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Synthesis, Characterization and Lpg Sensing Properties of Fe Doped Nano-Sized Tin Oxide

Physics

KEYWORDS:

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ABSTRACT

This paper reports the synthesis, characterization and LPG sensing properties of Fe doped nano-sized tin oxide. The Fe doped nano-sized SnO2 powder was synthesized by using a chemical co-precipitation method using stannic chloride (SnCl4, 5H2O), iron chloride (FeCl3) and ammonium hydroxide (NH4OH), as starting materials and water as a carrier. The resulting nano-sized powder was characterized by X-ray diffraction (XRD) measurements, transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The LPG sensing properties of the synthesized Fe doped nano-sized SnO2 powder were investigated at different operating temperatures and LPG concentrations. It was observed that doping of Fe significantly enhances the sensitivity of the nano-sized SnO2 to the LPG. The sensitivity of Fe doped nano-sized SnO2 to 75 ppm of LPG is maximum at an operating temperature 350 oC and it was found to be ~ 504.30 %. The response and recovery times were found to be nearly 3 sec and 5 sec, respectively. Finally, the plausible mechanism for the enhancement in the LPG sensing properties was discussed.

I. INTRODUCTION

Semiconductor gas sensors based on metal oxides have been used extensively to detect toxic and inflammable gases. The metal oxides such as SnO_2 [1], ZnO [2] and Fe_2O_3 [3] offer the potential for developing a portable and inexpensive gas sensing devices, which have the advantages of simplicity, high sensitivity and fast response. The working principle of these semiconductor gas sensors is based on conductivity changes produced when the material is exposed to target gases. The main emphasis of research works in most recent times is centered on developing new sensing materials/compositions to improve the sensitivity, selectivity and stability. Most of the sensor development work is centered on SnO_2 material, due to lower working temperature and its adaptability to sense many gases after dopant addition. The gas sensitivity is greatly improved with the nanostructured SnO_2 material as the sensitivity of the material increases as the grain size decreases [4]. This is because the nanosized SnO_2 shows a large surface to volume ratio and hence high surface activity and gas sensitivity. SnO_2 gas sensor could be highly sensitive when its crystallite size is comparable with or less than twice the depth of space charge layer [5]. The addition of second component in metal oxide semiconductor sensors either as a bulk doping or as a surface modification is one of the successful means to optimize and improve the gas sensor properties [6-11]. These dopants are used both as active positions for redox processes and as promoting free charge carriers that increases the electronic conductance of the metal oxides [6,7]. To increase sensitivity, one of the successful techniques is addition of the catalytically active metals such as Pt or Pd. In order to develop a highly sensitive gas sensor, the crystallite size of SnO_2 powder should remain small after heat treatments such as calcinations and sintering. For this purpose numbers of additives are reported as grain growth inhibitors [11-12]. Lee et al.[12] reported that nanosized sensing materials with high surface area can be prepared by co-precipitation process using Pt/ and or Ca doped powder. Out of these approaches, the successful synthesis of nano-crystalline semiconducting oxides with high surface area for gas adsorption opens up a new paradigm for sensor materials.

LPG is a combustible gas and it is widely used as a fuel for domestic heating and industrial use. Although it is one of the extensively used gases, it is hazardous. Hence, it is crucial to detect it in its early stages of the leakage and to perform the active suppression [14]. In order to accomplish this, more attention has been paid to develop the gas sensors for the detection of LPG, using several sensing materials such as Ag_2O doped γ-Fe_2O_3, Pt modified Al_2O_3 [15], $ZnGa_2O_4$ [16], Sb doped SnO_2 [17], $MgFe_2O_4$, $CdFe_2O_4$[18] etc. Recently, the thick films of the mixed oxide of WO_3, TiO_2, In_2O_3 and SnO_2 and doped with nobel metals Au, Pd and Pt were investigated as sensing materials by Chaudhari et al. [19] for the detection of LPG. Srivastava et al.[1] studied the influence of microwave irradiation on SnO_2 powder prepared by precipitation method using water as a medium. They observed that the microwave irradiation results into an increase in LPG sensitivity.

With an objective to increase the sensitivity and selectivity of SnO_2 sensing materials for the detection of LPG, we have made an attempt to synthesize Fe doped nano-sized SnO_2 by a simple chemical co-precipitation method. The LPG sensing properties of the Fe doped nano-sized SnO_2 powder were investigated and compared with those of nano-sized SnO_2 and commercially available SnO_2.

II. EXPERIMENTAL

The Fe doped nano-sized SnO_2 powder was prepared by a simple co-precipitation method. In this method, a diluted NH_4OH solution was used to hydrolyze the metal salt precursors at a certain solution pH value. Fig. 1 is a schematic representation of the synthesis procedure.

In this work, the aqueous solution of 0.5 M $SnCl_4$, $5H_2O$ and 0.1 M $FeCl_3$ was prepared in double distilled water. To this, the solution of NH_4OH was added drop-wise under stirring until the final solution pH value of about 8 was achieved. The resulting precipitate was filtered and washed three to four times using double distilled water to remove impurities.

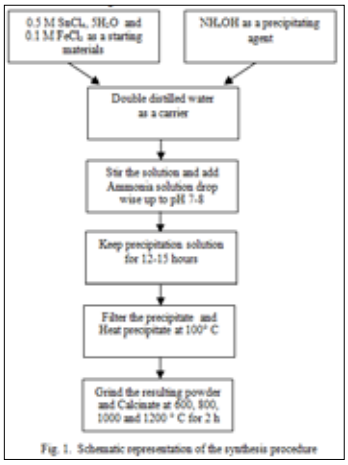


Fig. 1. Schematic representation of the synthesis procedure

The hydroxide, thus formed was dried at 100 °C and grinded into a powder, which is the precursor. The precursor was calcined in air at different temperatures of 600°C, 800°C, 1000°C and 1200°C for 2 h to produce nanocrystalline powders with different grain size. During the calcinations, the as-prepared powder was decomposed as follows –

$$SnCl_4 + FeCl_3 + NH_4OH \rightarrow SnFe(OH)x \downarrow + NH_4Cl$$
$$SnFe(OH)x \xrightarrow{>600^{\circ}C} SnO_2 + Fe_2O_3$$

The structure of the calcined powder was investigated by using XRD technique. The XRD patterns were recorded with a Rigaku diffractometer (Miniflex Model, Rigaku, Japan) having Cu K_α (λ = 0.1542 nm) radiation. The crystalline size was estimated from the broadening of SnO_2 (211) diffraction peak ($2\theta = 51.20^o$) using Debye-Scherrer's formula. The TEM was used to determine the particle size and the morphology of the nano-sized powder with JEOL 1200 EX. A TGA analysis of hydrate precipitate was performed to confirm at what temperature the precipitate have completely turned into oxide.

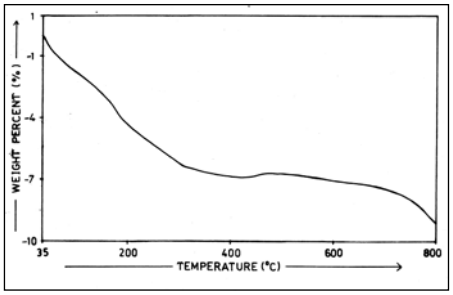
The Fe doped nano-sized SnO2 powder was pressed into pellets under a pressure of 15 MPa and the ohmic contacts were made with the help of silver paste to form the sensing element. The LPG sensing studies were carried out on these sensing elements in a static gas chamber in air ambient. The sensing element was kept directly on a heater in the gas chamber and the temperature was varied from 200 to 500oC. The temperature of the sensing element was monitored by chromel-alumel thermocouple placed in contact with the sensor. The known volume of the gas was introduced into the gas chamber pre-filled with air and it was maintained at atmospheric pressure.

$$S(\%) = \frac{R_a}{R_g} \times 100$$

The electrical resistance of the sensing element was measured before and after exposure to measuring gas using a sensitive digital multi meter (Scientific SW5015, India). The sensitivity (S) of the sensing element is defined as :
where Ra and Rg are the resistance values of the sensor element in air and in the presence of gaseous environment.

III. Results and Discussion

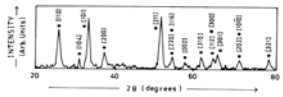
A. Synthesis of nano-sized Fe doped SnO2
The TGA curve of the hydroxide SnFe(OH)x is shown in Fig. 2.



A drastic weight loss was observed around 300°C and a constant weight region is obtained above 500°C. This indicates that the decomposition temperature of $SnFe(OH)_x$ into oxide completely is around 600°C. Therefore, in the present study, the hydroxide $SnFe(OH)_x$ was calcined at the temperatures between 600 and 1200 °C.

The XRD pattern of the calcinied powder at 800°C for 2 h is shown in Fig.3.

The analysis of different diffraction peaks indicates presence of SnO2 and Fe2O3 phases in the composite. It is to be noted that all the d values corresponding to these diffraction peaks are in close agreement with those reported by JCPDS-ICDD. The presence of mixture of phases makes the quantitative phase analysis difficult, but the identification of the above two phases can be achieved due to their explicit contribution to certain diffraction peaks. For instance, the diffraction peaks at 2θ values of 25.80o, 33.20o, 37.20o, 51.00o, 61.20o, 65.40o and 78.00o indicate the SnO2; whereas the peak at 2θ value of 31.00o clearly reveal the formation of Fe2O3 phase. The crystallite size was calculated by using the Scherrer formula –



$$t = \frac{k\lambda}{B\cos\theta}$$

where t is the average size of the crystallite, assuming that the grains are spherical, k is 0.9, λ is the wavelength of X-ray radiation, B is the peak full width at half maximum (FWHM) and θ is the angle of diffraction. The crystalline size of the powder calcinied at 800 °C is found to be ~ 12.46 nm.

The TEM micrograph of the powder calcinied at 800°C along with the electron diffraction (ED) pattern is shown in Fig.4. The TEM micrograph shows clearly that the particle size of powder calcinied at 800°C is ~ 12 nm. This result is in well agreement with the crystallite size calculated using the XRD data. The ED pattern gives the d spacing consistent with those obtained from XRD data.

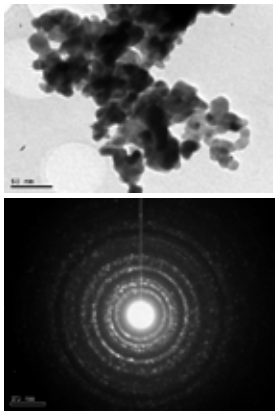


Fig. 4. TEM Micrograph with ED pattern of Fe doped nano-sized SnO_2 at 800°C for 2 h.

In order to study the effect of the calcination temperature on the crystallite size, the as-prepared powder was calcinied at 600oC, 800oC, 1000oC and 1200oC for 2 h in air. The crystallite size is found to be smallest when the as-prepared powder was calcinied at 800°C for 2 h. However, the crystallite size increases with the increase in the calcinations temperature after 800°C. This observation may be attributed to the particles growth and a lot small particles aggregation after being calcinied at higher temperatures. Indeed, the TEM micrograph of the powder calcinied at 1000°C [Fig.5] clearly shows the aggregation of small particles.

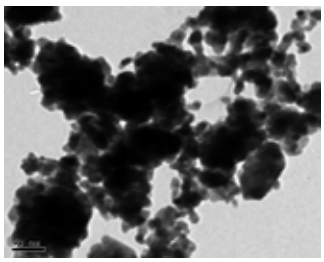


Fig.5. TEM micrograph of the powder calcinied at 1000 °C

The EDX spectrum of the Fe doped nano-sized SnO_2 is shown in Fig. 6. As expected, the EDX analysis indicates the presence of the signals due to the Sn (21.57 at.%), O (74.70 at.%) and Fe (4.04 at.%), which proves that the formation of Fe doped SnO_2.

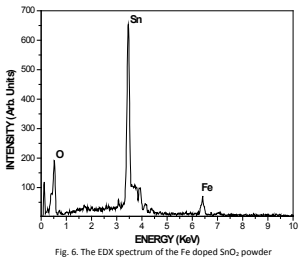


Fig. 6. The EDX spectrum of the Fe doped SnO_2 powder

B. LPG sensing properties of synthesized Fe doped nano-sized SnO_2
In this study, the LPG sensing properties of the Fe doped nano-

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sized SnO_2 synthesized by chemical co-precipitation method were investigated. For comparison, the LPG sensing properties of the commercially available SnO_2 and nano-sized SnO_2 were also studied under identical experimental conditions.

Fig.7 shows the effect of an operating temperature on the sensitivity of nano-sized SnO2, Fe doped nano-sized SnO2 powder and the commercially available SnO2 towards LPG. It is obvious from Fig.6 that the nano-sized Fe doped SnO2 powder exhibits an excellent sensitivity to LPG than nano-sized SnO2 and commercially available SnO2. When the commercially available SnO2 powder was used, the maximum sensitivity to 75 ppm of LPG occurs at 425oC and it is ~202.50%. On the other hand, when nano-sized SnO2 was used, the maximum sensitivity to 75 ppm of LPG is found to be ~254.60% at the operating temperature 375oC. Interestingly, the sensitivity of Fe doped nano-sized SnO2 to 75 ppm of LPG is maximum at an operating temperature 350 oC and it was found to be ~ 504.30 %.

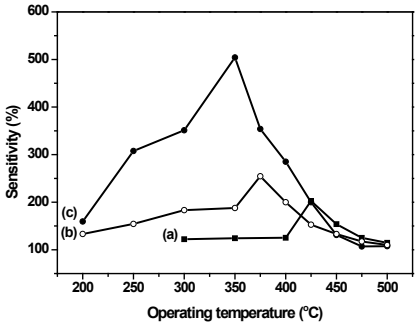

Fig. 7. Effect of operating temperature on the sensitivity of (a) commercially available SnO_2 , (b) nano-sized SnO_2 and (c) Fe doped nano-sized SnO_2 to 75 ppm of LPG

The relationship between the sensitivity of the Fe doped nano-sized SnO2 and the LPG concentration for an operating temperature 350 oC is shown in Fig. 8.

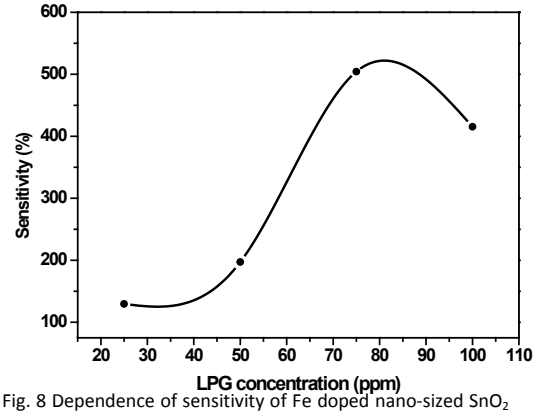

Fig. 8 Dependence of sensitivity of Fe doped nano-sized SnO_2 on the LPG concentration at 350^0C

It is observed that the sensitivity increases almost linearly as the LPG concentration increases from 25 to 75 ppm and then decreases with further increase in the LPG concentration. The linearity of the sensitivity in the low LPG concentration range (25-75 ppm) suggests that the Fe doped nano-sized SnO2 can be reliably used to monitor the concentration of LPG over this range. The linear relationship between the sensitivity and the LPG concentration at low concentrations may be attributed to the availability of sufficient number of sensing sites on the film to act upon the LPG. The low gas concentration implies a lower surface coverage of gas molecules, resulting into lower surface reaction between the surface adsorbed oxygen species and the gas molecules. The increase in the gas concentration increases the surface reaction due to a large surface coverage. Further increase in the surface reaction will be gradual when saturation of the surface coverage of gas molecules is reached. Thus, the maximum sensitivity was obtained at an operating temperature of 350 oC for the exposure of 75 ppm of LPG.

The response and recovery curves of the undoped and Fe doped nano-sized SnO2 for 75 ppm LPG at the operating temperature 350 oC are shown in Fig.9. Five samples

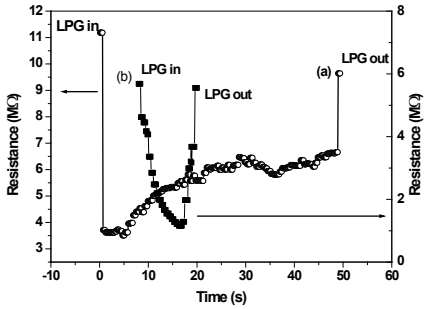

Fig.9. Response and recovery curves of (a) nano-sized SnO_2 (b) Fe doped nano-sized SnO_2 at operating temperature

were tested from each bath and each sample was tested three times, the repeatable and stable response was observed. The response time was small for both undoped and Fe doped SnO2 and it was observed to be ~ 3-5 s. However, the recovery was fast in the case of doped SnO2 and the recovery time was observed to be ~ 4 s.

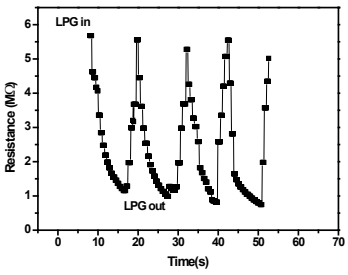

Fig.10. Gas sensing response of Fe doped nano-sized SnO_2 at operating temperature 350^0C

Fig. 10 shows the reproducibility of the sensor based on Fe doped SnO2 when exposed to 75 ppm of LPG for four times at an operating temperature 350 oC. It is clearly seen that the response and recovery characteristics are almost reproducible and stable.

Here, we first discuss a possible mechanism to explain qualitatively the observed LPG sensing properties of nano-sized SnO2. The LPG sensing mechanism is a complex process and it is believed that it proceeds through several intermediate steps which are not yet understood. It is based on the changes in the resistance of the SnO2 which is controlled by the LPG species and the amount of the chemisorbed oxygen on the surface. It is known that a certain amount of oxygen from air is adsorbed on the surface of the SnO2. The nano-sized SnO2 interacts with the oxygen, by transferring the electrons from the conduction band to adsorbed oxygen atoms, resulting into the formation of ionic species such as O2- or O-. The reaction kinematics may be explained by the following reactions [20-27]-

$$O_2(gas) \Leftrightarrow O_2(absorbed)$$
$$O_2(absorbed) + e^- \Leftrightarrow O_2^-$$
$$O_2^- + e^- \Leftrightarrow 2O^-$$

The electron transfer from the conduction band to the chemisorbed oxygen results into the decrease in the electron concentration. As a consequence, an increase in the resistance of the SnO2 is observed.

It is well known that the LPG consists of CH_4, C_3H_8 and C_4H_{10} etc. In these molecules the reducing hydrogen species are bound to carbon therefore the LPG dissociates less easily into the reactive reducing components on the SnO_2 surface. When the SnO_2 is exposed to reducing gas like LPG, the LPG reacts with the chemisorbed oxygen thereby releasing an electron back to the conduction band which decreases the resistance of the SnO_2[20-27]. The overall reaction of the LPG with the chemisorbed oxy-

gen can be explained as follows –

$$C_nH_{2n+2} + 2O^- \rightarrow H_2O + C_nH_{2n}O^- + e^-$$

When the nano-sized SnO_2 is heated at a temperature of 200-350°C, the reaction products do not desorb from the film surface. Nevertheless, they cover the sensing sites on the surface of the film which prevents the further reaction of the LPG with chemisorbed oxygen. Subsequently, no appreciable change in the resistance of the film is observed.

At temperature 375°C, the reaction products may get desorbed immediately after their formation providing the opportunity for new gas species to react with the sensing sites on the film surface. Thus, the LPG reacts most effectively with chemisorbed oxygen at such particular temperature, which results in the significant decrease in the resistance of the film. Therefore, the maximum sensitivity of the nano-sized SnO_2 towards LPG is expected at such particular temperature.

At higher temperatures (>375°C), the amount of the adsorbed oxygen is less and therefore, a lesser amount of ionic species are formed. Therefore, in presence of the LPG, the probability of the reduction reaction of the gas with chemisorbed oxygen is less, which results into a very small change in resistance of the film at higher temperatures. Therefore, the nano-sized SnO_2 operates as a sensing element to the LPG only within a specific temperature window. In the present case, the optimum operating temperature for the nano-sized SnO_2 is 375 °C at which the sensor sensitivity attains its maximum value.

When the nano-sized SnO_2 was doped with Fe, the improvement in the sensitivity to LPG is observed at all the operating temperatures. It is known that the reactivity of oxides in acid-base reactions depends on the electronegativity of cations M^{n+} : $\chi = \chi_o (2n+1)$, where χ_o is the Pauling electronegativity and n is the ion charge [28-30]. The Pauling electronegativities of Fe-O and Sn-O are 1.83 and 1.96 in Pauling units [29]. Therefore, the adsorption of gas molecules at Lewis acid sites increases when the SnO_2 doped with Fe. Also, the Fe_2O_3 facilitates the changing of the metal oxidation state with preserving the original oxide phase. As a result, the complete oxidation of intermediates occurs effectively at the center of Fe_2O_3. Due to the above mentioned two reasons the improvement in the LPG sensitivity of Fe doped nano-sized SnO_2 was observed.

IV. CONCLUSIONS

The Fe doped nano-sized SnO_2 powder was synthesized by a simple chemical co-precipitation method and its LPG sensing properties were investigated. The following main findings resulted from the present investigation –

- We have successfully synthesized the Fe doped nano-sized SnO_2 powder at low cost by using a chemical co-precipitation method using $SnCl_4$, $5H_2O$, $FeCl_3$ and NH_4OH, as starting materials and water as a carrier. The resulting powder was characterized by XRD measurements, TGA and TEM.
- The crystallite size is found to be smallest when the as-prepared powder was calcinied at 800 °C for 2 h. However, the crystallite size increases with the increase in the calcination temperature.
- The operating temperature significantly affects the sensitivity of the synthesized Fe doped nano-sized SnO_2 powder to the LPG. The sensitivity to 75 ppm of LPG is maximum at an operating temperature 350 °C and it was found to be ~ 504.30 %.The response time was nearly 3 to 5 sec and the recovery time was found to be 8 to 10 sec.
- It was shown that the Fe doped nano-sized SnO_2 can be reliably used to monitor the concentration of LPG over the range (25-75 ppm).

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