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# *$H_2S$ Gas Sensing Studies of $Cd_XZn_{1-X}O$ Thin Films Synthesized at Low Temperature by Advanced Spray Pyrolysis Technique*

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***Abstract* - Cadmium zinc oxide ($Cd_XZn_{1-X}O$) thin films were deposited at low substrate temperature using advanced spray pyrolysis technique. Aqueous solution of cadmium acetate and zinc acetate were used as initial ingredients. The films were prepared by keeping optimized preparative parameters constant. Influence of variation of zinc in the '$Cd_XZn_{1-X}O$' system on the structural, electrical and gas sensing properties of the films has been investigated. X-ray diffraction studies indicate polycrystalline nature of the films. Field emission scanning electron micrograph measurements reveal that the grain size decreases with increase in zinc content. It is found that films are sensitive to $H_2S$ gas and maximum response is observed at the operating temperature of 300ºC.**

***Keywords: Cadmium Zinc Oxide, Advanced spray pyrolysis technique, H2S gas.***

## I. INTRODUCTION

Gas sensing devices generally used metal-oxide semiconductor, because of their response to oxidizing and reducing gases. Now a day's much attention is given by the researcher to the development of metal-oxide gas sensors that detects the toxic gases such as $H_2S$, $(CH_3)SH$ and $(CH_3)S$. Among this Hydrogen sulfide ($H_2S$) is one having typical bad smell and even generated from dump, sewage etc. Metal oxides in the form of pellets, thick films and thin films were used in the fabrication of the gas sensors. Many materials were tried by the researchers to obtain required properties [1], [2]. Zinc oxide is vital metal-oxide semiconductor used for detection of combustible and toxic gases. The principle of gas sensing in case of ZnO is based on the change in conductivity, when interact with gas molecules. Furthermore they have generally the disadvantage of low sensitivity/response at lower concentration of $H_2S$ gas and poor gas selectivity [3], [4]. Therefore different approaches like synthesis methods of material, dopants/additives and sensatization were used in fabrication of sensor to overcome these problems. Some achievements were reported by salunke et al. [1], [2], ]5]. They have studied the gas sensors based on CdO thin films synthesized by Chemical Bath Deposition (CBD), SILAR and Spray pyrolysis method. Shewale et. al. [6]-[8] prepared ZnO by advanced spray pyrolysis technique and observed the effect of Cu and Sn doping on $H_2S$ gas sensing performance. However, the mixed oxide system was not used by any researchers in $H_2S$ gas sensing. In the present investigation the thin film of cadmium and zinc mixed oxide were prepared by advanced spray pyrolysis technique. The Crystal structure and surface morphology of these films were studied with XRD and FESEM techniques. The hydrogen sulfide gas sensing performance of the mixed oxide films was studied by varying the operating temperature and gas concentration and results are explained at length.

## II. EXPERIMENTAL

Advanced spray pyrolysis (ASP) technique was used to synthesis $Cd_xZn_{1-x}O$ thin film [9]. A 0.02 M aqueous solutions of high purity cadmium acetate ($Cd(CH_3COO)_2.2H_2O$) (Thomas Baker, India) and equimolar solution of zinc acetate ($Zn(CH_3COO)_2.2H_2O$) (Thomas Baker, India) were used as a initial ingredients. The solutions were prepared in double distilled water. The solutions were mixed in appropriate volume to achieve final solution of 300 ml. The required ration is obtained by varying the value of x from 1 to zero by step of 0.1. The spraying solution was atomized through a glass nozzle. During the process of deposition, compressed air is used as carrier gas and spray rate was maintained at ~5 ml/min. All the samples were deposited by keeping substrate temperature and reaction chamber temperature at 210ºC and 325ºC respectively. The reaction chamber temperature is the

decomposition temperature of zinc acetate. Because cadmium acetate decompose at lower temperature as compared to zinc acetate. When the sprayed solution comes in to the reaction chamber, the reactant undergoes pyrolytic decomposition inside the core of furnace and oxide particles were formed. These particles are pushed upward i.e. towards the glass substrates and uniform films were formed on the glass substrate. The substrate to nozzle distance was set at optimized value of 41 cm. The films deposited with different concentration of zinc (x=1, x=0.8, x=0.6, x=0.4 and x=0 ) are denoted by $M_0$, $M_{20}$, $M_{40}$, $M_{60}$, $M_{80}$ and $M_{100}$ respectively. Structural, morphological and electrical properties of these films were studied with reference to the variation in composition of films. The crystal structure of $Cd_xZn_{1-x}O$ thin film was studied by using German make Bruker AXS D-8 Advance X-ray diffractormeter with Cu kα radiation having wavelength 1.5406 Å. The diffraction patterns were studied by varying diffraction angle from 20º to 80º in steps of 0.2º. The film thickness was measured by Ambios XP-1 surface profiler. The surface morphology was examined by the field emission scanning electron micrograph (FESEM). The home made gas sensing unit was used to test the $H_2S$ gas detection. It consists of hot plate which is enclosed in airtight stainless still housing. The gas is inserted into the chamber from septum with a rubber gasket. A Rigol DM 3062 Digital multimeter is used to measure the resistance with and without $H_2S$ gas exposure. The details of the setup explained elsewhere [9].

## III. Results and Discussion

### A. *X-ray diffraction and morphology studies*

Fig.1 shows the X-ray diffraction pattern for the typical samples. It is observed that when x=1films are grown along (111) and (002), with some less intense peaks along (220), (311) and (222) planes. However, at x=0 films grow along (100), (002) and (101) plane with some minor peaks (102), (110) and (103). This indicates the polycrystalline nature of the films. The standard d values from JCPDS card no. 05-640 are compared with observed d values and it indicates that films exhibits rock salt type crystal structure with preferential orientation along (111) direction. This also indicates the formation of pure CdO initially for x=1, i.e. for sample $M_0$.

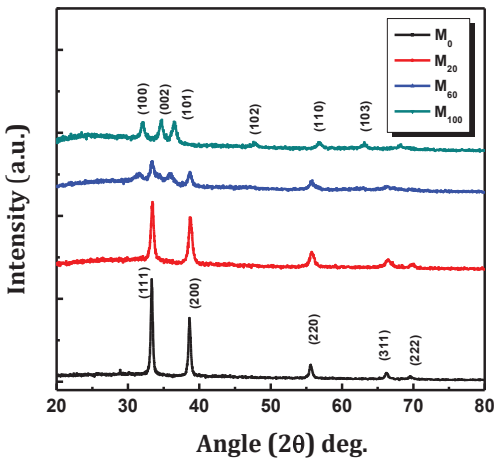


**Fig. 1 X-ray diffraction patterns for the typical Samples.**

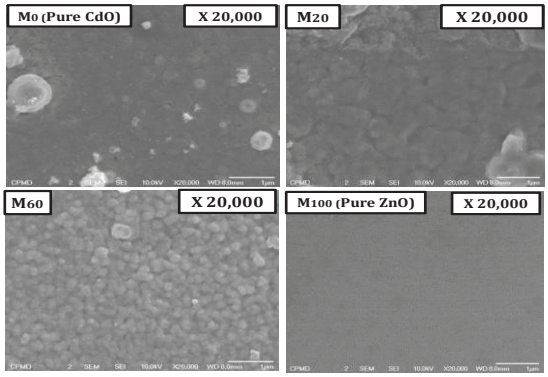


**Fig. 2 FESEM Images of the typical sample**

As x tends to zero, i.e. for sample $M_{100}$ there is a complete shift in structure from rock salt to wurtzite with change in preferential orientation and peak matchs with those given in JCPDS card no. 05-664 indicating the formation of pure ZnO. It is further seen that with increased in zinc concentration the degrees of polycrystallinity of the film decreases. Sample $M_{60}$ shows the existence of mixed phase with decrease in intensity of different peaks with decreases in orientation. While the peak intensity for sample $M_{100}$ is notably greater than one of sample $M_{60}$. Such type of behavior is reported by Vigil et. al. [10].

Fig.2 shows the FE-SEM images of $Cd_XZn_{1-X}O$ thin film with different Zn concentration. The images were obtained at magnification of x 20,000. From FESEM images it is observed that all film are free from cracks and are compact. It is further observed that sample $M_{60}$ exhibits the well defines grains and are circular; however, surface looks somewhat porous. It is also observed that grain size decreases up to ~48 nm indicating that the sample is nanocrystalline with relatively large surface ratio and that is the requisite for good sensing performance of the sensor. These results are in good

agreement with X-ray diffraction results.

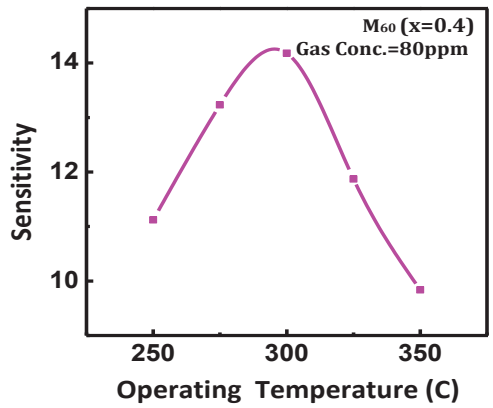


**Fig. 3. Variation of sensitivity with operating temperature for typical sample**

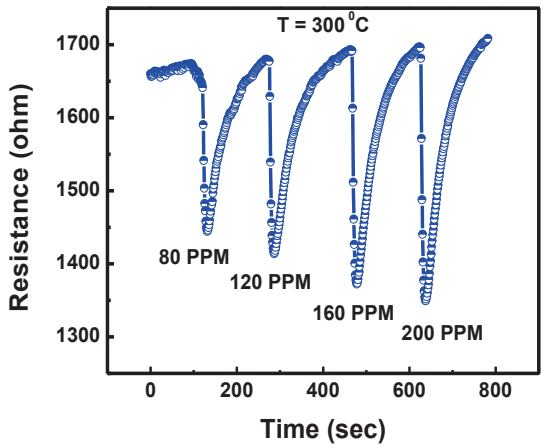


**Fig. 4. Variation of resistance verses time for typical sample**

## B. *Gas sensing characteristics*

It is known that the gas response gets considerably influenced by the surface morphology, crystallinity, doping and operating temperature of the metal-oxide semiconductors. In the present case the crystallnity and surface morphology is considerably changed by addition of zinc oxide in cadmium oxide. In order to obtain the performance of these films to sensing the hydrogen sulfide gas, the resistance of the film was measured in air and in hydrogen sulfide gas environment and sensitivity of the sensor can be calculated by using the following equation.

$$S = \frac{(Ra - Rg)}{Ra} \times 100 \qquad \text{----------} \quad (1)$$

Where '$R_a$' is the resistance of sensor in ambient environment, '$R_g$' is the resistance of sensor measured when exposed to the $H_2S$ gas. The sensitivity of the sensors was determined using the measured values of resistance.

In order to study the effect of zinc addition on the $H_2S$ gas detection all the samples were exposed to 50 100 ppm of $H_2S$ at 250$^o$C operating temperature. From this experiment it is observed pure CdO and pure ZnO exhibits poor response, however, sample with 40% of zinc exhibits better performance. This may happens because of the favorable structure and morphology of this films for gas sensor. These observations force us to study detail performance of the typical sample $M_{60}$. These observations are controversial to our previous observations; because we have reported good sensitivity for the ZnO films. However, this observed controversy may be due to the change in deposition procedure of ZnO films. From the pilot experiments it is found that films of cadmium oxide and mixed oxide are not responding at low concentration of $H_2S$. So it is decided to perform the experiment above 80 ppm. In order to obtain the optimum operating temperature of the mixed oxide, sample $M_{60}$ was used. The resistance of this film was measured in air and when exposed to the $H_2S$ gas at different operating temperature and sensitivity was obtained using the above equation 1. Fig.3 shows the variation of sensitivity of the sensor with operating temperature to 80 ppm of $H_2S$ gas, for typical sample $M_{60}$. The sensitivity curve is in Gaussian shape. Initially the sensitivity increases with the operating temperature, attend maximum value at 300$^o$C and for further increase in temperature it decreases. The low response to $H_2S$ gas at low operating temperature may be due to slow reaction of gas molecules with surface adsorbed oxygen species. This happens due to the low thermal energy of gas molecules. At the optimal operating temperature, $H_2S$ reacts to the film surface to inject the electron into conduction band, because of that electron concentration increases and resistivity of the film decreases. On the other hand at the higher operating temperature causes to increases the carrier concentration, which reduces the Debye length and this might be one of the reason for decreased in sensitivity at higher operating temperature that is above 300ºC. The other possibility is that at higher operating temperature there will not be enough oxygen species to react with the gas.

In order to determine the response and recovery time of the typical ($M_{60}$) sample resistance was measured as a function of concentration of the Hydrogen sulfide gas at optimum operating temperature. Fig. 4 shows the variation of resistance with time for the typical sample. It is seen that resistance decreases when the film is exposed to the hydrogen sulfide gas.

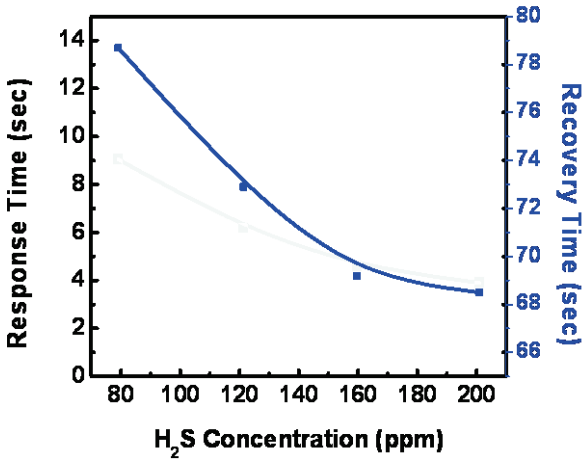


**Fig. 5 Variation of response and recovery time with gas concentration**

The resistance of the film decreases with increase in gas concentration. It is noteworthy that, variation in resistance is almost linear when exposed to the gas. However, the recovery path of the film is not linear. This is observed for all gas concentration. The injection of $H_2S$ induced a remarkable variation in the electrical resistance of the sensing layer. It is also observed that the resistance value returns to its initial baseline value after release of $H_2S$ gas from the chamber. This concludes that the adsorption of $H_2S$ on the surface layer is reversible. It is further observed that there is no saturation in the sensor response at the highest concentration of $H_2S$ (200 ppm).

From the Fig. 4 response time and recovery time of $M_{60}$ sample at all concentration of hydrogen sulfide was calculated and are plotted in Fig. 5. It is seen that response time is very short as compared to the recovery time. The response time is slightly varies with gas concentration for the sample $M_{60}$, however, the recovery time increases with increase in concentration of the hydrogen sulfide gas. With increase in gas concentration slight decrease in response time may be due to the increase in availability of gas molecules with increase in concentration of gas. From the Fig. 5 it is observed that recovery time varies from 67 to 79 seconds. This slight increase in the recovery time may be due to the increase in desorption time due to the large number of adsorbed gas molecules; when exposed to higher concentration of $H_2S$ gas.

Fig. 6 shows the bar chart and it indicates the variation of sensitivity with $H_2S$ gas concentration at an operating temperature of 300ºC for typical sample $M_{60}$. It is found that sensitivity varies from ~14% to 20% when the sensor is exposed in the range of 80 to 200 ppm of $H_2S$. The increase in sensitivity with gas concentration is attributed to the availability of the large number of gas molecules with increase in gas concentration. These films are tested for gas sensing for three months at an interval of a week. Very small edging is observed after three months. This exhibits that films shows good response after three month. That confirms the stability of the films for gas sensing.

## IV. Conclusion

$Cd_XZn_{1-X}O$ thin films were synthesized at low substrate temperature using advanced spray pyrolysis technique. The film grown at low substrate temperature 210ºC and at various Cd and Zn ratio are polycrystalline in nature. FE-SEM measurement reveals that the surface morphology of the film changes continuously with decrease in the grain size due to Zn addition and it is low for pure zinc oxide. The measured grain proves that the films are nanocrystalline in nature. The sensitivity measurement study exhibits that films are sensitive to hydrogen sulfide gas and exhibits 20% sensitivity at 300ºC operating temperature. This is promising for the future development of these devices for practical application in $H_2S$ gas sensing.

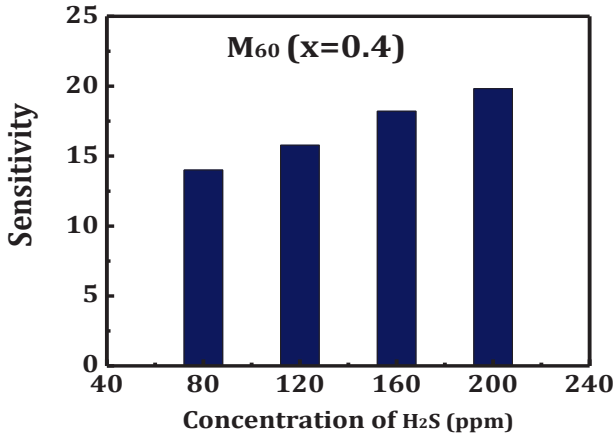


**Fig. 6. Variation of sensitivity with concentration of $H_2S$ Gas for typical sample**

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