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Nanostructured Spray Pyrolysis Zinc Doped CdO Thin Films for LPG Gas Sensor

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ABSTRACT

Semiconductor metal oxide fabricated for application in chemiresistor gas sensors and approaches used for synthesis of metal oxides and with surface modified is improved gas sensing performance. In present work, nanostructured pure CdO and Zn doped CdO thin films has been synthesized by employing spray pyrolysis technique and evaluated for LPG gas sensing (Gas response = $S \sim 1900$) at operating temperature 350 °C with 500 ppm. Prepared thin films were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray (EDAX) spectroscopy, transmission electron microscopy (TEM) and UV-spectroscopy. Sensor showed the quick response (6 s) and fast recovery times (8 s) respectively.

1. Introduction

Recently the atmospheric pollution has become a global issue. Gases from auto and industrial exhausts are polluting the environment. The sensors are required basically for measurement of physical quantities and for monitoring working environments. Depending on the gas and its concentration in the atmosphere the electrical conductivity is different. It has been demonstrated that the sensor response could remarkably increase as the average crystallite size decreased to below 10 nm. Among them nanostructured materials exhibiting small particle size and large surface area may be applied for various gas sensors application [1]. Nanostructured CdO is known as a potential material for gas sensor applications. It is inevitable to have a continuous control of these hazardous gases in an atmosphere [2].

CdO is an n type semiconductor with a well-established direct band gap at approximately 2.5 eV [3] and an indirect one experimentally found at 1.98 eV [4]. Faizullah studied on the (Al, N) doped CdO thin films for optical and electrical properties [5]. Zhou et al reports on CdO-ZnO nanocomposites for enhanced detection for ethanol and CO gas sensor [6, 7].

Semiconductor metal oxide gas sensors improve their gas response, selectivity, response and recovery time due to nanocrystalline nature of the material associated, which is the most attractive quality of nanomaterials. Basically the improvements are because of the high surface area to volume ratio and smaller crystallite size compared to conventional microcrystalline materials [8].

In present work we have modified the surface of CdO thin films using Zn catalyst to improve gas sensing performance. Therefore, spray pyrolysis technique was employed to prepare pure and Zn doped CdO thin films because the technique is simple and involves low cost equipment and raw materials. The technique involves a simple technology in which an ionic solution (containing the constituent elements of a compound in the form of soluble salts) is sprayed over heated substrates [9]. By this method dopants can be easily introduced into the matrix of the film by using appropriate precursors. Additives or dopants enhance the properties of the sensors, such as gas response, selectivity, lowering the operating temperature, response and recovery time etc. [10-12].

2. Experimental Methods

2.1 Preparation of Pure Nanostructured CdO Thin Films

The glass substrate was cleaned by an ultrasonic cleaner to make surface hydrophilic. 0.05 M of cadmium acetate dihydrates ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) was dissolved in deionized water. Solution was filled in a spray gun and was allowed to spray onto heated glass substrate at constant temperature 300 °C thus the films with spraying time of 20 min was obtained and referred to pure CdO. Details of spray pyrolysis were discussed elsewhere [13].

2.2 Preparation of Nanostructured Zn-Modified CdO Thin Films

As prepared mixture of precursor solution of cadmium acetate dihydrates (0.05 M) and doping solution of zinc acetate dihydrate (0.05 M) in mentioned percentage variation was sprayed through a glass nozzle of 0.1 mm bore diameter on heated glass substrate at 300 °C \pm 10 °C temperature with constant flow spray rate 7 mL/min by means of air as a carrier gas. Thus the modified films of 20 min spraying time with different dopant volume (% Zn) 3, 5 and 7 were obtained and referred to R1, R2, and R3 respectively. Optimized parameters for the spray deposition of nanostructure pure CdO and Zn doped CdO thin films were tabulated in Table 1.

Table 1 Process parameters for the spray deposition of nanostructure CdO and Zn doped CdO thin films

Spray parameter	Optimum value/item
Nozzle	Glass
Nozzle to substrate distance	30 cm
Cadmium acetate dihydrate solution concentration	0.05 M
Zinc acetate dihydrate solution concentration	0.05 M
Volume % of Zn	3, 5 and 7
Spray deposition time	20 min.
Solvent	Deionised water
Solution flow rate	7 mL/min
Carrier gas	Compressed air
Substrate temperature	300 °C

2.3 Optimized Parameters

As the prepared nanostructured pure CdO and Zn-CdO, thin film samples were annealed at 500 °C for 1 h.

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2.4 Details of Gas Sensing System

The gas sensing performance were carried out using a static gas chamber to sense LPG in air ambient and the experimental set up is described elsewhere [13]. The nanostructured pure CdO and Zn doped CdO thin films were used as the sensing elements. Cr-Al thermocouple is mounted to measure the temperature. The output of thermocouple is connected to temperature indicator. Gas inlet valve fitted at one of the ports of the base plate. The air was allowed to pass into the glass chamber before start of every new gas exposure cycle. Gas concentration (500 ppm) inside the static system is achieved by injecting a known volume of test gas in gas injecting syringe. The conductance of the sensor in dry air was measured by means of conventional circuitry by applying constant voltage (5 V) and measuring the current by picoammeter. The conductance was measured both in the presence and absence of test gas.

The gas response (S) is defined as the ratio of change in conductance in gas to air to the original conductance in air.

$$S = G_g - G_a / G_a \quad (1)$$

Where, G_a = the conductance of the sensor in air, G_g = the conductance on exposure of a target gas.

3. Results and Discussion

3.1 Structural Studies

The crystal structure of films was analyzed with X-ray diffractometer (Miniflex Model, Rigaku, Japan, Advanced D8) by using Cu-K α lines ($\lambda = 1.542 \text{ \AA}$). Fig. 1 shows XRD pattern of pure CdO and Zn doped CdO thin films. The film show different planes of orientation along (111), (200), (220) and (311) deposited at 300 °C indicating the formation of CdO nano particles having cubic structure. All the films indicate a preferred orientation along (111) plane. All the planes are very well matches with the standard JCPDS data (JCPDS data card no. 05 - 0640) of CdO. The average crystallite size of pure CdO and Zn doped CdO have been obtained from the full width at half maximum (β) by applying Scherrer's formula [13], and tabulated in Table 2.

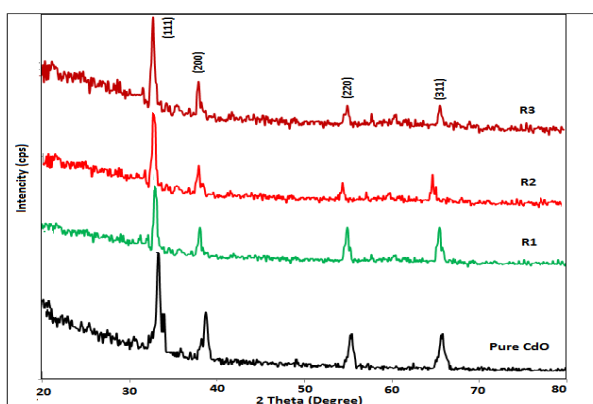


Fig. 1 X-ray diffractogram: (a) pure CdO and (b) Zn doped CdO (R1,R2 and R3) nanostructured thin film

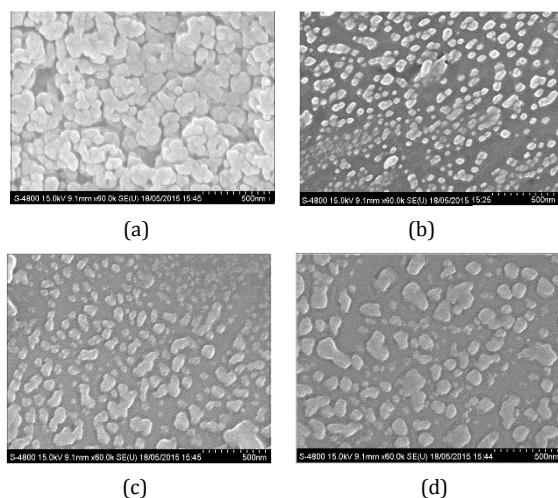


Fig. 2 FESEM morphology of deposited nanostructured (a) pure CdO and (b-d) Zn doped CdO thin films

3.2 Morphological Studies

Surface morphology was examined by field emission scanning electron microscope (FE-SEM Hitachi S 4800) coupled with EDAX. The FESEM micrograph shows the surface topography of pure CdO and Zn doped CdO nanocrystalline thin film in Fig. 2(a-d). The film shows the nanocrystalline nature and uniform distribution of mixed spherical and cubical grains were observed. The average grain size estimated from FE-SEM were represented in Table 2.

Table 2 Measurement of Zn content, crystallite size, grain size, optical band gap energy and activation energy

Sample	Zn%	Crystalline size from XRD (nm)	Grain size from FESEM (nm)	Optical band gap energy eV	Activation energy (ΔE) eV
Pure CdO	-	17	19	2.61	0.44
R1	3	18	21	2.75	0.41
R2	5	20	22	2.83	0.37
R3	7	23	24	2.96	0.31

The crystallite sizes were found to be within the range from 17 to 23 nm. This confirms the good crystallinity of the samples. The grain size obtained from FE-SEM slightly matches with the crystallite size obtained from XRD. Activation energy is related to conductivity of the samples. From Table 2 it was found that crystallite size, grain size and optical band gap energy goes on increasing with increase of Zn % in CdO while activation energy decreases. This behavior may be due to the improvement in crystalline size, grain size and change in structural parameters.

3.3 Elemental Compositional Studies

Table 2 shows the elemental composition of the films determined by EDAX. Theoretically expected stoichiometric mass % of Cd and O in CdO are 50.00 and 50.00 respectively. Observed mass % and at % of Zn, Cd and O was represented in Table 3.

Table 3 Elemental compositions of thin films

Element	Observed							
	Pure CdO		R1		R2		R3	
	mass %	at %	mass %	at %	mass %	at %	mass %	at %
Cd	54.67	53.12	31.57	49.29	39.73	40.44	50.82	46.59
O	45.33	46.88	55.78	50.59	39.52	59.40	27.54	53.21
Zn	-	-	12.65	00.12	20.75	00.16	21.64	00.20
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

All the deposited thin films were observed to be nonstoichiometric in nature. It is clear from Table 2 that at % of Zn goes on increasing with decreasing at % of oxygen goes on decreasing with the Zn % in CdO.

3.4 Microstructural Studies

Microstructure property was studied using transmission electron microscope (TEM, TECNAI G220-TWIN FET, NETHERLAND: CM 200 Philips 200 kV HT).

It is clear from TEM image (Fig. 3) that the grains are nanocrystalline in nature which are smaller than 20 nm with nearly spherical in shape.

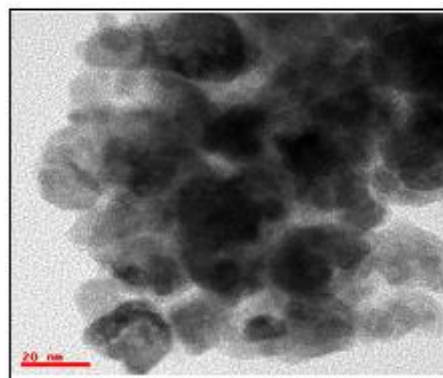


Fig. 3 TEM images of the nanostructured of most sensitive thin sample R2

3.5 Optical Band Gap Studies

Optical band gap studies were conducted using UV-VIS absorption spectroscopy (Shimadzu 2450 UV-VIS).

Fig. 4 shows the absorption spectra of pure CdO and Zn doped CdO. The absorption of deposited thin films were studied in the wavelength range 300 - 900 nm. The optical absorbance of the films decreases with the wavelength. These spectra reveal that as-grown pure CdO and Zn doped CdO thin films have more absorbance in the UV region and less absorbance in the visible and high wavelength region. The band gap energies of the samples were calculated from the absorption edges of the spectra. The slope drawn from the start of an absorption edge (the onset of absorbance) and horizontal tangent had drawn on absorption minimum and intercepted each other at some point. The vertical line drawn from this point on wavelength axis gave the absorption edge wavelength.

The value of λ (nm) was then used in the following relation to know band gap energy:

$$E_g = h\nu = hc/\lambda = (1240)/\lambda \text{ (nm)} \text{ eV} \quad (2)$$

Optical band gap energy was found to be 2.61 to 2.96 eV.

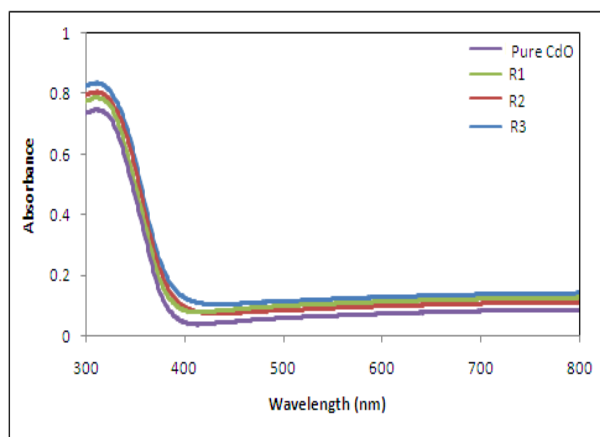


Fig. 4 The variation of relative absorbance with wavelength (nm) for nanostructured pure CdO and Zn doped CdO (R1-R3) thin films

3.6 Electrical Properties of the Pure and Modified Sensor

Electrical conductivity and gas sensing properties were checked using a static gas sensing system for different conventional gases.

3.6.1 Thermoelectric Power (TEP) Measurements

Measurement of thermo electrical power was conducted using TEP set up (Made-Pushpa agency-Hydrabad). Using TEP measurement set up, it indicates that as prepared pure and Zn-doped CdO thin films was n-type semi conductivity in nature.

3.6.2 I-V Characteristics

Fig. 5 shows the I-V characteristics of pure CdO and Zn doped CdO thin film at room temperature in the air atmosphere. The linearity in the graph indicate the ohmic nature of contact.

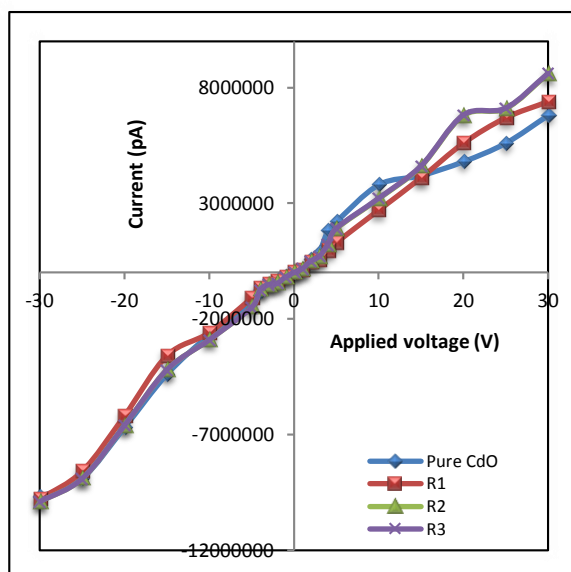


Fig. 5 I-V characteristics of nanostructured thin film sensors

3.6.3 Electrical Conductivity

Fig. 6 represents the variation of conductivity with temperature for pure CdO and Zn doped CdO thin films in air ambience for different operating temperature. The conductivity of these films goes on increasing with increase in temperature, indicating negative temperature coefficient (NTC) of resistance. This shows the semiconducting nature of the films. Electrical conductivity was calculated using the relation:

$$\sigma = \sigma_0 \exp(-\Delta E/kT) \quad (3)$$

Where, σ = conductivity, σ_0 = conductivity constant, k = Boltzmann constant, T = Temperature.

Activation energy (ΔE) was calculated from slope of $\log(\sigma)$ versus inverse of temperature curve at high and low temperature range. Activation energy was tabulated in Table 2.

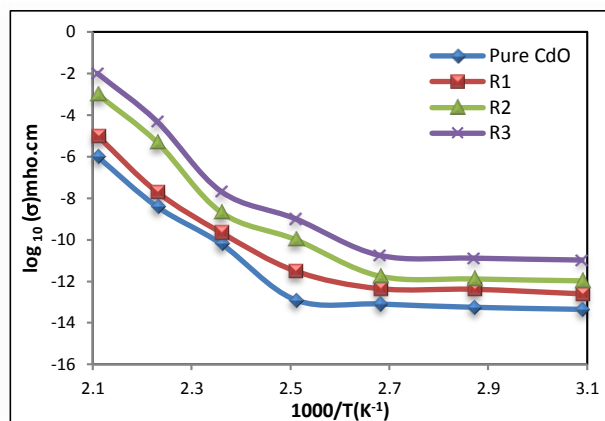


Fig. 6 Electrical conductivity of nanostructured thin film sensors

3.7 Sensing Performance of Zn-Modified Thin Film Sensors

3.7.1 Gas Response with Operating Temperature

Fig. 7 represents the variation in the gas response for different range of temperature for LPG gas. The temperature is an important parameter for gas sensing materials and designing of the sensor. The sensing materials have to appropriate temperature to achieve crystallization and structural evaluation. A number of experiments (5 cycles) have been carried out to measure the gas response as a function of operating temperature. All the time gas response of the sensor element has approximately constant value indicating the repeatability of the sensor at the same operating temperature. Among the pure CdO and Zn doped CdO samples (B1 and B3), the response of sample B2 is highest ($S = 1900$) at 350 °C. It may be due to optimum microstructural feature of sample B2.

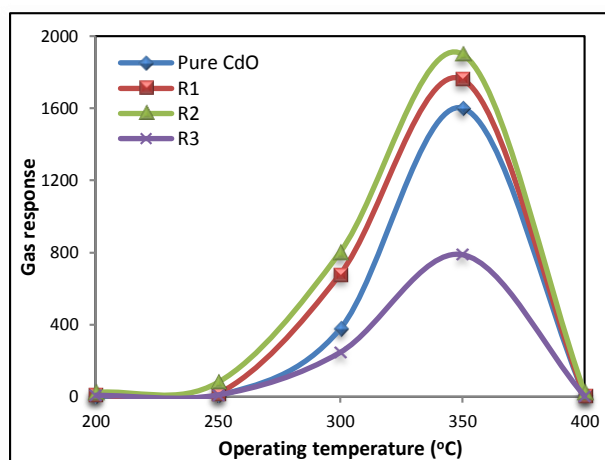


Fig. 7 Representing variation of gas response with operating temperature °C

3.7.2 Selectivity

It is clear from Fig. 8 that, Zn-modified thin film sample doped with (vol. 5%) Zn (sample R2), was observed to be the best LPG sensor, showing highest LPG response, highly selective against other gases along with highest speed of response. This could be the potential material (Zn doped CdO) to developed LPG sensor.

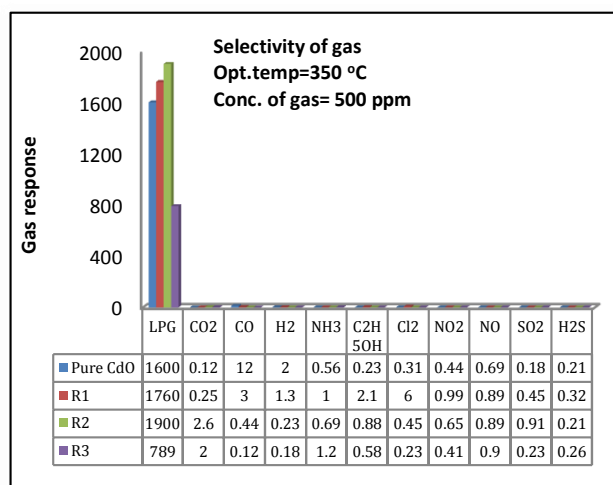


Fig. 8 Selectivity profile of nanostructured modified Zn doped CdO against various gases

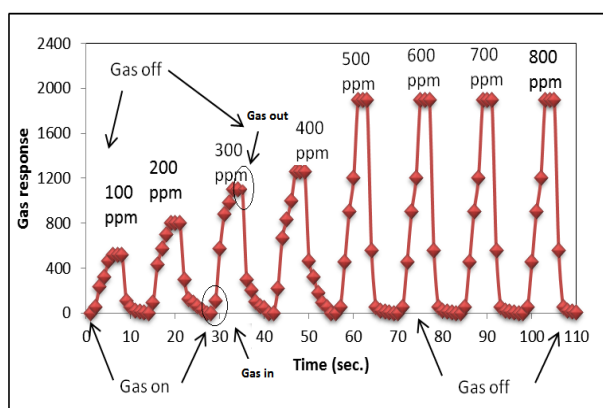


Fig. 9 Response and recovery time of (Most sensitive = R2) thin film sensor

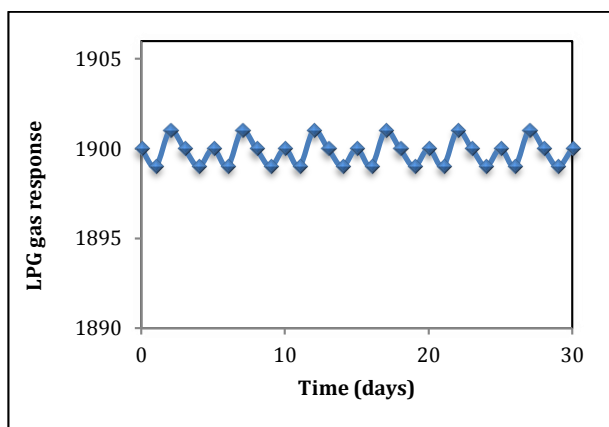


Fig. 10 The long term stability studies for (most sensitive sample = R2) thin film

3.7.3 Response and Recovery Time With Concentration of Gas (ppm)

Fig. 9 shows the response and recovery profile of thin film sample R2 (5% Zn-CdO) in presence of LPG gas at 350 °C. The variation of response of modified Zn doped CdO sample with LPG gas concentration is represented in Fig. 9. It is clear from the figure that the gas response goes on increasing with gas concentration up to 500 ppm (active region from 100 – 500 ppm) at 350 °C. The rate of increase in response was relatively larger up to 500 ppm and smaller beyond 500 ppm. Thus the active region of the sensor would be up to 500 ppm. This may be due to a restricted number of active sites, due to large lateral diameter and small amounts of oxygen vacancies on the surface. Very short response (6 s) and recovery times (8 s) are the important feature of the nanostructured Zn doped CdO sensor. The negligible quantity of the surface reaction products and their high volatility explain the fast recovery of the sensor.

3.7.4 Stability of Sensor

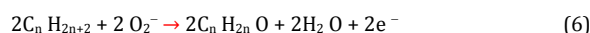
The long-term stability of sensors has also been investigated. Our sensors have been continuously operating for over one month for this experiment. Time dependence of average response for LPG gas concentration (500 ppm) at 350 °C is depicted in Fig. 10. The stable performance of the sensors is evident from this figure.

3.8 Gas Sensing Mechanism of LPG Sensor

The gas sensing mechanism of Zn doped CdO based LPG sensor is a surface controlled phenomenon i.e., it is based on the surface area of the thin film at which the LPG molecules adsorb and reacts with pre-adsorbed oxygen molecules. The oxygen chemisorption centers viz., oxygen vacancies, localized donor and acceptor states and other defects are formed on the surface during synthesis. These centers are filled by adsorbing oxygen from air. After some time equilibrium state is achieved between oxygen of Zn doped CdO thin film and atmospheric oxygen through the chemisorption process at room temperature [14]. The Zn doped CdO thin film interacts with oxygen by transferring the electrons from the conduction band to adsorbed oxygen atoms, resulting into the formation of ionic species such as O_2 , O_2^- , O^{2-} . The reaction kinematics may be explained by the following reactions:



The electron transfer from the conduction band to the chemisorbed oxygen results in the decrease in the electron concentration at surface of the thin film. As a consequence, an increase in the resistance of the thin film is observed. The conduction process in gas sensing is electronic and the chemisorption of atmospheric gases take place only at the surface of the Zn doped CdO thin film. The overall conduction in a sensing element, which will monitor the sensor resistance, is determined by the surface reactions resulting out from the charge transfer processes with the sensing element. In LPG molecules the reducing hydrogen species are bound to carbon, therefore, LPG dissociates less easily into the reactive reducing components on the thin film surface. When the thin film is exposed to reducing gas like LPG, the LPG reacts with the chemisorbed oxygen and is adsorbed on the surface of thin film then the exchange of electrons between the LPG and oxide surface upon adsorption would be taken place, i.e., a surface charge layer will be formed [2]. When the LPG reacts with the surface oxygen ions then the combustion products such as water depart and a potential barrier to charge transport would be developed. i.e., this mechanism involves the displacement of adsorbed oxygen species by formation of water. The overall reaction of LPG with the chemisorbed oxygen may be taken place as shown below:



Where, $C_n H_{2n+2}$ represent the various hydrocarbons. These liberated electrons recombine with the majority carriers (holes) of sensing thin film resulting in a decrease in conductivity. The formation of barrier is due to reduction in the concentration of conduction carriers and thereby, results in an increase in resistance of the sensing element with time. As the pressure of the gas inside the chamber increases, the rate of the formation of such product increases and potential barrier to charge transport becomes strong which has stopped the further formation of water constituting the resistance constant. The free charge carriers have to overcome the surface barriers appearing at the surface of the grains.

4. Conclusion

Spray pyrolysis technique is simple, inexpensive was successfully use for preparation of pure nanostructured CdO and modified Zn doped CdO thin films. It may be useful for the large scale production of nanostructured thin films. XRD analysis shows that the films are nanocrystalline nature with cubic structure. The crystallite sizes were found to be in the range of ~17 nm to 23 nm. FE-SEM analysis revealed that, the grains were mixed with spherical and cubical in nature and a size distribution in the range of ~19 to 24 nm. Elemental analysis confirmed that the as-prepared nanostructured CdO and Zn doped CdO thin films are nonstoichiometric in nature. TEM images showed nearly spherical particles with a size ~20 nm. The band gap energy was calculated from absorption spectrum. It was observed to be varying from 2.61 to 2.96 eV. The crystallite size, grain size and band gap energy was observed to be increased with increase of volume 3-7% of Zn in CdO while activation energy goes on decreases. Pure nanocrystalline CdO thin film was observed to be the most sensitive to LPG. Response of Zn doped CdO to LPG was observed to be higher than the response of the unmodified CdO to LPG at 350 °C. Doping of Zn into CdO

helped to enhance the response, selectivity towards LPG gas. The sensor showed quick response (6 s) and fast recovery (8 s) for LPG. Overall it summarized that, doping improved selectivity, response and recovery time of the sensor.

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