Hydrogen and LPG sensing properties of SnO_2 films obtained by direct oxidation of SILAR deposited SnS

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Abstract. Hydrogen (H_2) and liquid petroleum gas (LPG) sensing properties of SnO_2 thin films obtained by direct oxidation of chemically deposited SnS films has been studied. The SnS film was prepared by a chemical technique called SILAR (Successive Ionic Layer Adsorption and Reaction). The sensor element comprises of a layer of chemically deposited SnO_2 film with an overlayer of palladium (Pd) sensitiser. The Pd sensitiser layer was also formed following a chemical technique. The double layer element so formed shows significantly high sensitivity to H_2 and LPG. The temperature variation of sensitivity was studied and the maximum sensitivity of 99.7% was observed at around 200°C for 1 vol% H_2 in air. The response time to target gas was about 10 seconds and the sensor element was found to recover to its original resistance reasonably fast. The maximum sensitivity of 98% for 1.6 vol% LPG was observed at around 325°C. The sensor response and recovery was reasonably fast (less than one minute) at this temperature.

Key words: SILAR, SnO_2 film, Pd catalyst, H_2, LPG.

1. Introduction

SnO_2 is the most extensively studied gas sensor material and the most commercially available gas sensors utilize a SnO_2 element [1]. SnO_2 based sensors has been fabricated in different physical forms such as single crystal [2], sintered pellets [1, 3], whiskers [4], thick films [5–7] and thin films [8–13]. The sensitivity, selectivity and optimum operating temperature of these sensors made in different physical forms vary considerably. However, the thin film form is expected to produce highest sensitivity, as sensing is essentially a surface phenomenon. Different techniques have been employed to prepare SnO_2 thin films for sensor applications. These includes rf sputtering from a metallic target or from a SnO_2 target, thermal evaporation, CVD, spray pyrolysis, sol-gel, rheotaxial growth of tin oxide (RGTO). RGTO technique, a relatively new technique [14–15], has been used to grow tin dioxide films particularly for gas sensor applications. The properties of the resulting films depend markedly on the deposition parameters of each technique. The films have been utilized for the detection of CO, CH_4, H_2S, NH_3, H_2, C_4H_{10} etc. Thus it may be noted that various methods, ranging from a simple to a sophisticated one, have been utilized by researches to obtain device quality SnO_2 films for gas sensing applications.

Although the oxides themselves are catalytically active, they are rarely used in isolation as their gas sensing characteristics are usually enhanced by using a small amount of noble metal catalyst such as palladium (Pd) and platinum (Pt). Conventional SnO_2 sensors almost always use Pd [16]. Gold (Au) or silver (Ag) is also utilized to enhance sensitivity [17]. Different techniques of catalyst loading have been employed by workers. These include spray technique [18], im-

pregnation technique (which is particularly suitable for bulk doping) [16], chemical vapor deposition [5], dipping technique [11], photo deposition [19], sputtering and evaporation [2, 20–21].

In this work, we have reported the hydrogen and LPG sensing properties of tin oxide thin film. The SnO_2 film was obtained by direct oxidation of tin sulphide (SnS) thin film; the later was prepared by SILAR (Successive Ionic Layer Adsorption and Reaction) technique. The technique involves multiple dipping of a substrate in cationic and anionic precursors. Compared to physical techniques, chemical techniques are much simpler and cheaper and thus can offer the desirable cheapness as far as the cost of the sensor material is concerned. The process is relatively simple to carry out and less energy expensive and therefore can be easily transferred to industrial level. The sensitization with palladium (Pd) catalyst was also carried out following a novel wet chemical method. Earlier we have reported the LPG and methane sensing characteristics of ZnO films sensitized with Pd following this technique [22–23].

2. Experiments

The SnO_2 films were prepared by direct oxidation of tin sulphide (SnS) layer prepared by a chemical dipping technique. The SnS layer was formed by alternate dipping of a substrate in stannous chloride ($SnCl_2$) and sodium sulphide (Na_2S) bath. The technique was originally reported by Call et al. [24] for zinc oxide film deposition. The process was given the name SILAR by Nicolau et al. [25] since it involves adsorption of a layer of ion on the substrate followed by reaction of the absorbed ion layer. The technique has been employed to develop zinc sulphide (ZnS), zinc cadmium sulphide (ZnCdS)

and cadmium sulphide (CdS) by Nicolau et al. [26–27] We have used the technique to produce tin sulphide thin films. For this the substrate was introduced in 0.1 M (Molar) $SnCl_2$ solution where adsorption of Sn^{2+} takes place. Upon placing it in 0.1 M sodium sulphide solution, reaction between tin ion (Sn^{2+}) takes place with sulphide ion (S^{2-}) ion leading to the formation of SnS. A part of the SnS so formed was deposited onto the substrate as a strongly adherent film and another part of it forms precipitate in the bath solutions. Thus the bath solution needs to be changed at regular intervals. The film growth rate is slow and 50 (fifty) dipping gives approximately 0.6 μm thick film. The details of film growth process and its dependence on deposition parameters (e.g. concentration of the solutions, temperature of deposition etc.) have been reported elsewhere [28].
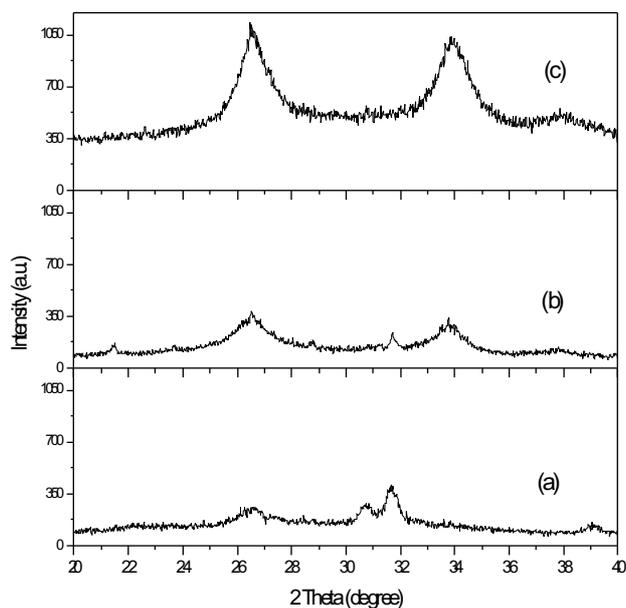
Fig. 1. XRD pattern of (a) as-deposited SnS; (b) heat treated SnS (300°C, 1 hr.); (c) heat treated SnS (400°C, 1 hr.) leading to complete conversion to SnO_2

Thermal oxidation of the SnS layer in air at 400°C for one hour directly leads to the formation of SnO_2. Figure 1 shows the XRD pattern of SnS and its conversion to SnO_2 due to heat treatment. The material was scanned in the range 20–40° with CuK_α radiation. Figure 1(a) shows the XRD pattern of as deposited SnS. The peaks at 26.62°, 30.94° and 31.62° are in good agreement with the Joint committee on powder diffraction standard (JCPDS) data belonging to SnS [29]. The corresponding planes are (120), (101) and (111). Figure 1b shows the XRD of SnS film heat treated at 300°C for 1 hr. The SnS peaks at 30.94° and 31.62° decreases in intensity and a peak at 33.84° appears indicating formation of SnO_2. Heat treatment at 400°C for 1 hour results in complete conversion to SnO_2. The peaks at 26.34° and 33.84° corresponding to reflections from (110) and (101) plane are in agreement for SnO_2 [30]. It is seen from the XRD pattern that the SnO_2 film is phase pure with (110) plane having maximum intensity as expected for a casseterite crystal structure [30].

The particle size was measured using "Scherrer equation" which is given by

$$D = \frac{0.89\lambda}{\beta \cos\theta}$$

where λ is the wavelength of radiation used ($CuK\alpha$ in this case), β is the full width at half maximum intensity of the diffraction pattern (FWHM), θ is the Bragg angle and D is the crystallite dimension or particle size.

Using Scherrer equation, particle size estimation was carried out for the peaks of SnO_2 at 26.34° and 33.84° corresponding to the planes (110) and (101) respectively. The measured particle sizes were 55.97 Å and 61.83 Å respectively. The average of these two values is 58.9 Å or 5.9 nm.
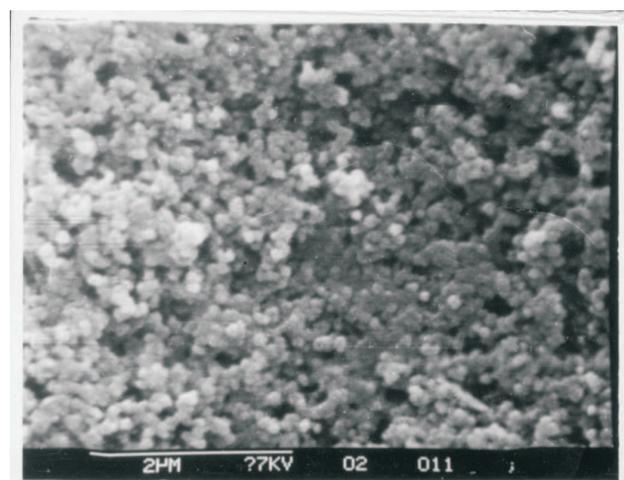
Fig. 2. SEM of SnO_2 film (thickness ∼0.6 μm)

SEM photograph also illustrates the formation of nanocrystalline particles. Figure 2 shows the typical micrograph (SEM) of a SnO_2 film of thickness approximately 0.6 μm. The structure is polycrystalline with very fine pores distributed fairly uniformly on the film surface.

2.1. Surface sensitization of the films. The surface of SnO_2 thin films was sensitized by a dipping technique. The process involved multiple dipping of the film in a 50 cc solution of 1 wt.% palladium chloride ($PdCl_2$) in ethyl alcohol (C_2H_5OH). After each dipping the film was withdrawn form the solution and the volatile solvent (alcohol) was allowed to evaporate leaving behind a coating of $PdCl_2$. The dipping time was 2–3 seconds each time in alcohol medium. The thickness of the Pd layer could be increased by increasing the number of dipping [22]. The Pd loaded films were subsequently heat treated at 250°C for 1 hr.

2.2. Fabrication of sensor element. The SnO_2 sensor element was deposited on a hollow cylindrical glass tubes (5 mm long, 2 mm external diameter and 1 mm internal diameter). The wall thickness was about 0.5 mm. A nichrome wire (80 gauge) used in the form of a heating coil, was placed inside the hollow tube in order to operate the sensor element at the requisite temperature. Finally electrical contacts on the

SnO$_2$ film were made at the two ends of the cylindrical sensor element by using silver (Ag) paste. The contacts were cured by heating to 200°C in air for 30 minutes. The solder connections were made on a standard 6-pin base and the sensor element was housed in a polycarbonate base with a polycarbonate cover (12 mm inner diameter and 8 mm height). Stainless steel (SS) wire gauge (100 mesh) was fixed on the polycarbonate frame through which the target gas could come in contact with the sensor element. Figure 3 shows as deposited and Pd treated sensor elements as well as few typical complete sensor assemblies.
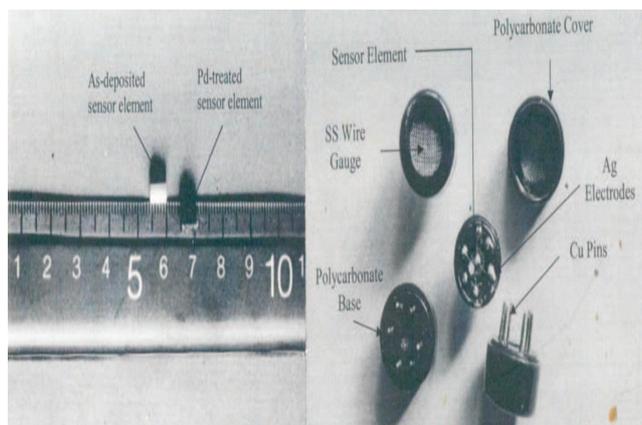
Fig. 3. As-deposited and Pd-treated sensor element on glass tube and sensor assembly housed inside a polycarbonate casing

The resistance values were measured using a digital multimeter (DMM). Two pins of the standard 6-pin base were used to hold the nichrome heater coil. A 5-volt dc source was used to supply power to the heater coil. The other four pins were used for silver electrodes. Any two (taking one from each side of the electrode) were used for resistance measurement. Copper (Cu) wires from these two pins were connected to the resistance-measuring instrument (DMM).

The gas sensing characteristics (response and recovery) of the Pd-sensitized SnO$_2$ film was carried out for H$_2$ and LPG. Calibrated cylinders with target gases diluted in air were used for gas sensing measurement. A known amount of target gas was introduced after the ohmic resistance of the sensor material gets stabilized. The recovery characteristics (when the target gas is withdrawn) were also monitored as a function of time.

The sensitivity has been defined in different ways in the literature. It has been defined as $\dfrac{R_{\text{air}}}{R_{\text{gas}}}$ [3, 6, 13], in which case it is a quantity greater than one (1) for reducing gases since the resistance of a sensor material decreases in presence of reducing gases. Here R_{air} is the initial sensor resistance in air, prior to gas exposure and R_{gas} is the sensor resistance in presence of the target gas. Sensitivity has also been defined as percent reduction of sensor resistance [12, 31–32]. The percent sensitivity (or the percent reduction of sensor resistance on exposure to target gas) can be expressed as

$$S\% = \left[1 - \frac{R_{\text{gas}}}{R_{\text{air}}}\right] \times 100.$$

In the present work, the sensing characteristic was carried out for a fixed concentration of target gas and we have used the above equation for calculation of sensitivity.

3. Results and discussions

3.1. Hydrogen sensitivity of SnO₂. SnO$_2$ film with 15 dipping Pd loading was used for gas sensing experiments. Although no optimization was carried out for palladium loading in the present experiment, it was found that for films loaded with more than 25 dipping Pd, a highly conducting surface of low resistance is formed suggesting formation of metallic Pd. It was also observed that for a 10 dipping Pd loaded sensor shows little sensitivity. Although not much systematic data was carried out in this direction, the observation is similar to that obtained for ZnO films loaded with Pd using identical technique [22] where 15 dipping was found to be optimized value. Lower number of dipping (i.e. lower amount of Pd catalyst) produced low sensitivity in ZnO films and higher number of dipping produced a highly conducting surface of metallic Pd, which is unsuitable for sensing activity. At this particular value of dipping, it was found that Pd is dispersed over the ZnO surface without forming a continuous metallic layer of low resistance. In the present experiments, exact value of number of Pd dipping for which maximum sensitivity could be obtained was not carried out. The optimized value lies somewhere between 10 and 25.

The catalytic effect of the noble metal on the sensitivity of the semiconducting oxides is explained by either a chemical or an electronic sensitization mechanism. However it is not easy to control the amount of doping (in other words, using controlled dose of doping) for thin films [20]. When noble metal catalyst (Pd, Pt etc.) is applied on thin film surface by sputtering technique, it is done by varying the sputtering time and power density. For our case, it is carried out by dipping technique. Using controlled dose of doping by optimizing exact number of dipping is extremely difficult. Experiments in this direction are in progress.
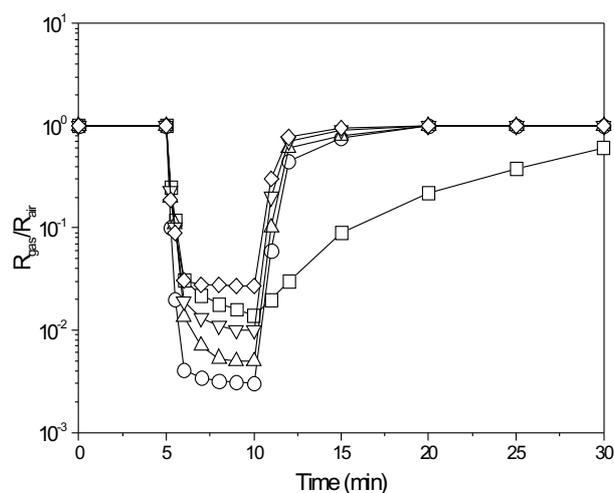
Fig. 4. Sensing and recovery characteristics of Pd sensitized SnO$_2$ film for different temperature in presence of 1 vol% H$_2$ in air: ($\square$) 150°C, ($\circ$) 210°C, ($\triangle$) 275°C, ($\triangledown$) 325°C and ($\diamond$) 375°C

Figure 4 shows the response and recovery characteristics of the Pd-sensitised SnO_2 film during 5 minutes exposure to 1 vol% H_2 in air at different operating temperatures. The resistance ratio $\dfrac{R_{gas}}{R_{air}}$ is plotted against time in Fig. 4. The resistance value of the sensor element in air (R_{air}) is a function of temperature and it varies from few $M\Omega$ (Mega-ohm) to a few $k\Omega$ (kilo-ohm) as the temperature is raised from 150°C to 375°C. The distance between the Ag electrodes were approximately 3 mm.

Figure 5 shows the variation of percent sensitivity against temperature of the Pd sensitized SnO_2 thin film during 5 minutes exposure to 1 vol.% H_2 in air.
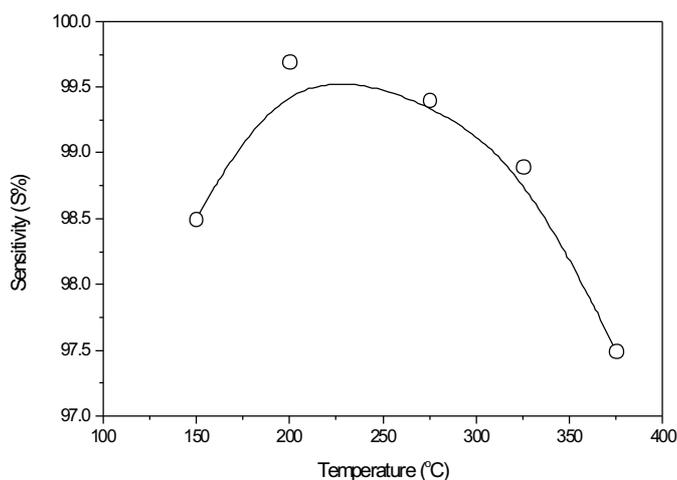
Fig. 5. Variation of percent sensitivity with sensor operating temperature for 1 vol% H_2 in air

Generally, the response time is defined as the time required to reach 90% of the difference ($R_{air} - R_{gas}$) after sudden change of the atmosphere from a state with no gas (i.e. air) to that containing the target gas [33]. The recovery time has been defined as the time it takes to reach 90% of the difference ($R_{air} - R_{gas}$) after the reverse change of atmosphere [33]. In this way, the response time and the recovery time under different operating temperatures can be evaluated. The sensitivity as well as response time is temperature dependent since the chemical kinetics governing the solid-gas interface reaction is temperature dependent.

It is seen from Fig. 5 that the peak sensitivity occurred at around 200°C and the value of maximum sensitivity is 99.7%. The response time to the target gas was approximately 10 seconds. The complete recovery of the sensor element took about five (5) minutes. However, 80% recovery occurred in about one minute. The sensitivity decreases above 200°C temperature and it was 97.5% at 375°C. The recovery at high temperatures is relatively faster. Although a reasonable sensitivity of 98.5% was obtained at 150°C, the response time was very high as the resistance reduction continued even after 5 minutes of gas exposure. The recovery process was also incomplete. The recovery after 20 minutes was found to be 60%.

3.2. LPG sensitivity of SnO_2. Figure 6 shows the response and recovery characteristics of the Pd-sensitized SnO_2 film during 5 minutes exposure to 1.6 vol% LPG in air at different operating temperatures. Figure 7 on the other hand, shows the variation of percent sensitivity with sensor operating temperature. The sensitivity increases rapidly above the sensor operating temperature of 100°C and reaches the maximum of 98% at around 325°C. The sensitivity however decreases above this temperature. The recovery is slow at low operating temperatures. It takes about 30 minutes for complete recovery at 100°C. With increasing operating temperature, the recovery gets faster.
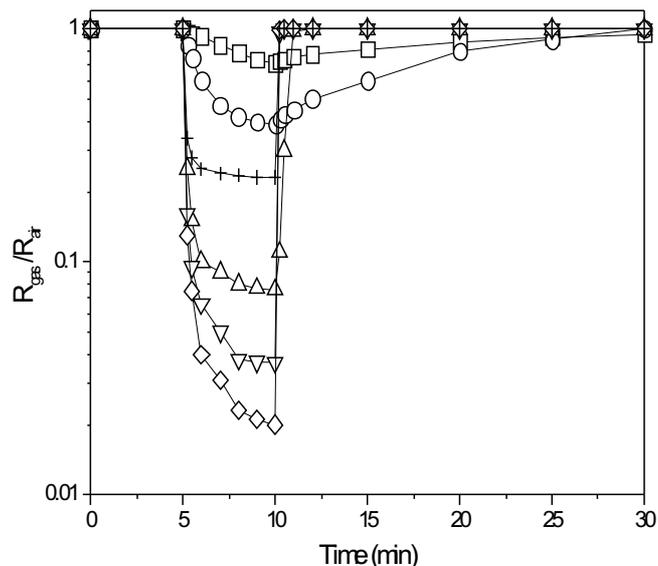
Fig. 6. Response and recovery characteristics of Pd sensitized SnO_2 film for different operating temperatures for 1.6 vol% LPG in air: 100°C ($\square$), 200°C ($\circ$), 300°C (∇), 325°C ($\Diamond$), 375°C ($\triangle$) and 425°C (+)
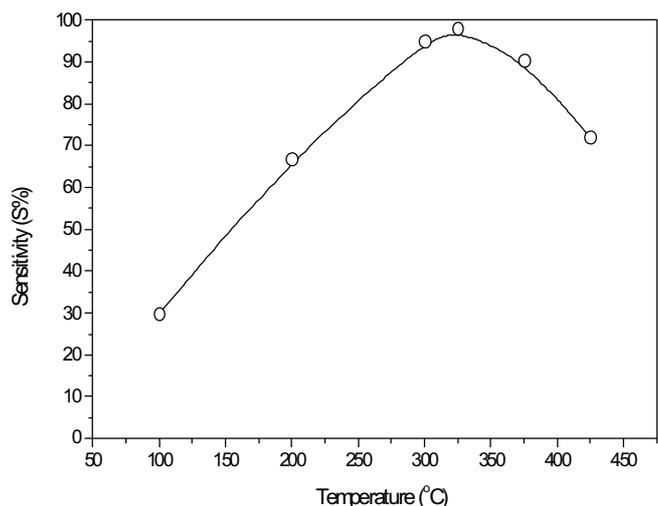
Fig. 7. Variation of percent sensitivity with sensor operating temperature for 1.6 vol% LPG in air

The response time (which is generally defined as time required for 90% resistance reduction of total resistance change)

is less than one minute at 325°C and also complete recovery requires less than one minute at this temperature.

Earlier we have reported maximum sensitivity of Pd-treated ZnO films at 350°C in presence of 1.6 vol% LPG [22]. The sensitivity at this temperature was 98%. The present SnO₂ films show maximum sensitivity of 98% at a relatively low operating temperature of 325°C.

Malyshev et al. [33] observed highest sensitivity of sputtered undoped SnO₂ thin films at 450°C in presence of butane and propane. Lee et al. [12] reported maximum sensitivity for (Pd+Pt) doped SnO₂ films at 400°C in presence of C_3H_8 and C_4H_{10}. The films were prepared by sputtering technique. Thus the observed maximum sensitivity at 325°C for the present Pd doped SnO₂ sensor elements in presence of LPG (which is a mixture of propane and butane) is somewhat on the lower side. The maximum sensitivity for sputtered Pd doped SnO₂ films in presence of H_2 was reported at 300°C by Baik et al. [13] and at 150°C by Yamazoe [16]. Thus our observation of maximum sensitivity at 200°C is comparable to those reported by others. Song et al. [6] on the other hand reported maximum sensitivity at room temperature for platinum (Pt) doped SnO₂ films. The effect of crystallite size and use of noble metals on temperature of maximum sensitivity has been discussed by Song et al. [6], Baik et al. [13] and Malyshev et al. [33]. Experiments in these directions for the present sensor elements are in progress.

4. Conclusions

The present investigation shows that porous SnO₂ thin films, prepared by oxidation of SnS film obtained from a simple low-cost chemical process can act as a very good hydrogen sensor. The maximum sensitivity to 1 vol% hydrogen is 99.7% at 200°C. Thus the films respond strongly to 1 vol% H_2, which is on the lower side of the hazardous explosion range for H_2 (4–75%). The response time at this temperature is about 10 seconds and time for 80% recovery is about one minute.

The sensor also respond strongly to 1.6 vol% LPG, which is equivalent to 80% LEL (lower explosive limit) of LPG. The maximum sensitivity to 1.6 vol% LPG is 98% at 325°C. The response at this temperature is less than one minute and also the recovery is complete within one minute. The high sensitivity to H_2 and LPG may be attributed to low thickness (approximately 0.6 μm), low crystallite dimension (approximately 5.9 nm calculated using Scherrer equation) and porosity. The stability of the sensor elements has not been checked. Also use of other catalyst (e.g. Pt, Au etc.) and proper optimization of catalyst loading can improve the sensor performance.

The simplicity and low cost of the chemical deposition method and high degree of sensitivity of the deposited films can make the process attractive for industries. The films can be deposited on any shape and size of the substrate and the process can be easily carried out in a large scale. The process of catalyst loading by chemical dipping is also simple to carry out and the amount of loading can also be varied with great ease.

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