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Detection of liquid petroleum gas using mixed nanosized tungsten oxide-based thick-film semiconductor sensor

G.N. Chaudhari [a,*], A.M. Bende [a], A.B. Bodade [a], S.S. Patil [a], S.V. Manorama [b]

[a] *Gas Sensor and Thin Films Laboratory, Department of Chemistry, Shri Shivaji Science College, Amravati 444601, Maharashtra, India*
[b] *Materials Science Laboratory, Indian Institute of Chemical Technology, Hyderabad 500007, Andhra Pradesh, India*

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Abstract

The thick-film semiconductor sensor for liquid petroleum gas (LPG) detection was fabricated using a mixed WO_3-based sensor. We present the characterization of both their structural properties by means of XRD measurements and the electrical characteristics by using gas-sensing properties. The sensing characteristics such as sensitivity, working range, cross-sensitivity and response time were studied by using nanosized WO_3-based mixed with different metal oxides (SnO_2, TiO_2 and In_2O_3) and doped with noble metals (Au, Pd and Pt). The WO_3-based mixed with 5 wt.% In_2O_3 and 0.5 wt.% Pd showed the higher sensing characteristic at low concentration of LPG sensor at an operating temperature 225 °C.

Keywords: LPG sensor; WO_3; In_2O_3; Sensitivity; Response characteristics

1. Introduction

Since the discovery nearly half a century ago that the charge-carrier concentration on the surface of a semiconductor is sensitive to the composition of the surrounding atmosphere [1]. Considerable research has been carried out on the development of novel solid-state gas sensors based on semiconducting metal oxides. As a result many such commercial gas sensors have been developed and marketed [2–4]. The currently acceptable levels of performance are used increasingly to monitor gases in various fields such as industrial and environmental control [5,6].

Different hydrocarbons are widely used for several industrial and domestic applications. These gases are potentially hazardous because they can cause explosions if they leak out accidentally or by mistake. Hence there is a great deal of worldwide interest in developing reliable and efficient hydrocarbon sensors having good sensitivity and selectivity.

For the last three decades, wide-gap semiconducting oxides such as SnO_2 and ZnO have been extensively studied for making efficient hydrocarbon sensors with suitable noble metal additives such as palladium [7,8] and platinum [9,10]. Other well-known materials for fabricating hydrocarbon sensors include WO_3 [9], CO-doped Fe_2O_3 [11] and In_2O_3–Al_2O_3 doped with Pd [12]. However, the above-mentioned materials are still not as selective as one would expect, since they sense several other reducing gases such as liquid petroleum gas (LPG), H_2, CO and CH_4 with good sensitivity values. In addition, the stability of some of these materials is not very good resulting in poor reliability due to aging and humidity-induced effects, involving grain growth and poisoning. These are manifested as a change in resistance over several weeks and hence are not suitable, since they do not offer the good combination of high sensitivity, selectivity and rapid response time reliably required for several applications.

Recently, Wang et al. [13] developed a thick-film gas sensor to detect LPG and hydrogen gas based on γ-Fe_2O_3. Further studies and developments of WO_3-based gas sensors have been accomplished by Barrett et al. [14], Miura et al. [15] and Akiyama et al. [16]. Barrett et al. prepared WO_3-based gas sensors of the metal oxide semiconductor (MOS) type by decomposing ammonium tungsten. It was found that the WO_3-based gas sensor was sensitive to H_2S even at concentrations down to 50 ppm. At the same time, Miura et al. [15] developed a pair of Pt-loaded oxide electrodes as a proton-conductor gas sensor. It was

* Corresponding author.
E-mail addresses: gnc4@indiatimes.com, gnchau@rediffmail.com (G.N. Chaudhari).

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selective and sensitive to CO even at room temperature. It was reported that the CO sensitivity of this type of WO_3-based sensor was seven times higher than the H_2, sensitivity and the 90% response time was about 3 min in 1000 ppm CO gas and 1 min in 1% H. In 1991, Akiyama et al. [16] found that the tungsten oxide-based semiconductor sensor was highly sensitive to NO and NO_x.

Considering the LPG gas sensor market needs (low cost, small size, maintenance free and long durability) gas sensors based on semiconducting oxides and manufactured by the screen-printing method have certain advantages with respect to other types of gas sensors. Among published works, considering this sensor from the practical point of view, none of these showed sufficient sensing characteristics for determination of LPG using mixed oxides as the sensing materials by thick-film method [17].

In the present works, the mixed oxide of WO_3, TiO_2, In_2O_3 and SnO_2 and doped with noble metals (Au, Pd and Pt) as sensing material by thick-film technique were studied. The basic characteristics of LPG gas sensor using WO_3/In_2O_3/Pd as sensing material, such as, sensitivity, working range, cross-sensitivity and response characteristics were further studied. Detail results on the gas-sensing properties and the mechanism involved are discussed in the following sections.

2. Experimental details

The precursors of WO_3 and mixed oxide doped WO_3 nanocrystallites were prepared by the sol-precipitation method considering the reactive conditions such as the concentration of the reactants, pH value, calcination temperature and time. The solution of WCl_6 was mixed with ammonia hydroxide to form $W(OH)_6$ and sol with pH 7. The sol was centrifuged and washed. It was dried at 120 °C for 6 h to prepare the precursors of WO_3 nanocrystallites. The dried powder then calcined with different temperatures in the range of 350–750 °C in order to improve the crystallinity of WO_3. The solution of $InCl_6$, $SnCl_4{\cdot}5H_2O$ or $TiCl_4$ was used as an additive in the precursors of WO_3. The homogeneity of the compound was confirmed by X-ray diffraction using SIEMEN D.5000 with copper target, Kα radiation (λ = 1.5406 Å).

3. Sensor fabrication

Fabrication of mixed WO_3-based sensor began by weighing the correct quantities of adding various 1 g metal oxides (TiO_2, In_2O_3 and SnO_2), 1 ml noble metals of 0.5 wt.% solution in weight (Au, Pd and Pt) and 10 g WO_3 powders and then mixing them. The mixture was dried at 120 °C for 3 h and then calcined at 650 °C for 6 h in an air stream. The calcined compound was mixed with 2% polyvinylalcohol (PVA) binder to make a paste and coated onto alumina tube substrates which were already provided with platinum wire electrodes for electrical contacts. The PVA decomposes and the strength of the final element markedly increases.

The sensors were subjected to measurements of their electrical resistance in dry air or a sample gas for 5000 ppm of gas concentration in dry air at various operating temperatures. The sample gas was prepared by mixing air with LPG, H_2, CO and CH_4. The gas sensitivity (S) is defined as the ratio of the change of resistance in presence of gas (R_g) to that in air (R_a), $(R_a - R_g)/R_a = \Delta R/R_a$.

4. Results and discussions

4.1. Structural characterization

Fig. 1(a)–(d) shows X-ray diffraction patterns obtained from WO_3 after calcination at 350, 450, 550 and 650 °C with reflection peaks of both monoclinic (m) and tetragonal phases of WO_3. The grain size was estimated from Scherrer's formula [11]. At lower calcination temperature of WO_3, it was observed that twin peaks for (0 0 1) and (1 1 0) reflection shows metastable tetragonal phase crystallites. As shown in Fig. 1(d), there are peaks at 2Ø values of 23.20, 28.88 and 34.17. The existence of these peaks means that the crystalline phase of the WO_3 is monoclinic (JCPDS 431035). For calcination temperature above 450 °C, there is a phase transition with a monoclinic phase appearing with grain growth. At calcination temperature of 650 °C, the monoclinic structure is dominating, and the grain size is 55 nm. Wang et al. [18] shows the average grain size of about 24–26 nm for WO_3 at calcination temperature 800 °C. Fig. 1(e) shows that XRD pattern of 5 wt.% In_2O_3 doped WO_3 calcined at 650 °C for 6 h shows complete phase formation of In_2O_3:WO_3 nanocrystallites. No diffraction peaks originated from In_2O_3 crystallites were detected.

4.2. Gas-sensing mechanism

The gas-sensing mechanism is based on the changes in the conductance of WO_3. The reducing gas reacted with oxygen adsorbed on the surface of the sensor. The reducing gas acting on the WO_3 sensor surface can be explained as [19]:

$$R + O_{ads}^{-} \leftrightarrow RO + e^{-}$$

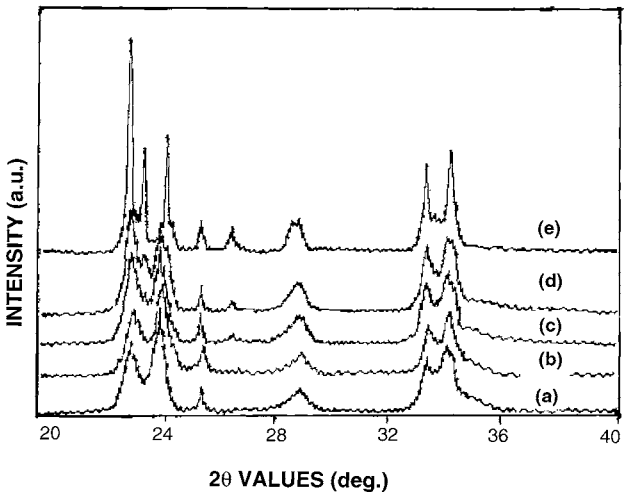

Fig. 1. X-ray diffraction patterns obtained from WO_3 calcined at (a) 350 °C; (b) 450 °C; (c) 550 °C; (d) 650 °C; and (e) 650 °C with addition of 5 wt.% In_2O_3.

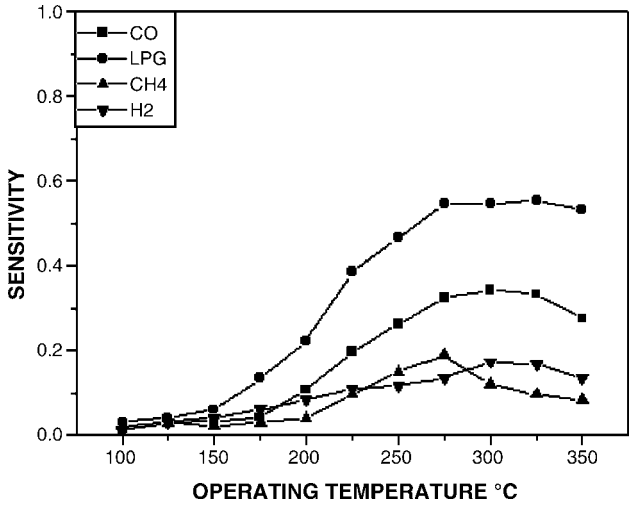

Fig. 2. Sensitivity of undoped WO_3 for LPG, CO, CH_4 and H_2 sensor calcined at 650 °C.

To maintain neutrality, the electrons release back WO_3 material, resulting in the increase of the electron concentration and the decrease of the resistance. This change of the electrical resistance determined sensitivity of the WO_3-based sensor to reducing gases. Fig. 2 shows the sensitivity of undoped WO_3 for LPG, CO and CH_4 and H_2.

4.3. Effect of additives

In order to promote gas sensitivity, additives were shown to effectively influence the semiconductive properties of sensor materials. WO_3-based elements doped with various metal oxides with different weight percentage were subjected to measurements of the LPG-sensing characteristics at 320 °C. Fig. 3 shows that the LPG sensitivity changed with metal oxide. Obviously many additives promoted sensitivity. Among the examined metal oxides, 5 wt.% In_2O_3 was singularly outstanding in promoting the sensitivity. So 5 wt.% of In_2O_3 was the optimal dopant for WO_3-based LPG-sensing element.

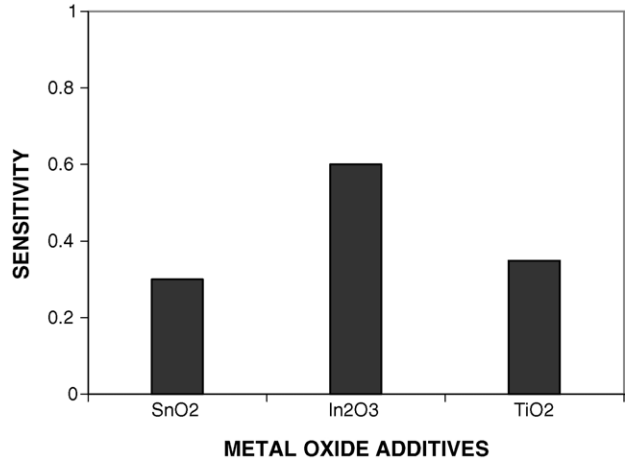

Fig. 3. Sensitivity of metal oxide additives doped WO_3 for LPG sensor at an operating temperature 300 °C.

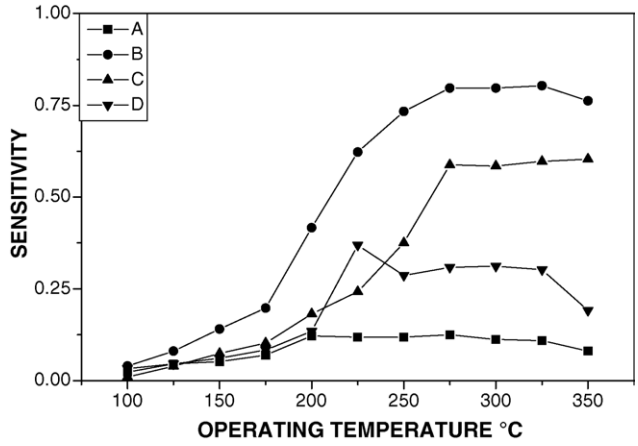

Fig. 4. Sensitivity of WO_3 doped with different amount of In_2O_3 for LPG sensor calcined at 650 °C. (A) 2 wt.% In_2O_3, (B) 5 wt.% In_2O_3, (C) 7 wt.% In_2O_3 and (D) 10 wt.% In_2O_3.

4.4. Effect of In_2O_3 loading

In order to obtain the optimal LPG-sensing characteristics, we studied the relationships between the sensitivity and the operating temperature of the elements with different In_2O_3 concentration. Fig. 4 shows that the sensitivity increased with increasing concentration of In_2O_3. However, the curves of sensitivity as a function of operating temperature shows the sensitivity intensively changed with the temperature when the loading is 5 wt.% of In_2O_3 doped WO_3.

4.5. Sensor cross-sensitivity for 5 wt.% In_2O_3:WO_3

The sensor cross-sensitivity effect played by LPG, CO, CH_4 and H_2 interfering gases at various temperature is shown in Fig. 5. It is clear from the graph that the sensitivity for LPG is more than the other reducing gases. As expected, the sensitivity increased with an increase in the operating temperature. For LPG, the sensitivity increased and reached saturation values around 250 °C.

LPG is a mixture of hydrocarbons like *n*-propane and *n*-butane and one of the by products after partial combustion is

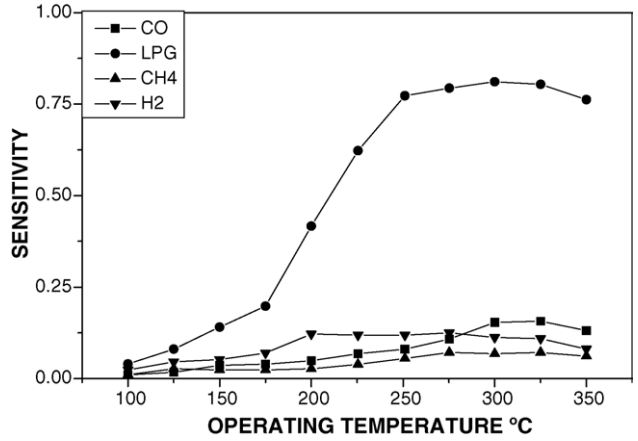

Fig. 5. Cross-sensitivity of LPG, CO, CH_4 and H_2 gases at various operating temperatures.

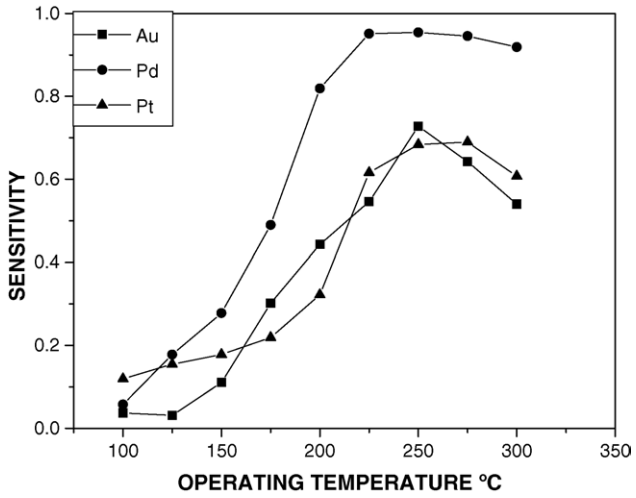

Fig. 6. Sensitivity of WO_3–5 wt.% In_2O_3 with addition of 0.5 wt.% of Pt, Au and Pd.

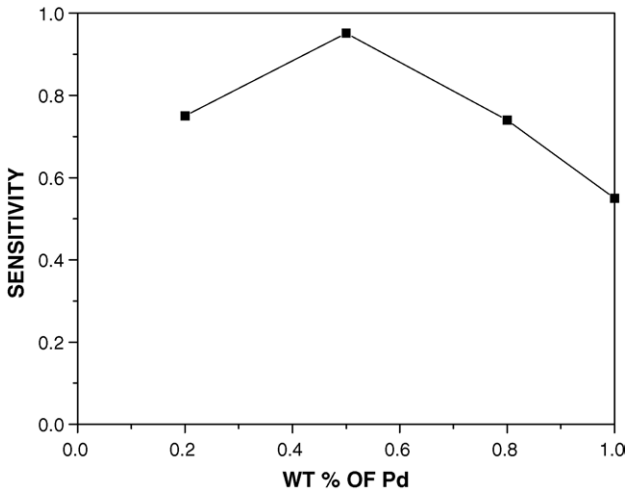

Fig. 7. Sensitivity as a function of amount of Pd doped 5 wt.% In_2O_3:WO_3.

CO and after complete combustion, it is CO_2 and H_2O. Hence, the sensitivity of the sensor to other reducing gases like CO and CH_4 were also measured as a function of operating temperature. As seen in Fig. 5, WO_3/In_2O_3 is highly selective to LPG though the sensitivity is low, while for the other gases, the sensitivity is almost negligible in the temperature range of interest. The sensitivity of the sensor to the other above-mentioned reducing gases at an operating temperature of 250 °C is negligible compared to that of LPG. For CH_4, the sensitivity was about 0.03847 whereas for CO, it was about 0.08. The low sensitivity to carbon monoxide and methane may be due to the fact that these gases are reactive only at temperatures much higher than those investigated in this study.

4.6. Sensor sensitivity of WO_3–In_2O_3 adding Au, Pd or Pt

In order to further increase the sensitivity, different noble metals were incorporated in In_2O_3:WO_3. For WO_3–5 wt.% In_2O_3 doped with noble metals, the maximum sensitivity for LPG gas was obtained with WO_3–5 wt.% In_2O_3–0.5 wt.% Pd. Fig. 6 shows the sensitivity as a function of operating temperature for WO_3–5 wt.% In_2O_3 doped with 0.5 wt.% of Pt, Au and Pd. The maximum value of sensitivity was observed for 0.5 wt.% Pd doped 5 wt.% In_2O_3:WO_3 for LPG sensor.

It was found to be extraordinarily large indicating that the LPG detection was sensitized quite effectively by the addition of Pd. The sensitivities to other gases remain almost unchanged with or without Pd addition. Such a feature seems to be favorable from the viewpoint of selective detection of LPG. The effect of Pd on the sensitivity for LPG detection was further studied as a function of Pd loading. The effect of palladium loading on the sensitivity of the sensor at an operating temperature of 225 °C is shown in Fig. 7. The palladium concentrations were varied from 0.2 to 1 wt.%. It was found that 0.5 wt.% Pd was the optimum concentration for maximum sensitivity to LPG at 225 °C. The sensitivity increases with Pd concentration up to 0.5 and then decreases above 0.5 wt.% Pd suggests the importance of the dispersion of Pd on the semiconductor surface.

4.7. Relation between the sensitivity and the gas concentration

Fig. 8 shows sensitivity versus gas concentration in ppm mixed in dry air for sensor element 0.5 wt.% Pd doped 5 wt.% In_2O_3:WO_3 calcined at 650 °C for 6 h. The sensor element exhibits significant increase in sensitivity even at lower concentration of LPG for an operating temperature of 225 °C.

4.8. Response characteristics of WO_3:5 wt.% In_2O_3:0.5 wt.% Pd

The time taken to reach the saturation value is apparent from its response characteristics, which gives the rise time in presence of gas and fall time once the gas leaves the system. The typical response characteristic of the sensor element was shown in Fig. 9. It is observed that the response to LPG shows a steep rise followed by steep fall in response to the presence and absence of gas. The element reaches its maximum value of sensitivity (0.95)

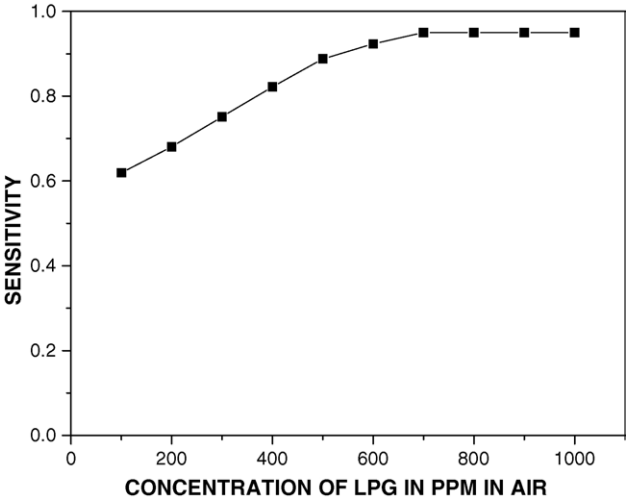

Fig. 8. Sensitivity of 0.5 wt.% of Pd doped 5 wt.% In_2O_3:WO_3 for LPG gas concentrations in ppm in air.

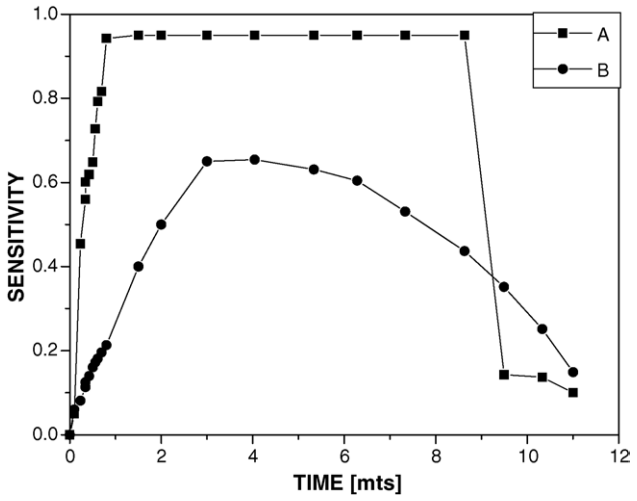

Fig. 9. Response characteristics of (A) WO_3:In_2O_3 (5 wt.%):Pd (0.5 wt.%) and (B) WO_3:In_2O_3 (5 wt.%).

also defined as the saturation values is less than one minute and comes to the original position in less than 10 min indicating reliability of sensor element for long time.

5. Conclusions

The basic characteristics of LPG sensor were clarified considering sensor market needs and other practical points by thick-film method. The sensitivity of the WO_3-based sensor was remarkably increased with mixed In_2O_3 doping and addition of Pd. The WO_3-based mixed with 5 wt.% In_2O_3 and 0.5 wt.% Pd shows higher sensitivity characteristic at low concentration of LPG sensor at an operating temperature 225 °C. The sensor having the best overall characteristics of good response, good sensitivity for low concentration, undesirable cross-sensitivity effect was obtained using 0.5 wt.% Pd:5 wt.% In_2O_3:WO_3 for LPG-sensing material.

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