Bulletin of Environment, Pharmacology and Life Sciences
Bull. Env. Pharmacol. Life Sci., Special Issue [1]2022 : 1380-1385

Online ISSN 2277-1808
Journal's URL:http://www.bepls.com
CODEN: BEPLAD

ORIGINAL ARTICLE **OPEN ACCESS**

Higher H_2S Gas Sensing Performance of Cadmium Zinc Mixed Oxide Thin Films Compared to Tin Doped and Pure Cadmium Oxide Thin Films Synthesized by Spray CVD Method

C. R. Bobade[1]*, V.S. Raut[1], P. P. Jadhav[1], D.K. Dhongade[1], R.S. More[1], U.K. Mohite[2]
[1]Department of Physics Balwant College Vita, Dist: Sangli 415311 (M.S.), India
[2]Department of Physics M.B.S.K. Mahavidyalaya, Kadegaon, Dist: Sangli (M.S.), India
***Corresponding Author:** chandrakant.bobade24@gmail.com

ABSTRACT
Polycrystalline, pure (undoped) cadmium oxide (CdO), cadmium zinc mixed oxide ($Cd_xZn_{1-x}O$) and tin-doped cadmium oxide (Sn:CdO) thin films were deposited onto glass by spray CVD technique at low substrate temperature. The films were grown using optimized preparative parameters. Pure (undoped) CdO films were synthesized using 0.02 M cadmium acetate Cd ($(CH_3COO)_2.2H_2O$. To synthesize mixed oxide thin films,0.02 M aqueous solutions of high purity cadmium acetate Cd(CH3COO)2.2H2O and zinc acetate $Zn(CH_3COO)_2.2H_2O$ were used as initial ingredients Tin (Sn) doping of 2 to 4 at% in cadmium acetate was achieved using stannic chloride. The structural, optical, morphological and gas sensing studies of as deposited films were done with the help of XRD, UV-Visible spectroscopy, FESEM & AFM techniques respectively while H2S gas sensing performance was studied using homemade gas sensing unit. XRD studies showed that all the films were polycrystalline in nature; while morphological studies confirmed that the films were compact in nature having granular morphology. The band gap values obtained from the optical data were in agreement with the reported data. From H2S gas sensing measurements show that mixed oxide films show high sensitivity ~33.4% than tin doped and undoped cadmium oxide thin films.
Keywords: *Mixed Oxide, doping, Spray CVD technique, gas sensing.*

Received 12.02.2022 Revised 16.03.2022 Accepted 26.04.2022

INTRODUCTION

Most recent and emerging field of research in thin films has been that of transparent conducting oxides (TCOs) due to their commercial importance. They are used for variety of applications like flat-panel displays, electro- chromic windows, thin film photovoltaics, etc [1-4].Metal oxides such as, zinc oxide (ZnO) [5], cadmium oxide (CdO)[6], tungsten oxide WO3 [7], tin oxide (SnO2)[8] and few other metal oxide semiconductors exhibit n-type conductivity. Such metal oxide thin films are transparent in the visible-region and show low electrical resistivity at optimized deposition conditions. Well known deposition techniques used to synthesize above metal oxides include- chemical bath deposition [9], sol-gel[10], thermal oxidation[11], , pulsed laser deposition [12], SILAR[13], spray pyrolysis [14-18] and spray CVD (advanced spray pyrolysis)[19]. Out of these, the spray pyrolysis is often used due to its simplicity, low cost, reproducibility and one can deposit large area films as compared to other techniques [18]. Till date, physical, optical, and other properties of pure and doped CdO thin films synthesized by spray pyrolysis technique have been studied by many researchers. They have reported that CdO films were grown on glass substrates above substrate temperature of 400^0C [14, 20]. Synthesis of films at high substrate temperature has restricted the use of conventional spray pyrolysis technique in device fabrication or in multilayer deposition.The spray CVD technique reported in this work is useful to synthesize uniform and crack free thin films at lower substrate temperature. Here, in this technique, the 'substrate temperature' and 'core temperature' play a vital role that govern film properties such as film thickness, grain size, particle size, etc. Therefore, these parameters must be optimized with great care to achieve high quality films. This work reports on synthesis of pure, tin-doped cadmium oxide (Sn:CdO) and cadmium zinc mixed oxide ($Cd_XZn_{1-X}O$) thin films onto glass substrate at low substrate temperature using spray CVD technique and to study their comparative response towards sensing hydrogen sulfide gas. The gas sensing studies were carried out for selected samples of each type.

MATERIAL AND METHODS

The SprayChemical Vapor Deposition (spray CVD) technique reported by Bobade is an augmentation of conventional spray pyrolysis technique [21]. It consists of: reaction chamber, substrate heater, nozzle assembly. The temperatures of reaction chamber and substrate are set to a desired value with the help of PID temperature controller. The temperature of substrate heater can be varied from 100 ^oC to 400 $^oC$and the reaction chamber temperature can be varied from 100 to 600^oC. Temperature of the reaction chamber of furnace and substrate heater is controlled to an accuracy of ±10^oC. The glass nozzle is fixed on a wooden frame. The spray rate can be varied by changing the height of the solution holder or by adjusting air flow which helps to atomize the solution to be sprayed. Nozzle to substrate distance is adjustable and can be set to a desired value. Pure (undoped) & tin doped cadmium oxide and cadmium zinc mixed oxide thin films were synthesized using spray CVD technique. A pre-optimized 300 ml, 0.02 M spray solution of high purity cadmium acetate was prepared using double distilled water. Tin (Sn) doping from 2 to 4 wt. % is achieved by using stannic chloride solution in double distilled water, the films deposited with 2, 3, and 4 atomic wt.% of Sn doping are denoted by S2,S3and S4, respectively. A0.02 M aqueous solutions of highly pure cadmium acetate $Cd(CH_3COO)_2.2H_2O$and zinc acetate $Zn(CH_3COO)_2.2H_2O$ were used to synthesize ($Cd_XZn_{1-X}O$) thin films. Mixing was done so as obtain pure CdO, 60% zinc oxide mixed CdO and pure ZnO and the samples were designated by M0, M60, and M100, respectively. Optimized quantity (300 ml.) of desired solution was sprayed through a glass nozzle into the reaction chamber kept at 325^oC. The solution enters into the reaction chamber and undergoes thermal decomposition to form oxide particles. These aerosols are further forced upwards and reach towards the hot glass substrates kept at relatively low substrate temperature. The film formation is achieved when fine metal oxide particles reach the substrate. Deposition is achieved by forcing in moisture free air using an air compressor so as to get a sprayrate of ~5 to 6 ml/min. The substrate to nozzle distance was fixed at a height of 37cm.

The crystal structure of as deposited films was determined using XRD technique. XRD analysis was done by using X-ray diffractometer [Bruker axs D-8 Germany] /Cu $K\alpha$ (λ = 1.5406 Å) radiation. The diffraction angle was varied from 20 to 80° at a step size of 0.1^o. To determine the band gap, transmittance of selected samples was measured in the range 300-900nm by UV-VIS spectrophotometer. Surface morphology and surface topography of as deposited films was studied by field emission microscopy FESEMand atomic force microscopy AFM techniques respectively. Hydrogen sulfide (H_2S) gas sensing measurements, at different gas concentrations and different operating temperatures were carried out using a homemade gas sensing unit.

RESULTS AND DISCUSSION

Structural and Morphological

Studies X-ray diffraction analysis

Fig.1. shows the XRD patterns of films viz: pure (undoped) CdO, 3% Sn doped CdO (SampleS3), and cadmium zinc mixed oxide (Samples M60 and M100). The undopedCdO and Sn:CdO films were polycrystalline in nature showing intensity peaks along (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes with preferential orientation along (111) plane [22].There was decrease in intensity of corresponding peaks due to Sn doping. The observed 'd' values were found to be in excellent agreement with those reported in the JCPDS card (No.05- 0640[23].However, in case of mixed oxide films, notable shift in peak positions was observed for sample M60 indicating the shift from cubic to wurtzite crystal structure, the sample M100 (Pure ZnO) showed intensity peaks at (1 0 0), (00 2), (1 0 1), (1 0 2), (1 1 0),(1 0 3) planes indicating presence of wurtzite structure and observed 'd' values matched with JCPDS card no 05-664. Further, the crystallite size was calculated using Scherrer formula [22].

$$D = \frac{0.9\lambda}{\beta \cos\theta_B}$$

Where, D =particle size, λ =wavelength of X- rays, θ_B= angle of diffraction and β= line width. It was observed that crystallite size of above samples was in the range of 50 to 60 nm which reveals that the films were nano crystalline in nature.

Surface morphological analysis

Some typical samples were characterized for morphological studies by using FESEM technique as shown in Figure .2.It is observed from FESEM images that the surface morphology is granular and that tiny crystallites have coalesced together to form larger crystallites/grains. It is clearly seen that pure CdO and sample M60 of mixed oxide are more crystalline and porous as compared with Sn doped sample S3 indicating that these samples might show relatively higher gas sensing performance.Further, that sample M60 shows uniform nano flower like morphology with sufficient inter granular separations leading to exposure of larger surface area when film is subjected to analyte gas this might show improved sensing performance. Pure (undoped) CdO, 3% Sn doped CdO (Sample S3), and cadmium zinc mixed oxide (Samples M60 and M100) were characterized for studying surface topography using atomic force microscopy (AFM) as shown in Figure 3. Surface roughness was observed to be greater for undopedCdO and cadmium zinc mixed oxide (Samples M60 and M100) than 3% Sn doped CdO (Sample S3).

Optical Studies

Using optical absorbance studies for doped CdO, 3% Sn doped CdO (Sample S3) and cadmium zinc mixed oxide (Samples M60 and M100), the optical band gap was calculated using the relation given below [23]

$$\alpha = A\frac{(h\nu - E_g)^n}{h\nu}$$

where, A is a constant, 'hν' is the energy of a photon, 'Eg' is the band gap energy, 'n' is constant and n =1/2 for direct and allowed transitions. The band gap energy 'Eg' is estimated by extrapolating the straight-line part of $(\alpha h\nu)^2$ against 'hν' curve on energy axis. The band gap values obtained from the graph are: 2.4 eV, 2.48 eV, 2.63 eV and 3.18 eV for pure CdO, 3% Sn doped CdO (Sample S3), and cadmium zinc mixed oxide (Samples M60 and M100) respectively and in agree with the values reported by other researchers [24]. This indicates that the films are semiconducting in nature having n type conductivity.

Gas Sensing Studies

Gas sensing experiments were performed with the helpof a homemade gas sensing unit reported elsewhere. The response of pure (undoped) CdO thin film to hydrogen sulfide (H_2S) gas was tested at various concentrations of H_2S gas and at different operating temperatures. It is seen that pure CdO sample shows notable response to H_2S. Figure 5. shows variation in % sensitivity versus temperature for 200 ppm of H2S and it is found to be maximum at 250°C. The increase in response with increase in temperature may be due to the supply of adequate thermal energy to overcome inter- granular barrier height. The decrease in response at higher temperature (300°C) is attributed to the excess thermal energy that may slow down the process of interaction with oxygen.of H2S gas by M60 sample was studied at various operating temperatures and at different concentrations. The sensitivity was found to vary from ~ 21.8 to 33.4 % when the sample is exposed to H_2S gas in the concentration ranging from 80 to 200 ppm and it remains nearly constant for concentrations greater than 200 ppm. Fig.6. shows variation in maximum response to H_2S gas for different concentrations at an operating temperature of 250°C exhibited by the sample M60. H_2S sensing studies were carried out in similar way for 3 at % doped CdO (sample S3). After carrying out rigorous experimental studies it was observed that no appreciable variation in resistance of the film was observed at above gas concentrations and at different operating temperatures in the range of 200 to 350°C.

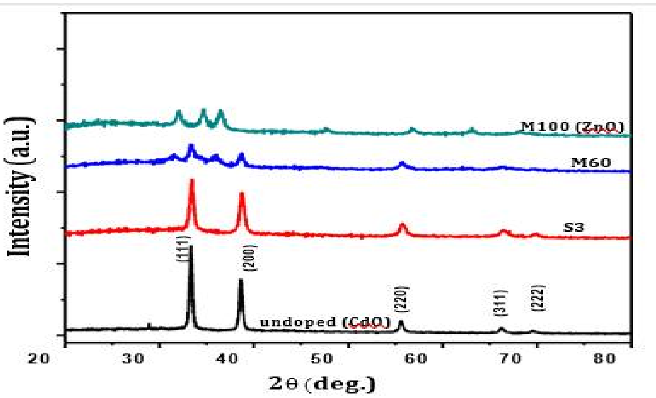

Figure1: Intensity patterns of pure CdO, Sn: CdO (sample S3), CdxZn1-xO (Samples M60 and M100 [22]

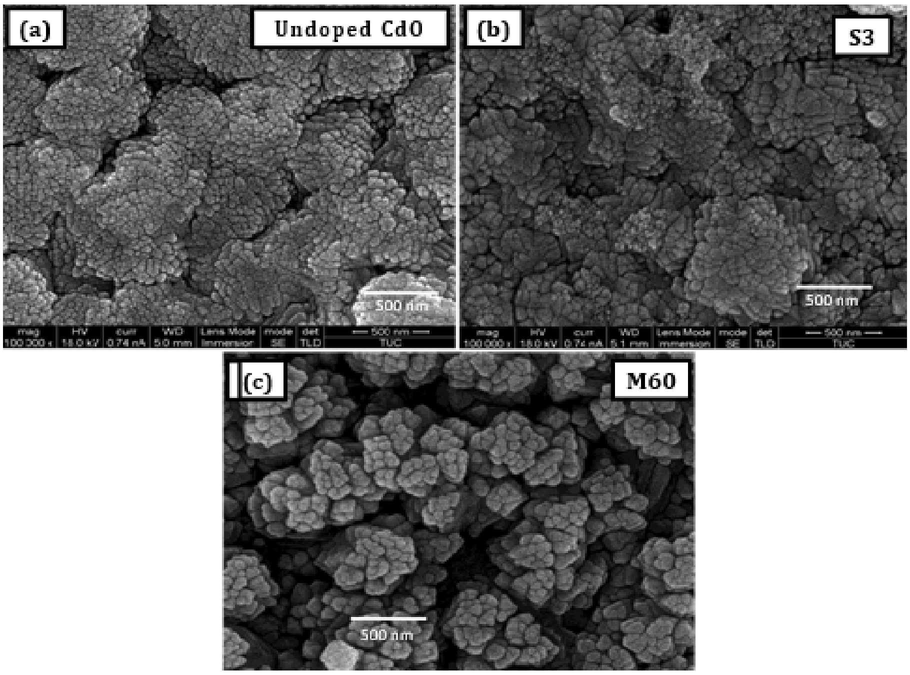

Figure2: FESEM images of pure CdO, Sn: CdO (sample S3), $Cd_xZn_{1-X}O$ (Samples M60)

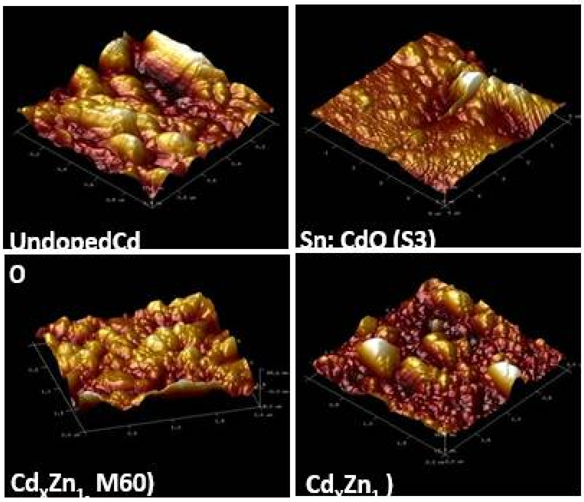

Figure3: AFM images of undoped CdO, Sn: CdO (sample S3), CdxZn1-XO (Samples M60)

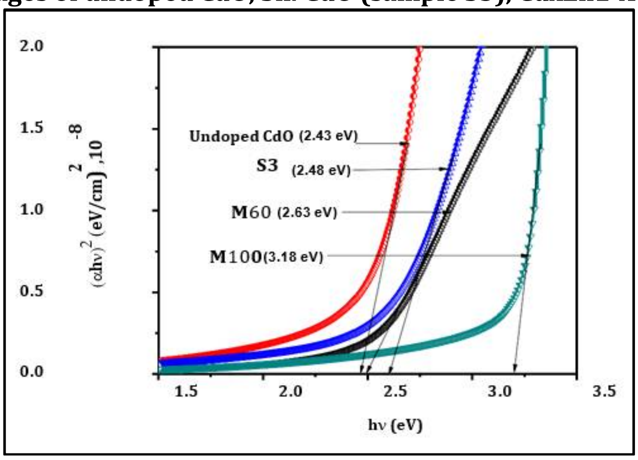

Figure 4: Tauc's plots for undopedCdO, Sn: CdO (sample S3), CdxZn1-XO (Samples M60) [22]

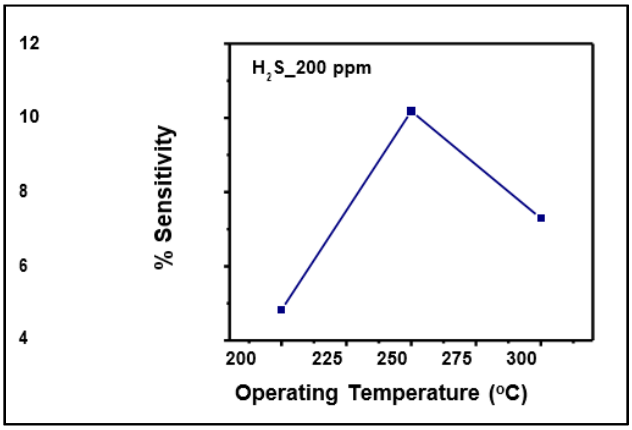

Figure 5: Percentage sensitivity vs temperature plot for 200 ppm H_2S shown by pure CdO sample [22]

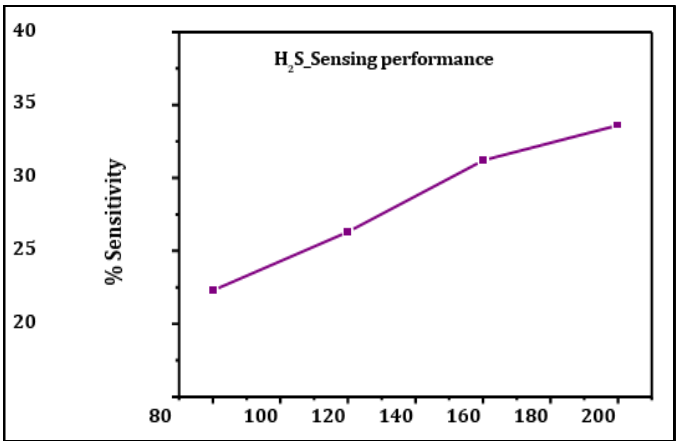

Figure 6: Variation in % sensitivity with different concentrations of H2S shown by mixed oxide sample M60[22]

CONCLUSION

It was possible to synthesize pure (undoped) cadmium oxide (CdO), tin-doped cadmium oxide (Sn:CdO) and cadmium zinc mixed oxide ($Cd_XZn_{1-X}O$) nano crystalline thin films were using novel spray CVD technique at low substrate temperature. As synthesized films were nanocrystalline, uniform, porous with rough surface topography. The energy gap varied in the range of 2.43 eV to 3.18 eV indicating that the films were semiconducting in nature, and they were transparent in the region 300 to 900 nm. Gas sensing studies indicate that pure CdO films showed maximum sensitivity of 10.2 % at 250oC when subjected to 200 ppm of H2S gas while cadmium zinc mixed oxide ($Cd_XZn_{1-X}O$) showed maximum sensitivity of 33.4 % at same concentration and operating temperature. No notable gas response was observed for tin doped CdO (Sn:CdO) in this study. Overall, this study reveals that mixed oxide thin films show higher response than pure (undoped) and tin doped CdO thin films.

REFERENCES

1. Ali H. M. (2005). Characterization of a new transparent-conducting material of ZnO doped ITO thin films.Phys. Status Solidi. A.202:2742-2752.
2. Ali H. M, Mohamed H. A., Wakkad M. M. and Hasaneen M. F .(2009). Optical and Electrical Properties of Tin-Doped Cadmium Oxide Films Prepared by Electron Beam Technique. Japanese J. Appl. Phys. 48:104.
3. SahaB.,Thapa R., and Chattopadhyay K. K. (2008). Bandgap widening in highly conducting CdO thin film by Ti incorporation through radio frequency magnetron sputtering technique. Solid State Commun..145 : 33-37.
4. Kul M., Aybek A. S., Turan E., Zor M. and Irmak S. (2007). Effects of fluorine doping on the structural properties of the CdO films deposited by ultrasonic spray pyrolysis. Sol. Energ. Mat. Sol. C. 91: 1927-1933.
5. Lupan, O.,Chow L., Shishiyanu S., Monaico E., Shishiyanu T., SonteaV.,RoldanCueny B.,Naitabdi A., Park S., Schulte A. (2009). Nanostructured zinc oxide films synthesized by successive chemical solution depositon for gas sensor application. Mater. Res. Bull. 44 : 63-69.
6. Salunkhe R. R., Lokhande C. D. (2008). Effect of film thickness on liquefied petroleum gas (LPG) sensing properties of SILAR deposited CdO thin films. Sens. Actuators B, 129:345-351.
7. Tamaki J.HayashiA.,Yamamoto Y., Matsuoka M. (2003). Detection of dilute nitrogen dioxide and thickness effect of tungsten oxide thin film sensors. Sens. Actuators B, 95: 111-115.

8. YamazakiT., Okumura H.,Jin C.-J., Nakayama A., Kikuta T., Nakatani N. (2005). Effect of density and thickness on H2-gas sensing property of sputtered SnO2 films.Vacuum.77:237-243.
9. de León-Gutiérrez, L.R.,Cayente-Romero J. J.,Peza-Tapia J. M.,Barrera- CalvaE.,Martínez Flores J. C.,Ortega-López M. (2006). Some physical properties of Sn-doped CdO thin films prepared by chemical bath deposition. Materials Letters.60 :3866- 3870.
10. Dantus C., Rusu G. G., Dobromir M., Rusu M. (2008). Preparation and characterization of CdO thin films obtained by thermal oxidation of evaporated Cd thin films. Appl. Surf. Sci. 255: 2665-2670.
11. GuptaR. K., Ghosh K., Patel R., Kohol P.K. (2009). Highly conducting and transparent Ti-doped CdO films by pulsed laser deposition. Appl. Surf. Sci. 255: 6252-6255.
12. Salunkhe R. R., Lokhande C. D. (2008). Effect of film thickness on liquefied petroleum gas (LPG) sensing properties of SILAR deposited CdO thin films. Sensors and Actuators B: Chemical.129 : 345-351.
13. Bhosale C.H., Kambale A.V., Kokate A.V., RajpureK.Y. (2005). Structural, Optical and electrical properties of chemically sprayed CdO thin films. Materials Science and Engineering B. 122: 67-71.
14. Kumaravel R., RamamurthiK. (2010). Effect of indium doping in CdO thin films prepared by spray pyrolysis technique. Journal of Physics and Chemistry of Solids. 1545-1549.
15. Khan M. K. R., Azizar Rahman M., Shahjahan M., Mozibur Rahman M.,. Hakim M.A, Saha Dilipkumar.,KhanJasimuddin. (2010). Effect of Al-doping on optical and electrical properties of spray pyrolytic nano-crystalline CdO thin films. Current Applied Physics.10:790-796.
16. Ferro R., Rodriguez J. A. (1999). Some physical properties of F-doped CdO thin films deposited by spray pyrolysis. Thin Solid Films.347: 295-298.
17. Patil P. S. (1999). Versatility of chemical spray pyrolysis technique. Mater. Chem. Phys. 59:185-198.
18. Shewale P.S., Yu Y.S., KimJ.H., Bobade C. R., Uplane M.D. H2S gas sensitive Sn-doped ZnO thin films: Synthesis and characterization. Journal of Analytical and Applied Pyrolysis 2015.112: 348-356.
19. DeokateR .J. Pawar S. M., MoholkarA .V., Sawant V .S., Pawar C. A., Bhosale C. H., Rajpure K. Y. (2008). Spray deposition of highly transparent fluorine doped cadmium oxide thin films Appl. Surf. Sci.254: 2187-2195.
20. BobadeC.R. (2017). Synthesis and characterization of Sn doped CdO thin films by novel advanced spray pyrolysis technique. IJRBAT, Vol V Issue 3:123-129.
21. BobadeC.R. (2015). Thesis entitled :Synthesis of cadmium oxide thin films by Advanced spray pyrolysis technique and their use in gas sensor PhD Thesis.
22. Micheltti F. and Mark P. (1967). Effects Of Chemisorbed Oxygen On The Electrical Properties Of Chemically Sprayed Cds Thin Films. J. Appl. Phys. Lett. 10: 136-138.
23. Cullity B. D. and Stock S.R. (2001). Elements of X- ray Diffraction. Prentice Hall Third Edition, London.
24. SahaB., DasS., Chattopadhyay K. K. (2000). Electrical and optical properties of Al doped cadmium oxide thin films deposited by radio frequency magnetron sputtering. Sol. Energ. Mat.Sol.C. 91: 1692-1697.

CITATION OF THIS ARTICLE

C. R. Bobade, V.S. Raut, P. P. Jadhav, D.K. Dhongade, R.S. More, U.K. Mohite. Higher H_2S Gas Sensing Performance of Cadmium Zinc Mixed Oxide Thin Films Compared to Tin Doped and Pure Cadmium Oxide Thin Films Synthesized by Spray CVD Method. Bull. Env.Pharmacol. Life Sci., Spl Issue [1] 2022 : 1380-1385