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Selectivity of organic vapour for nanostructured CdO thin films prepared by sol-gel dip coating technique

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Abstract The objective of the present paper is to investigate the effect of dipping cycle interval (5, 10, and 15) on the structural, morphological, and gas sensing properties of nanostuctured CdO thin films prepared by simple sol-gel deposition technique. The structural, microstructural and elemental composition have been revealed by X-ray diffractogram (XRD), field emission scanning electron microscopy (FE-SEM), and energy dispersive spectrophotometer (EDAX) respectively. The nanostructured CdO film showed selectivity for ethanol over methanol compared to ammonia ($S_{ethanol}$ /$S_{methanol}$ = 6.4 and $S_{ethanol}$/$S_{ammonia}$ = 31.24). It is found that the sensing response increased monotonically with increasing operating temperature and gas concentration. The maximum ethanol response of 1353 for the sample S2 for gas concentration of 500 ppm at 300 ^{o}C was achieved. The quick response ($T_{Response}$ = 4 s) and fast recovery ($T_{Recovery}$ = 9 s) are the main features of this film. Moreover, the repeatability of the experiments was tested for the most sensitive sample (S2). Additionally, the stability of the prepared sensor has been studied. Effect of dipping cycle interval on physical, structural, microstructural, electrical and gas sensing properties of these films were studied and presented in the present investigation.
Keywords: Sol-gel technique, Nanostuctured CdO, surface morphology, thin films, organic vapour, gas response, selectivity.

1. Introduction

Presently 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 the working of environment. 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 be increased as the average crystallite size decreased to below 10 nm. Among them nanostuctured materials exhibiting small particle size and large surface area may be applied for various gas sensors application [1]. Nanostuctured 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].Semiconductor metal oxide (SMO) such as SnO_2 and ZnO have wide band gap energy, which can be efficiently used for gas sensors with suitable metal additives like platinum [3] and palladium [4]. In addition, the stability of some of the materials is not very good, resulting poor reliability due to aging and humidity- induced effects. Among thin films of semiconductor metal oxide, cadmium oxide (CdO) has received less attention because of its relatively narrow optical band gap energy varying between 2.2 to 2.7 eV [5].

Among the IIB-VI compound, CdO is of special interest. While other members of Cd and Zn are based on tetrahedral of metal cations in wurtzite and zinc blende structure. This compound adopts a face centered-

cubic rock salt structure based on octahedral coordination around (Cd).It has important electronic, structural and optical properties. It occurs naturally as the rare mineral monteponite, [6] and has special features such as high conductivity, high transmission and low band gap which made it applicable in photodiodes, phototransistors, photovoltaic cell, transparent electrodes, liquid crystal displays, IR detectors and anti reflection coatings [7].

A number of techniques are reported for the deposition of CdO including ion beam sputtering [8], spray pyrolysis [9], SILAR method [10] are used by different researcher for the preparation of nanostuctured thin films and powders. Among these, the sol-gel coating technique is simple and economical which needs no sophisticated instrumentation and has been used in the present work [11].

In this study, sol-gel dip coating technique was adopted to deposit nanostuctured CdO thin films on glass substrate at different dipping cycle interval. Nanostuctured thin films produced were characterized by different analytical techniques. The performance of nanostuctured CdO gas sensors can be improved notably and also study the influence of the process thickness on the structural, morphological and electrical properties of these films. The results were discussed and interpreted in the present investigations.

2. Experimental

2.1 Preparation of nanostuctured CdO thin films

All chemicals were of analytical grade purchased from Loba Chem. (Made-Mumbai), which are used without further purification. CdO thin films have been deposited on glass substrates using sol–gel dip-coating process as described elsewhere [11-12].Cadmium oxide thin films (CdO) have been prepared by the sol-gel technique. Cadmium acetate dehydrate [Cd $(COOCH_3)_2.2H_2O$] has been taken as the source cadmium. The precursor solution for preparing the CdO films has been obtained by dissolving 0.5 M cadmium acetate dihydrate in100 ml ethanol and 2 ml of lactic acid has been added to the solution to avoid turbidity and to obtain a clear solution. The solution is refluxed at 65 ^{0}C for 2 hours. Now the sol is ready. It is kept in an open beaker for gelation. After 3 days of gelation the sol-gel is used for dip coating.

Before dip coating, the glass substrates were first degreased by detergent, rinsed thoroughly by deionized water and then in boiled water. In order to remove macroscopic contaminations, the substrates were cleaned ultrasonically in a mixture of ethanol and acetone (each of 50% in volume) for 15 min. The latter procedure then was repeated in deionized water. Glass substrate was immersed into the solution draw vertically, laid flately and then wet thin films formed. Thus the films with different dipping cycle of 5, 10, and 15 were obtained and referred as sample S1, S2 and S3 respectively. After the dip coating the film were dried at 120 ^{o}C for 30 min in an oven to remove solvent and impurity traces.

The as prepared nanostuctured CdO thin film samples were fired at 500 ^{o}C for 1 h. After 1 h, the films were slowly cooled to room temperature and later on used for the characterization and gas sensing performance.

3. Result and discussion

3.1. Determination of film thickness

The film thickness was measured by a weight difference method [13] in which weight of the sample, area and densities were considered. In order to measure the thickness of the thin films by using weight difference method, error and accuracy was found to be ± 5 % nm. The thickness, sample weight and sample area are related as:

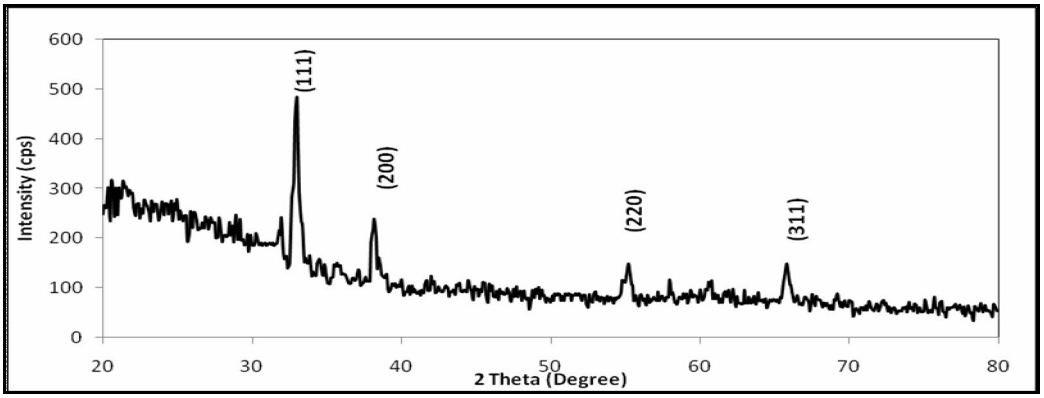
$t = M/A.\rho$ ---------- (1)
Where, M is the weight of the sample in gm,
A the area of the sample in cm^2
and ρ the materials density in gm cm^{-3}.
The values of the film thickness are given in Table 1.

3.2 Structural properties

3.2.1 Crystal structure

Crystalline structure of the nanostuctured CdO sensing layer were studied using Bragg–Brentano (θ–2θ) scan of a X-ray diffraction (Miniflex Model, Rigaku, Japan) using CuKα radiation with a wavelength, λ = 1·542 Å. The average crystallite size of nanostuctured CdO thin film samples were calculated by using the Scherrer formula

$D = 0{\cdot}9\lambda/\beta\cos\theta$ ---------- (2)
Where, D = Average crystallite size
λ = X-ray wavelength (1·542 Å)
β = FWHM of the peak
θ= Diffraction peak position.



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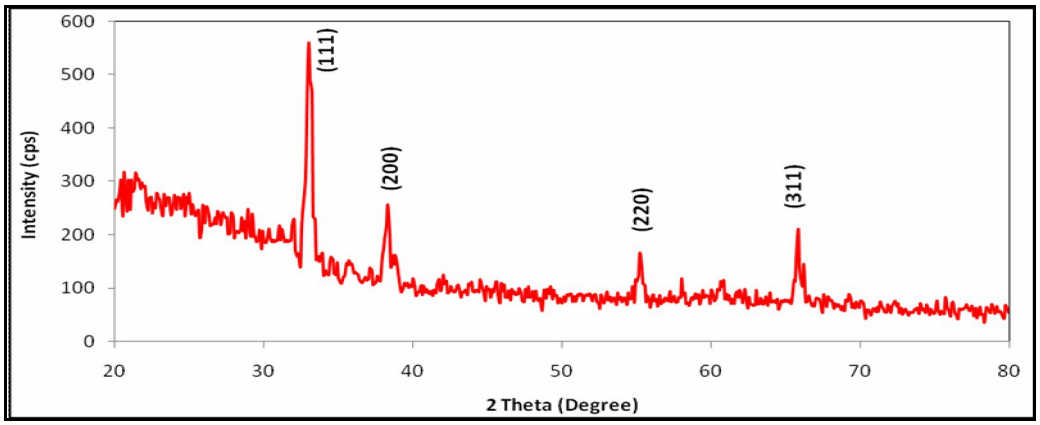

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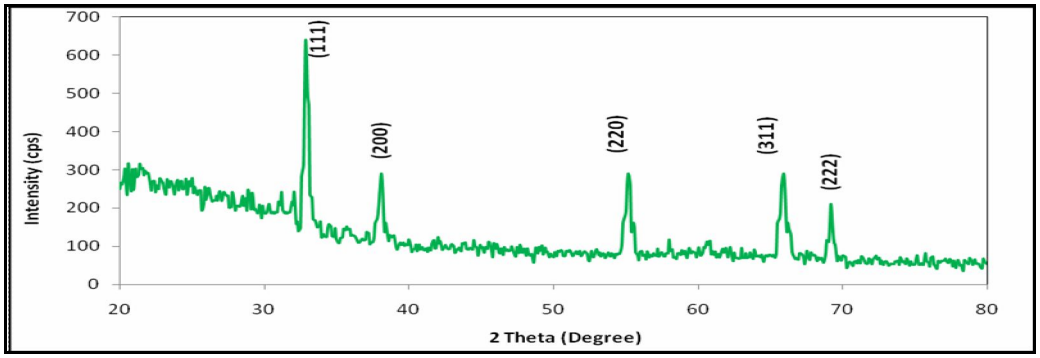


(c)

Figure 1. X-ray diffractogram of nanostructured CdO thin films samples: (a) S1, (b) S2, and (c) S3.

Figure 1 shows the X-ray diffractogram of pattern of the film prepared at different dipping cycle interval (5, 10, and 15). The X-ray diffraction patterns were scanned in the 2θ range of 20-80^{o}. All the peaks were well consistent with JCPDS data of CdO [14], confirming the thin films as cubic CdO phase formation. It shows presence of different strong diffraction peaks. It is not the result of structural changes in the films and it can be seen that the XRD peaks were broadened. With the Scherrer equation using full width at half maximum of (111), (200), (220), (311), and (222) peaks, the average crystallite of nanostructured CdO was tabulated in Table 3.

The various crystallographic and microstructural parameters such as dislocation density, number of crystallites, and microstain were estimated by using the standard relations were [15, 16]:

Dislocation density (δ) = $1/D^2$ ----------(3)
Number of crystallites (N): t/D^3 ----------(4)
Microstain (ε) = $\beta / (4 \tan\theta)$ ---------- (5)

The dislocation density, number of crystallites, and microstain value was tabulated in Table 1.

Table 1: Measurement of dipping cycle, film thickness, dislocation density, number of crystallites, and microstrain.

Sample	Dipping cycle	Thickness (nm)	Dislocation density	Number of crystallites	Microstrain (arb. unit)
S1	5	139	4.8×10^{15}	1.3×10^{26}	2.29×10^{-3}
S2	10	165	6.5×10^{15}	8.7×10^{25}	1.45×10^{-3}
S3	15	211	9.6×10^{15}	7×10^{25}	0.76×10^{-3}

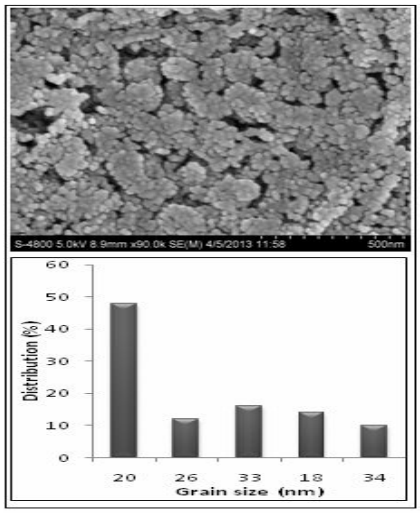
It is observed from Table 1 that as increasing dipping cycle interval, the film thickness, dislocation density went on increasing with decrease in number of crystallites and microstrain (ε).This type of change in microstrain and number of crystallites may be due to the predominant recrystallization process in the nanostrctured films [15]. In present investigation the negative value of the microstrain (2.29×10^{-3} to 0.76×10^{-3}) shows presence of compressive strain in nanostructured CdO film. This very low value of compressive microstrain suggests that the synthesized nanostructured CdO thin film exhibits high-quality crystal geometry [16]. The various crystallographic parameters estimated are tabulated in table 1.

3.3 Microstructural Properties

3.3.1 Field emission scanning electron microscope

The microstructure and elemental composition of the films was analyzed using a field emission scanning electron microscope coupled with energy dispersive spectrophotometer (FE-SEM, JEOL. JED 6300).

Figure 2 show the FE-SEM images of nanostructured CdO thin film samples S1, S2, and S3 respectively. FE-SEM micrograph is showing topography of the film surface. The morphology of the grains was roughly spherical in shape. The grain size was observed to be increased with the increase in film thickness. The observed grain sizes were presented in Table 3.



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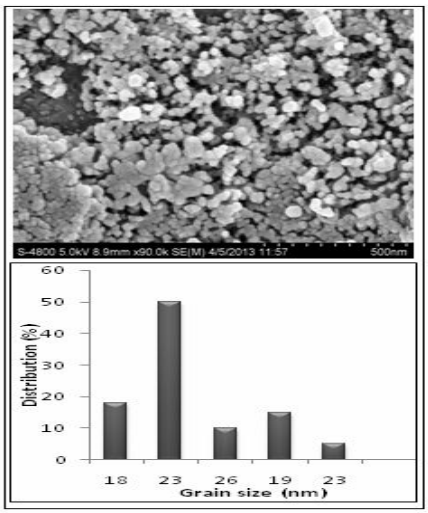

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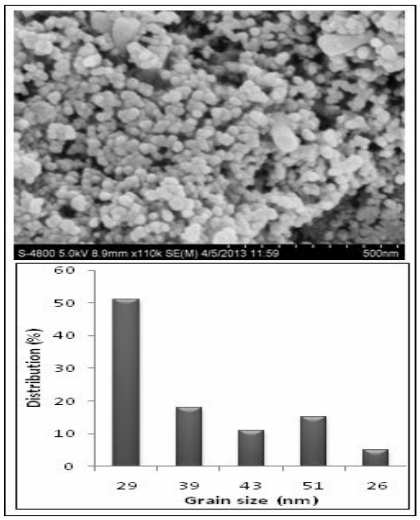

(c)

Figure 2. FE-SEM images of nanostructured CdO thin film samples with histogram to indicate grain size distribution: (a) S1, (b) S2, and (d) (c) S3.

3.4 Quantitative element analysis (EDAX)

Figure 3 shows the elemental analysis of most sensitive nanostructured CdO thin film (Sample= S2). It was analyzed using an energy dispersive spectrophotometer. The quantitative elemental analysis of the as deposited CdO films was carried out at room temperature.

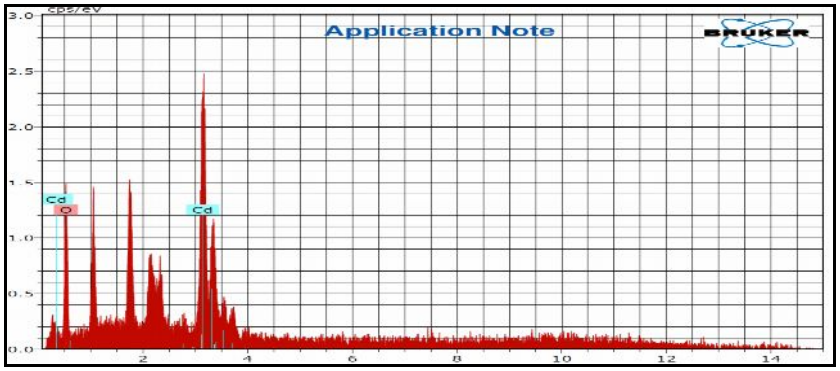

Fig.3. Elemental analysis of nanostructured CdO thin film sample (S2)

Table 2.: Quantative elemental analysis as prepared nanostructured CdO thin film

Sample No.	Cd (at%)	O (at%)	Remarks
S1	34.62	65.38	Nonstoichiometric
S2	43.07	56.93	Nonstoichiometric
S3	48.80	51.20	Nonstoichiometric

Stoichiometrically expected at% of Cd and O is 50:50. The observed at% of Cd and O were presented in Table 2. It is clear from table 2 that as prepared nanostructured CdO thin films were observed to be nonstichoimetric in nature. The nanostructured CdO thin films observed to be oxygen deficient. The oxygen deficient results suggests in the increase in the electrostatic interaction between the gas molecules and the surface of CdO thin film making it extremely useful for gas sensing applications.

4. Electrical properties

Electrical conductivity and gas sensing performance were measured using static gas sensing system at different operating temperature.

4.1 I-V Characteristics

The basic *I–V* characteristic of the nanostructured CdO thin film was performed on gas sensing set-up, using silver paste as contacts. *I–V* characteristics of the CdO thin film show an Ohmic behavior for both –ve and +ve applied potential as can be observed from Figure 4.

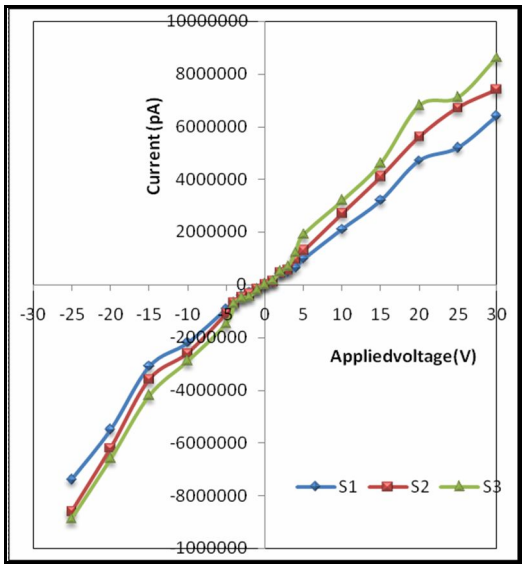

Fig. 4. I-V characteristics of nanostructured CdO thin film.

The non-linear I–V characteristics may be due to semiconducting nature of the thin films samples. The Ohmic behavior is very important the point of gas sensing applications, especially with different concentration of gases or other species [17].

4.2 Electrical conductivity

Conductivity was given by relation

$\sigma = \sigma_o \exp(-\Delta E/kT)$ ---------- (5)

Where, σ = conductivity

σ_o = conductivity constant

k= Boltzmann constant

T= Temperature

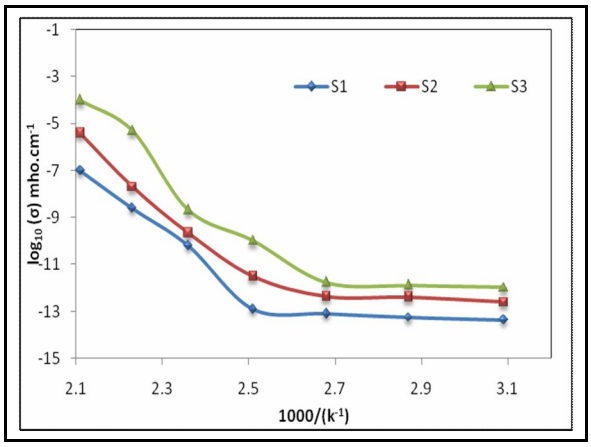

Figure 5. Variation of log (σ) with operating temperature (◦C).

Figure 5 shows the variation of log (σ) with operating temperature. The conductivity of each sample is observed to be increasing with an increase in temperature. The increase in conductivity with increase in temperature could be attributed to negative temperature coefficient of resistance and semiconducting nature of nanocrystallite CdO.

Table 3. Measurement of film thickness, crystallite size, grain size, and activation energy.

Sample	Thickness (nm)	Crystallite size from XRD (nm)	Grain size from FE-SEM (nm)	Activation energy (∆E)	
				473 K	673 K
S1	139	10.16	20.45	0.42 eV	0.47 eV
S2	165	12.36	22.89	0.36 eV	0.44 eV
S3	211	14.42	29.60	0.16 eV	0.21 eV

It is observed from Table 3 that as increased the film thickness, crystallite size, grain sizes goes on increasing with decrease in activation energy. This indicate that the film thickness contribute to the improvement in crystallinity with film thickness. Also the trend of increase in crystallite size may be interpreted in the terms of a columnar grain growth in the structure. It is reported [18, 19] as the thickness of the film increases activation energy goes on decreasing. It is clear from Table 3 that, as film thickness of the sample goes on increasing; the activation energy goes on decreasing. The decrease in activation energy with increasing film thickness may be due to the change in structural parameters, improvement in crystallite and grain size [20].

The activation energy calculated from slopes of line for deposited thin films at different dipping cycle interval 5, 10, and 15 were found to be 0.42 eV, 0.36 eV, 0.16 eV (at low temperature = 473 K) and 0.47 eV, 0.44 eV, 0.21 eV (at high temperature = 673 K) respectively.

4.3. Gas sensing system

The gas sensing studies were carried out using a static gas chamber to sense organic vapour gas in air ambient and the experimental set up is described elsewhere [1]. The nanocrystalline 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. 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 circuitary by applying constant (5 V) voltage and measuring the current by picoammeter. The conductance was measured both in the presence and absence of test gas.

The gas response detection (S) of the sensor active layer (nanostructured CdO thin films) can be evaluated using the relation:

$S = G_g - G_a / G_a$ ---------- (6)

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

5. Gas sensing performance of the nanostructured CdO thin films

The gas sensing study was initiated with a view to study the gas sensing performance of sol-gel deposited CdO thin films with varying dipping cycle interval. As the gas sensors are based on resistive material used in the form of thin film, an electrical characterization is related to the resistance measurements at various operating temperatures in different gaseous environments. The semiconductor sensors are based on an interaction between the metal oxide semiconductor and the gas ambient which produces a change in the conductivity of semiconductor. It is known [21, 22] for many years that the adsorption-dependent electrical properties of metal oxide semiconductors are often sensitive to many gaseous ambient. This phenomenon is the basis of present study.

The main characterization is the optimization of operating temperature of film sample for test gases. On the basis of measured data, the gas response and selectivity of thin film sensor for gas concentration in the range from 100-500 ppm in air ambient condition are calculated.

5.1. Effect of operating temperature and ethanol concentration

Fig. 6 shows the variation in resistance with time for CdO thin film based sensor structure at an operating temperature of 300 ^oC towards 500 ppm for ethanol gas. It is clear from Fig.6, that the ethanol response of sample S2 is higher at 300^oC as compared to those of S1, and S3. When target gas ethanol was inserted in the chamber, gas response of the film increases because of oxidizing behavior of ethanol gas. Due to the greater surface area of nanostructured materials, its interaction with the adsorbed gases is stronger, leading to higher gas response. Another reason that, from Ohm's law, the electrical resistance of the nanostructured CdO thin films sensor decreased and increased when the test gas (ethanol vapour) was turned on and off, respectively. The mechanism responsible for the gas sensing is considered to follow the surface conduction model [23]. Nanostructured CdO is an n-type semiconductor, in which the electrons are the majority carriers.

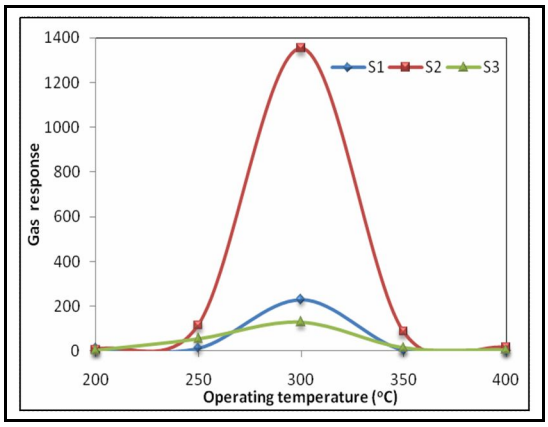

Figure 6. show the variation in gas response with the operating temperature to 500 ppm of ethanol for S1, S2 and S3 samples.

Its conductivity or electrical resistance can be changed by foreign gas molecule though turning the carrier density. Reducing molecule such as ethanol will donate electrons to the nanostructured CdO surface and thus decrease its resistance; the opposite holds true for oxidising molecule. In clean air, oxygen molecule adsorb on the surface of the nanostructured CdO thin film in the form of O_2^-,O^-, or O^{2-} by trapping free electrons form the surface, and incease the resistance of the nanostructured CdO sensor. On exposure to ethanol vapour, ethanol molecule will absorb and react with the ionic oxygen species, and thus inject electrons into the nanostructured CdO surface during the oxidation-reduction process, leading to decrease in its resistance [24, 25].

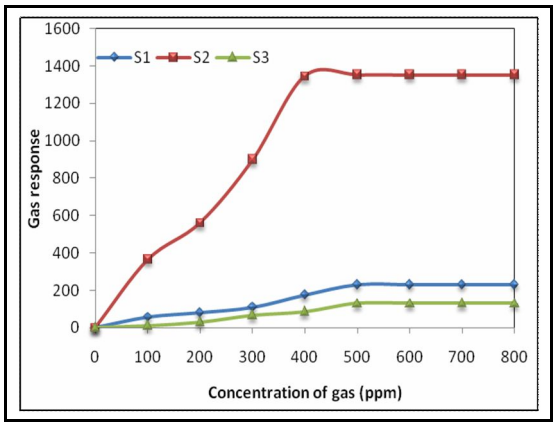

Fig. 7. Variation of response with gas concentration.

Once the operating temperature is fixed, the sensor response is studied at different ethanol concentrations. Fig. 7 shows the response of film sample S1, sample S2 and sample S3 as a function of ethanol concentration. Also Figure 7 shows the ethanol sensitivity of nanostructured CdO thin film sensor to varying concentrations of ethanol. The gas response of the sensors increases with increasing ethanol concentrations for 100–800 ppm ethanol. As the concentration of ethanol increased from 100 to 800 ppm, the gas response increased from 365 to 1353 at 300 ^{o}C. The sensor is capable of detecting concentrations as low as 100 ppm of ethanol vapors. 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 gas response was obtained at an operating temperature of 300 ^{o}C for the exposure of 500 ppm of ethanol.

5.2. Selectivity of organic vapour

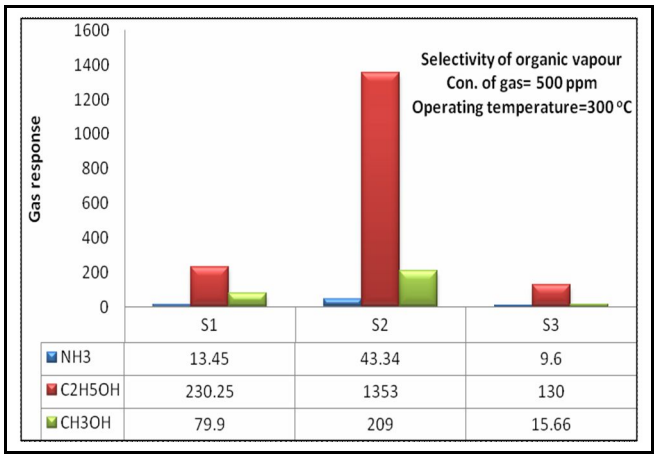

Figure 8. Selectivity of nanostructured CdO thin films for organic vapour

Figure 8 shows the histogram of gas response to different gases with operating temperature for the sample S1, S2 and S3. The table attached to the histogram indicates the response values of various gases at that particular operating temperature. The histogram revealed that the sensor offered maximum response to ethanol (1353), methanol (209) and ammonia (43.34) at same operating temperature 300 ^{o}C.

The sensor selects a particular gas at a particular temperature. Thus, by setting the temperature, one can use the sensor for particular gas detection. The same sensor could be used for the detection of different gases by operating it at particular temperature for a typical gas. Different gases have different energies for adsorption, desorption and reaction on the metal oxide surface and therefore, the response of the sensor at different temperatures would depend on the gas being sensed. The CdO film showed more selectivity for ethanol over methanol compared to ammonia ($S_{ethanol}$ / $S_{methanol}$ = 6.4 and $S_{ethanol}$ / $S_{ammonia}$ = 31.24) at an operating temperature of 300 ^{o}C. It revealed that ethanol is the more selective against methanol and poor selective against ammonia.

5.3. Response, recovery and repeatability of sensor

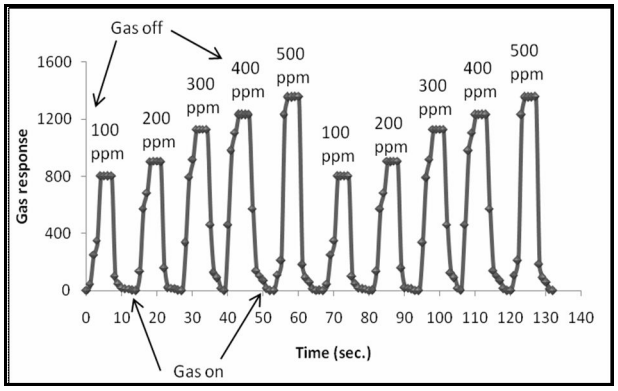

Fig.9. Repeatability of the sensor with response and recovery cycle

The response time was measured as the time taken by the sensor to acquire the 90% of its maximum resistance value in the presence of target oxidizing gas. Once the maximum resistance value is attained, the target gas was flushed out of the test chamber and sensor was allowed to regain its initial resistance value in atmospheric air while keeping the sensor at the same temperature. Time taken by the sensor to reacquire about 10% higher value of its initial resistance in the presence of atmospheric air is considered as the recovery time.

The cycle taken for the sensor to attain 90% of the maximum decrease in resistance on exposure to the target gas is the response cycle. The cycle taken for the sensor to get back 90% of original resistance is the recovery cycle.

The response and recovery of the most sensitive thin film S2 sensor on exposure of 500 ppm of ethanol at 300 ^{o}C are represented in Fig. 9. The response is quick (4 s) and recovery is fast (9 s). The high oxidizing ability of adsorbed oxygen species on the surface nanoparticles and high volatility of desorbed by-products explain the quick response to ethanol and fast recovery.

In order to check the repeatability of the sensor, the samples have been tested under a set of the gas concentration (100, 200, 300, 400 and 500 ppm respectively). Fig.9 shows that the response of the sensor for the set of two experiments remains the same.

5.4. Stability of sensor

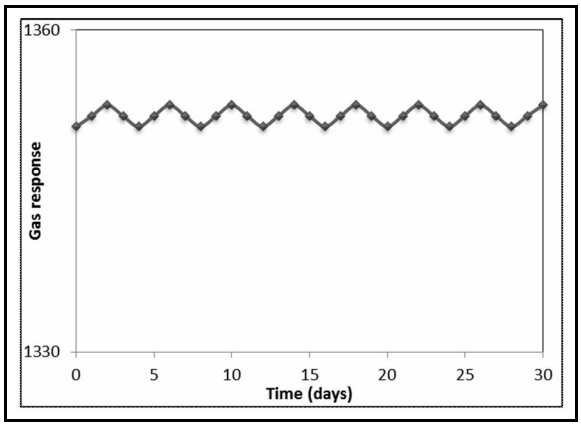

Figure 10. The sensing stability studies for CdO thin film at an operating temperature of 300 ^{o}C.

The stability behavior of nanostructured CdO thin film sample (S2= most sensitive) was tested by conducting the test many cycles (days). During the test, no significant variation was observed as shown in Figure 10.

The gas response value of sample (S2) sample was observed to be approximately similar. The obtained results show that gas response was reproducible.

6. Sensing mechanism

It is well known that the gas sensing mechanism is generally explained in terms of change in conductance due to the interaction of test gases with the semiconducting surface [26]. The change of conductance is either by adsorption of atmospheric oxygen on the surface and/or by direct reaction of lattice oxygen or interstitial oxygen with the test gases. In case of former, the atmospheric oxygen adsorbs on the surface by extracting an electron from the conduction band, in the form of super oxides or peroxide, which are mainly responsible for the detection of the test gases. Figure 11 shows the ethanol sensing mechanism (Fig. (a) before exposure of ethanol and (b) after exposure of ethanol).

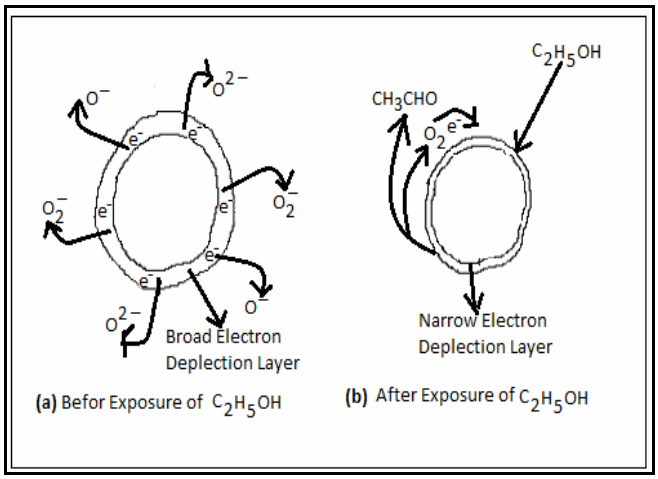

Figure 11. Ethanol sensing mechanism of nanostructured CdO thin film.

On adsorption of ethanol molecules tend to dissociate in to H atom form a surface hydroxyl and the former tends to be transformed further in to an aldehyde or a ketone. For the gas sensor to change its resistance, however, more important is the oxidation reaction of these adsorbates on the surface of nanostructured CdO. There are two general ways of ethanol conversion [27]: oxidative dehydrogenation and dehydration.

For n-type semiconductor sensors the sensing mechanism is interpreted as the sensing process probably involves at three-step process, i.e., an adsorption, oxidation and desorption process is shown in Fig. 11. Before exposure of ethanol, CdO nanoparticles are depleted of electrons from the conduction band by oxygen species (O_2^-, O^- and O^{2-}) adsorbed on particle surface [28, 29], forming an electron depletion layer on particle surface which increases the sensor resistance.

When the sensor is exposed to ethanol gas, the ethanol molecules are oxidized by oxygen species in to formaldehyde [26] and simultaneously the depleted electrons are feedback in to particles, resulting in an arrowed depletion layer and therefore the sensor resistance is decreased. When gas is out, the sensor is exposed to air again and thus refreshed by air at elevated temperature. The oxygen in atmospheric air will renewably capture electrons to deplete the particle surface.

The overall chemical reaction is as follows:

$C_2H_5OH + O \rightarrow CH_3CHO + H_2O + e$ ---------- (7)

7. Conclusions

1. Nanostructured cadmium oxide thin films can be synthesized on a large scale via sol-gel technique.
2. The technique is simple and inexpensive and it may be useful for the production of semiconductor metal oxide (SMO) thin film gas sensors.
3. The physical, structural, surface morphological and microstructural properties confirm that the as-prepared CdO thin films were nanostructured in nature.
4. The elemental analysis conferred that as prepared thin films were nonstiochiometric in nature.

5. As increasing dipping cycle interval, film thickness, crystallite size, grain size and dislocation density associated with films goes on increasing with decrease in number of crystallites, microstrain and activation energy.
6. *I–V* characteristics of the CdO thin film showed perfect Ohmic behaviour.
7. The different gas sensing behavior of the nonostrutured CdO thin film carried out on static gas sensing system.
8. Nanostructured CdO thin film sensor shows a high response (S2=1353) to ethanol gas in a wide concentration (500 ppm) range at operating temperature 300 ^{0}C.
9. Selectivity study showed that films were most selective to ethanol against methanol and ammonia.
10. Synthesized nonostrutured CdO thin films shows good response, selectivity towards organic vapour at same operating temperature.
11. Nanostrutured CdO thin film based sensor shows moderate response and recovery times.

8. Acknowledgements

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9. Reference

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