

LPG gas sensing performance of nanostructured CdSnO₃ thin films

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ABSTRACT

Nanostructured CdSnO₃ thin films were prepared by spray pyrolysis technique. The nanostructured CdSnO₃ film showed selectivity for LPG gas over other conventional gases. The maximum LPG response of 1460 for the sample S2 at 350 °C was achieved. The quick response ($T_{\text{Response}} = 5$ s) and fast recovery ($T_{\text{Recovery}} = 11$ s) are the main features of this film. Additionally, the stability of the prepared sensor has been studied. As prepared thin films were studied using XRD, FE-SEM, and EDAX to know crystal structure, surface morphology, and elemental composition, respectively. The results are discussed and interpreted.

Keywords: Nanostructured perovskite CdSnO₃; Microstructure property; Conductivity; LPG gas response; Stability; Response and recovery of sensor

1. INTRODUCTION

Increasing requirements for environmental monitoring, public security, domestic safety, space crafts, air-quality, medical diagnosis, detection of explosive toxic gases and sensor networks have led to growing interest in high- performance gas sensor. It is well known that the gas response, selectivity and response and recovery time are the three most important parameters in designing semiconductor metal oxide gas sensor [1]. Cadmium stannate also possesses excellent chemical and thermal stability. Nanostructured materials exhibiting small particle size and large surface area may be applied for various gas sensors application [2].

LPG (Liquefied petroleum gas) is highly inflammable gas. It is explosively utilized in industrial and domestic field as fuel. It is referred as town or cooking gas. This gas is potentially hazardous because explosion accidents might be caused when it leaks out easily. So it is a great demanded for accurate and emerged challenge for gas sensors to monitor LPG [3]. The focus is on the development of new sensing materials to improve gas response, selectivity and stability of sensors and also on the development of new and better fabrication techniques to ensure reliability, safety, and reproducibility and reduce the cost.

Cadmium oxide and tin oxide are both promising materials for their applications as windows and buffer layers in thin film solar cells. They are n-type semiconductor compounds and have good transparency in the visible region [4,5]. The band gap energy of the CdO film

lies between 2.29 to 2.73 eV depending on the growth conditions [6]. SnO₂ thin film have band gap energy about 3.6 eV. It is expected that the homogeneous alloying of these materials will have intermediate optical properties between those of pure CdO and SnO₂. Also interest in tin-based oxides with the perovskite crystalline phase of the form ABO₃ for gas-sensing applications has recently grown [7]. Perovskite materials exhibit many interesting and intriguing properties from both the theoretical and the application point of view. Magneto resistance, ferroelectricity, superconductivity, spin dependent transport, charge ordering, high thermo power and the interplay of structural, magnetic and transport properties are commonly observed features in this family. These compounds are used as sensors and catalyst electrodes in certain types of fuel cells [8] and are candidates for memory devices applications [9]. Cadmium stannate (CdSnO₃), a typical compound with a cubic perovskite lattice, shows quite attractive electrical properties [10].

A variety of techniques have been employed to prepare nanostructured CdSnO₃ thin films. These include solid-state reaction [11] and chemical co-precipitation method [12]. Among these techniques, spray pyrolysis has proved to be simple, reproducible and inexpensive, as well as suitable for large area applications. In addition, spray pyrolysis opens up the possibility to control the film morphology and particle size in the nanometer range [13-15]. Out of these approaches spray pyrolysis is a versatile technique for deposition of metal oxides. The deposition of nanostructured CdSnO₃ thin films using spray pyrolysis technique is advantage as it can produce highly crystalline and stratified structures [16]. This is important feature since high crystallinity and having layered formation can allow for greater gas response [17]. Current years have seen increased interest in gas sensing application of CdSnO₃. Moreover, some other studies have been performed concerning cross-sensitivity of CdSnO₃ with respect to butane, gasoline, carbon monoxide and methane [18].

In the present investigations, nanostructured CdSnO₃ thin films with different spraying time of the solution were prepared by spray pyrolysis technique. Structural properties, surface morphology, and elemental composition were studied using X-ray diffraction (XRD), field effect scanning electron microscope (FE-SEM), and energy dispersive of X-rays (EDAX) respectively. These nanostructured CdSnO₃ thin films were tested for sensing different conventional gases: LPG, CO₂, H₂, NH₃, C₂H₅OH, CH₃OH, acetone, Cl₂, H₂S and were observed to be most sensitive to LPG at 350 °C.

2. EXPERIMENTAL

2. 1. Preparation of nanostructured CdSnO₃ thin films

All chemicals were of analytical grade purchased from Loba Chem. (Made-Mumbai), which are used without further purification. All solutions were prepared with the deionized water. The glass substrates (75mm×25mm×1.2mm) supplied by Blue Star, Mumbai were used. CdSnO₃ thin films were prepared by using the spray pyrolysis setup as described elsewhere [17]. Aqueous solutions (0.05 M) of CdCl₂·2H₂O and SnCl₄·5H₂O in 1:1 proportion were chosen for preparation of the thin films. The stock solution was delivered to nozzle with constant and uniform flow rate of 70 ml/h. by compressed air. Various parameters such as nozzle-to-substrate distance (30cm), deposition time (10 min, 20 min, and 30 min) and flow rate of solution (5 ml min⁻¹), deposition temperature (350 °C) and concentration (0.05 M) were optimized to get good quality films. Thus the films with different spraying time of: 10 min, 20 min, and 30 min were obtained and referred to as S1, S2 and S3 respectively.

The as prepared nanostructured CdSnO₃ thin film samples were fired at 500 °C for 1 h. After 1 h, the films were slowly cooled to room temperature. The CdSnO₃ thin films samples were further used for structural, microstructural, electrical characterization and gas sensing performance.

2. 2. Characterization of nanostructured CdSnO₃ thin films

X-ray diffraction patterns (XRD) were recorded by a Miniflex model, Rigaku, Japan with CuK α radiation ($\lambda = 1.542 \text{ \AA}$) in the range of 20-80° (2θ). The surface morphology of the samples and the percentage of constituent elements were evaluated by using a field emission scanning electron microscope coupled with energy dispersive spectrophotometer (FE-SEM, JEOL. JED 6300). Gas sensing performance was examined at different operating temperature and concentration using static gas sensing system.

3. RESULT AND DISCUSSION

3. 1. Determination of film thickness

The film thickness was measured by a weight difference method [19]. In order to measure the thickness of the thin films by using weight difference method, error and accuracy was found to be $\pm 5 \%$ nm. The thickness, sample weight and sample area are related as:

$$t = M/A \cdot \rho \text{ ----- (1)}$$

where, M is the weight of the sample in gm,

A the area of the sample in cm²

ρ the materials density in gm cm⁻³.

Table 1. Variation of spray deposition time with thickness of the films (nm).

Sample No.	Spray deposition time (min)	Thickness (nm)
S1	10	128
S2	20	136
S3	30	143

It is observed from Table 1 that as spray deposition time goes on increasing, the thickness of the film increases.

3. 2. Structural properties

3. 2. 1. Crystal structure

The average crystallite size of nanostructured CdSnO₃ thin film samples were estimated by using the Scherrer formula.

$$D = 0.9\lambda/\beta\cos\theta \quad \text{-----} (2)$$

where,

D = Average crystallite size

λ = X-ray wavelength (1.542 Å)

β = FWHM of the peak

θ = Diffraction peak position.

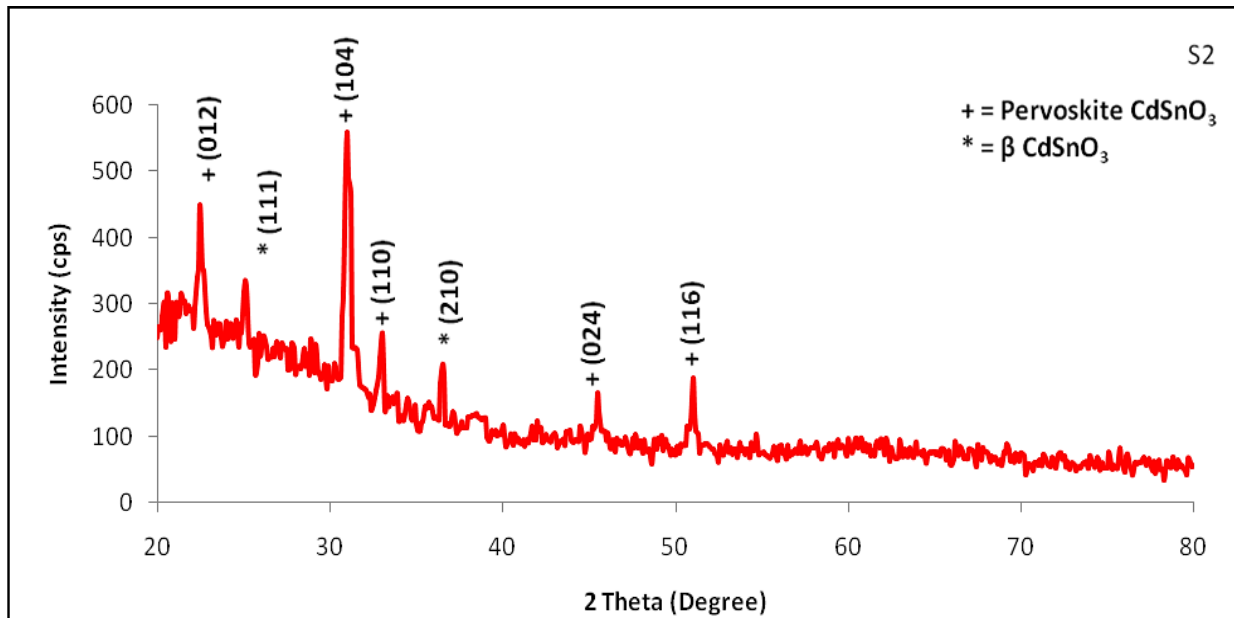


Fig. 1. X-ray diffractogram of most sensitive (Sample = S2) nanostructured CdSnO₃ thin film samples.

Fig. 1 shows the X-ray diffractogram of nanostructured CdSnO₃ thin film sample S2. The observed peaks are matching well with the standard JCPDS data of CdSnO₃ [20,21] possessing pervoskite and β - CdSnO₃ structure. No phases corresponding to impurities are detected in either pattern. It is clear from Figure 1 that, the films exhibited strong orientation along c-axis (104). The average crystalline size was observed to be 18.16 nm.

3. 3. Surface morphology using field emission scanning electron microscope (FE-SEM)

3. 3. 1. Field emission scanning electron microscope

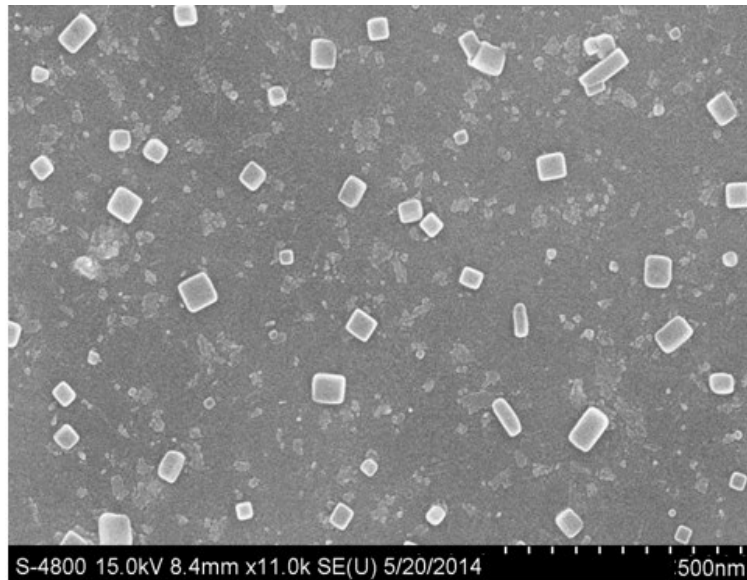


Fig. 2. FE-SEM images of nanostructured CdSnO₃ thin film samples (Most sensitive sample = S2).

Fig. 2 shows the FE-SEM image of most sensitive nanostructured CdSnO₃ thin film sample S2. FE-SEM micrograph is showing topography of the film surface. The morphology of the grains was cubic in shape. The grain size was observed to be 26.69 nm.

3. 4. Quantitative element analysis (EDAX).

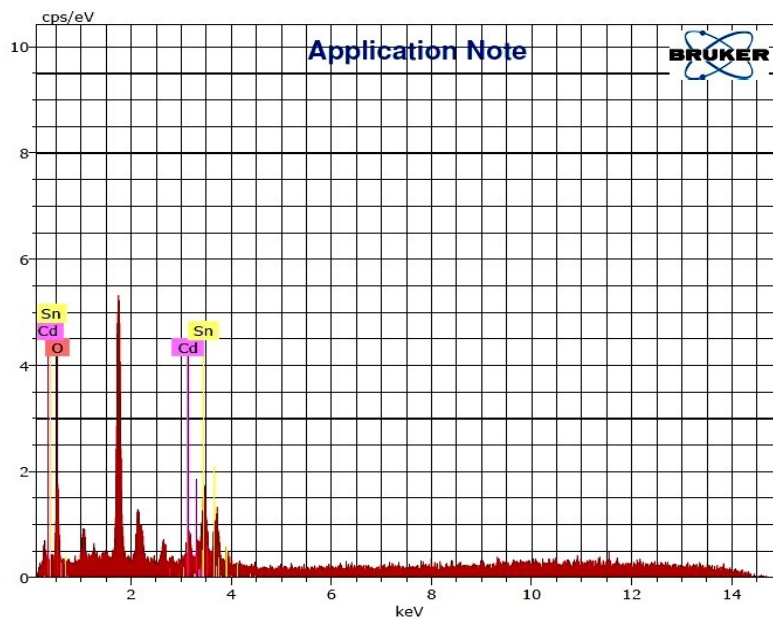


Fig. 3. Elemental analysis of nanostructured CdSnO₃ thin film (Most sensitive sample = S2).

The elemental compositions of the as prepared products were studied by EDAX and the results are displayed in Fig. 3. The data confirm that the sample (Most sensitive sample = S2) are composed of Cd, Sn and O.

Stoichiometrically expected at% of Cd, Sn and O is 20:20:60. The at % of Cd, Sn and O in our sample are 23.94, 17.90, and 58.16 which is not as per the stoichiometric proportion and observed to be the oxygen deficient, leading to the semiconducting nature of CdSnO₃.

4. GAS SENSING PERFORMANCE OF THE SENSORS

4. 1. Measurement of response

Gas response (S) of the sensor is defined as the ratio of change in conductance to the conductance of the sensor on exposure of target (at same operating conditions).

$$S = \frac{I_g - I_a}{I_a} \quad \text{----- (3)}$$

where,

I_a = the conductance of the sensor in air

I_g = the conductance on exposure of a target gas.

4. 2. Gas response and operating temperature

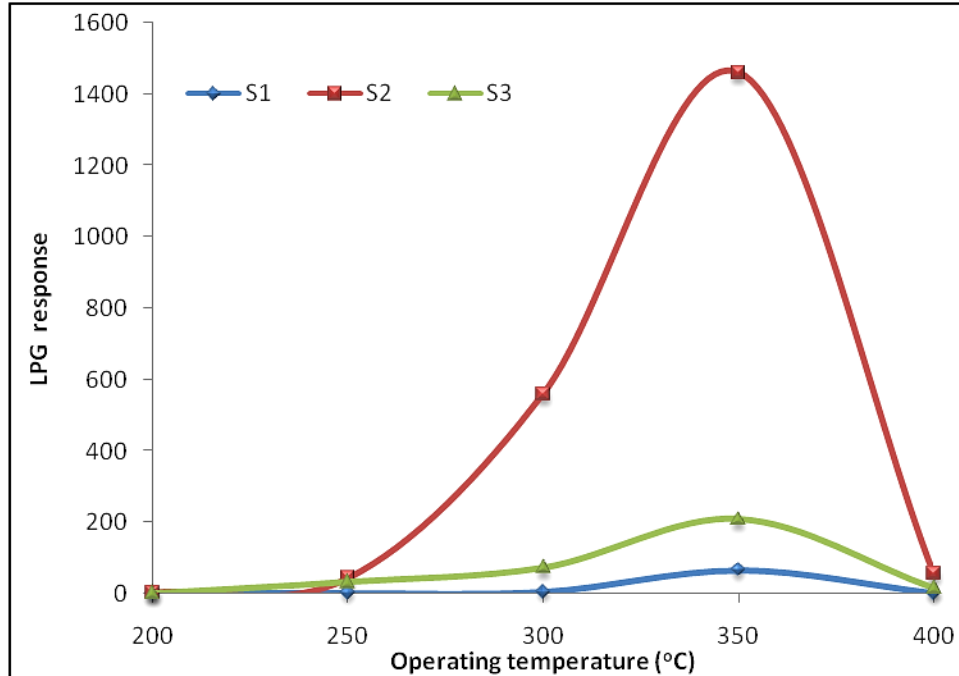


Fig. 4. Gas response of pure nanostructured CdSnO₃ thin films with operating temperature.

The gas-sensing performance of the nanostructured thin films was tested using static gas-sensing system [2]. The heater was fixed on the base plate to heat the sample under test.

Operating temperature was changed from room temperature to 500 °C. The current passed through the heating element. Cr–Al (Chromel-Alumel) thermocouple was used to sense the operating temperature of the sensor. The output of the thermocouple was connected to a digital temperature indicator. A gas inlet valve was fitted at one of the ports of the base plate. The required gas concentration inside the static system was achieved by injecting a known volume of a test gas using a gas-injecting syringe.

The electrical connections were brought out from the system to connect dc voltage source and digital picoammeter. A constant voltage (5V) was applied to the sensor, and the current was measured by a digital picoammeter. The air was allowed to pass into the glass chamber before start of (every) new gas exposure cycle. The required gas concentration (500 ppm) inside the dome was achieved by injecting predefined known volume of the test gas in chamber filled with ambient air at atmospheric pressure. Values of current before and after exposure of gas were recorded. Values of conductance were determined to obtain the gas response.

The operating temperature is an important functional characteristics for semiconductor metal oxides. Fig. 4 shows the relationship between the operating temperature and gas response of the sensors to 500 ppm LPG. It can be observed from Fig. 4, that the LPG response of sample S2 is higher at 350 °C as compared to those of S1, and S2. It is well-known that the response of the metal–oxide semiconductor sensors is mainly determined by the interactions between a target gas and the surface of the sensors. Due to the greater surface area of nanostructured materials, its interaction with the adsorbed gases is stronger, leading to higher gas response [13].

4. 3. Selectivity of LPG gas against other conventional gases

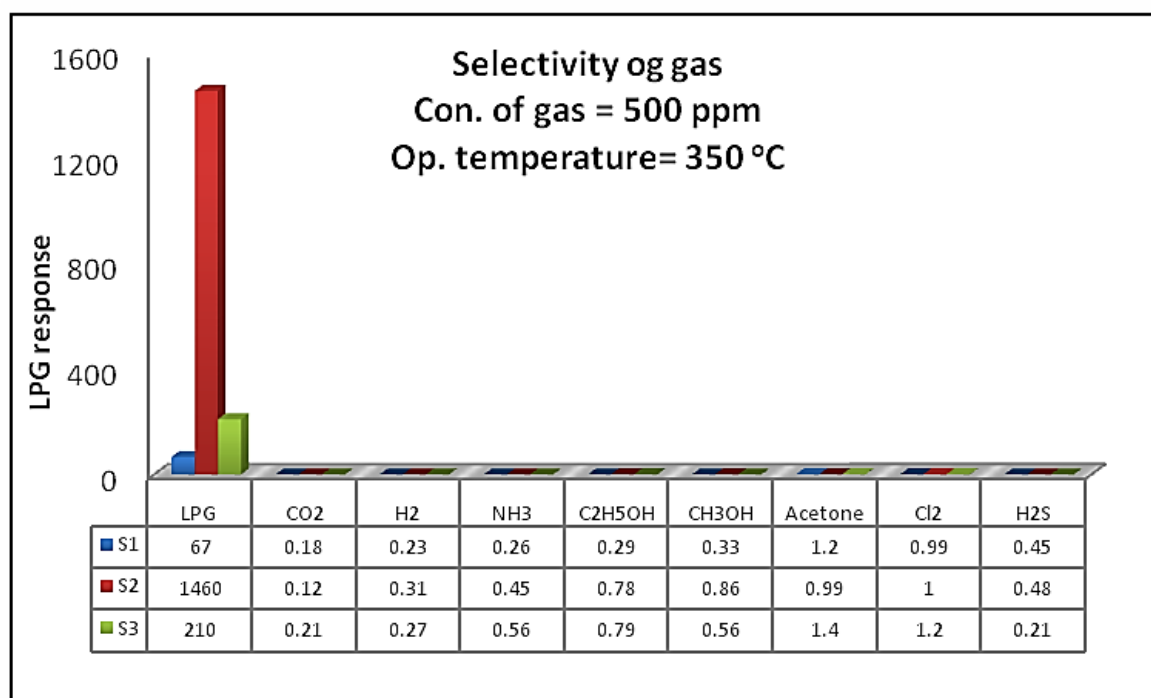


Fig. 5. Selectivity of nanostructured CdSnO₃ thin films for LPG gas.

Selectivity or specificity is defined as the ability of the sensor to respond to certain gas in the presence of the other gases. Selectivity of nanostructured CdSnO₃ thin film sensors is measured at an operating temperature of 350 °C.

Fig. 5 depicts the bar diagram to indicate LPG, selective ability of the sensor. It is clear from figure that the responses of all samples to CO₂, H₂, NH₃, C₂H₅OH, CH₃OH, acetone, Cl₂ and H₂S gases are lower as compared to their response to LPG.

4. 4. Response and recovery of sensor

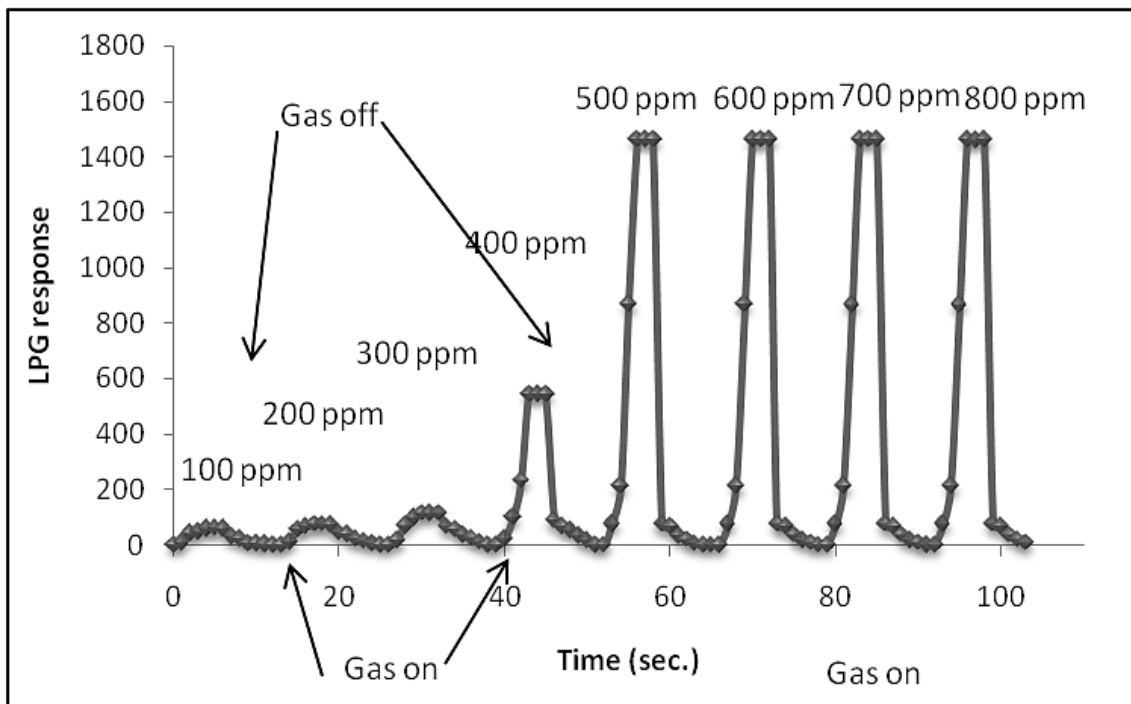


Fig. 6. Response and recovery of the sensor.

Response and recovery times are important factors of gas sensors: fast response and recovery can usually allow a real time detection.

The response and recovery of the nanostructured CdSnO₃ thin film (sample S2) sensor on exposure of various concentration (100 ppm to 800 ppm) of LPG at 350 °C are represented in Fig. 6.

The response is quick (5 s) and recovery is fast (11 s). The remarkably shorter sensor response and recovery time of the nanostructured CdSnO₃ thin film can be attributed to the rapid diffusion of the target gas toward their sensing surface.

4. 5. Stability of sensor

The stability of the CdSnO₃ sensor were measured by repeating the test many times (20 days). During the test, no significant variation was observed as shown in Fig. 7.

The obtained results show that both gas response and electrical conductance were reproducible.

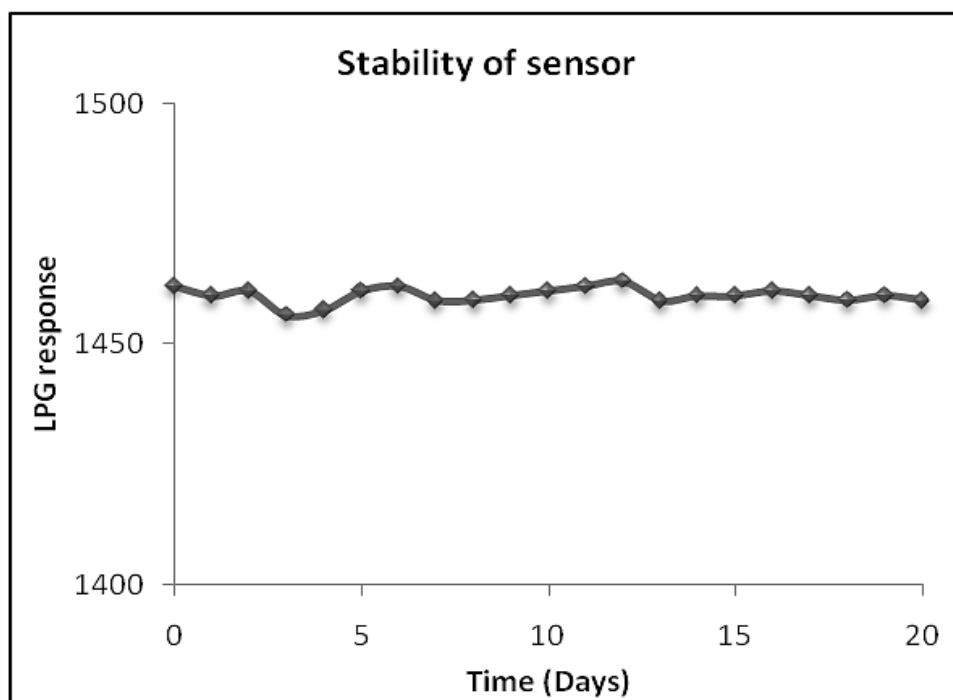
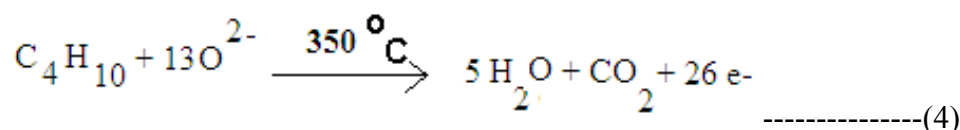


Fig. 7. The sensing stability studies for CdSnO₃ (most sensitive sample = S2) thin film at an operating temperature of 350 °C.

5. SENSING MECHANISM

When reducing gas such as LPG react with different oxygen species, complex series of reaction take place, ultimately oxidizing LPG as:



This shows n-type conduction mechanism. Thus on oxidation, single molecule of gas liberates number of electron in conduction band, results in increase in conductivity of the sensor.

We found that the gas response increases with operating temperature, reach to their respective maxima at particular temperature and then decreases with further increase in operating temperature. Increase in operating temperature causes oxidation of large number of gas molecules, producing very large number of electrons. Therefore, the conductivity increases.

This is the reason, why the gas response increases with operating temperature. The temperature at which the gas response is maximum, is the actual thermal energy needed to activate the material for progress the reaction.

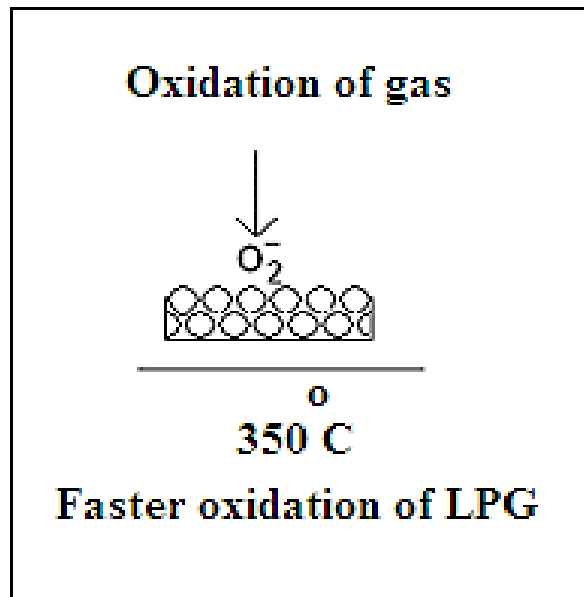
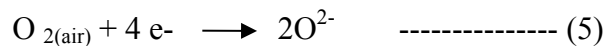


Fig. 8. Gas sensing mechanism.

However, the response decreases at higher operating temperature, as oxygen adsorbates are desorbed from the surface of the sensor. Also, at higher temperature, the carrier concentration increases due to intrinsic thermal excitation. This may be one of the reasons for decreased gas response at higher temperature [22]. For nanostructured CdSnO₃ thin film, a response to LPG at 350 °C is observed. The selective gas response of the sensor to LPG at 350 °C may be attributed to the oxidation of LPG gas by oxygen species on the surface (shown in Fig. 8).

The working principle of thin film semiconducting gas sensors is based on the change in the electronic conductivity of the semiconductor material upon exposure to the target gas. The interaction of the target gas molecule with the semiconductor surface adsorbates. Atmospheric oxygen molecules (O₂) are adsorbed on the surface of the thin film. They capture electrons from the conduction band of the thin film material as:



It results in decreasing electronic conductivity of the film.

6. CONCLUSIONS

- a) In summary, nanostructured CdSnO₃ thin films have been prepared by spray pyrolysis technique at different spray deposition times and the films were fired at 500 °C.
- b) The physical, structural, surface morphological and microstructural properties confirm that the as-prepared CdSnO₃ thin films were nanostructured in nature.
- c) The elemental analysis confirmed that the as-prepared thin films were nonstoichiometric in nature.
- d) Our results indicate that nanostructured CdSnO₃ can significantly improve the LPG sensing properties.

- e) The sensor based on nanostructured CdSnO₃ shows enhanced response and selectivity to LPG gas at operating temperature 350 °C.
- f) Rapid response, recovery and stability study indicates that nanostructured CdSnO₃ is potential material to be used as an effective for LPG sensor, which is one of the main features of this sensor.

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References

- [1] N. G. Cho, H. S. Woo, J. H. Lee, I. D. Kim, *Chem. Commu.* 47 (2011) 11300-11302.
- [2] G. H. Jain, L. A. Patil, M. S. Wagh, D. R. Patil, S. A. Patil, D. P. Amalnerkar, *Sensors and Actuators B: Chemical* 117 (2006) 159-165.
- [3] P. P. Sahay, R. K. Nath, *Sensors and Actuators B: Chemical* 117 (2006) 159-165.
- [4] B. G. Lewis and D. C. Paine, *MRS Bulletin* 25 (2000) 22-27.
- [5] X. Li, Timothy A. Gessert, and T. Coutts, *Applied Surface Science* 223 (2004) 138-143.
- [6] M. M. Islam, M. R. Islam, and J. Podder, *Journal of Bangladesh Academy of Science* 32 (2008) 97-105.
- [7] J. W. Fergus, *Sensors and Actuators B*, 123 (2007) 1169-1179.
- [8] A. Kulkarni, F.T. Ciacchi, S. Giddey, C. Munnings, S.P.S. Badwal, J.A. Kimpton, D. Fini, *Int. Journal of Hydrogen Energy* 37 (2012) 19092-19102.
- [9] J. M. D. Coey, M. Viret; S. Von Molnar, *Advances in Physics* 48 (1999) 167-293.
- [10] R.D. Shannon, J.L. Gillson, R.J. Bouchard, *J. Phys. Chem. Solids* 38 (1977) 819-824.
- [11] Y. Li Liua, Y. Xingb, H. Feng Yanga, Z. Min Liua, Y. Yanga, G. Li Shena, R. Qin Yua, *Anal. Chim. Acta* 527 (2004) 21-26.
- [12] T. S. Zhang, P. Hing, Y. Li, and J. C. Zhang, *Sensors and Actuators B* 60 (1999) 208-215.
- [13] R. H. Bari, S. B. Patil, A.R. Bari, G. E. Patil, J. Aambekar, *Journal of Sensors & Transducers*. 140 (2012) 124-132.
- [14] X. H. Wu, Y. D. Wang, Y. F. Li, and Z. L. Zhou, *Mater. Chem. Phys.* 77 (2002) 588-593.
- [15] T. S. Zhang, Y. S. Shen, R. F. Zhang, and X. Q. Liu, *Mater. Lett.* 27 (1996) 161-164.
- [16] T. S. Zhang, Y. S. Shen, and R. F. Zhang, *Mater. Lett.* 23 (1995) 69-71.
- [17] G. E. Patil, D. D. Kajale, S. D. Shinde, N. K. Pawar, V. B. Gaikwad, and G. H. Jain, *Journal. of Nanoengineering. and Nanomanufacturing* 2 (2012) 1.

- [18] L.A. Patil, A.R. Bari, M.D. Shinde, Vinita Deo, *Sensors and Actuators B: Chemical*, 149 (2010) 79-86.
- [19] V. B. Patil, G. S. Shahane and L. P. Deshmukh, *Mate. Chem. and Phys.* 80 (2003) 625-632.
- [20] JCPDS card no. 34-0758.
- [21] JCPDS card no. 34-0885.
- [22] Y. Li, W. Wlodarski, K. Galatsis, S. Moslih, J. Cole, S. Russa, N. Rockelmann, *Sensors and Actuators B: Chemical* 83 (2002) 160-163.

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