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Impact of Sputtering Power on Properties of CdO:ZnO Thin Films Synthesized by Composite Method for Oxygen Gas Sensing Application

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The present work reports the impact of RF sputtering power on CdO:ZnO (3:1) nanocomposite thin films deposited by sputtering. The structural, morphological, optical and electrical properties of CdO:ZnO thin films deposited at 40 W, 60 W, 80 W and 100 W RF sputtering power were investigated. The structural and morphological results show that high sputtering power improves the crystallinity of thin films. The thin film deposited at 80 W has (111) and (002) phases corresponding to mixed cubic and wurtzite crystal structure, whereas surface morphology of 100 W thin film shows that particles are densely agglomerate. The energy-dispersive x-ray spectrum shows the presence of Cd and Zn atoms in the CdO:ZnO nanocomposite samples. The films show 75–85% transparency in the visible region and a large variation in optical bandgaps from 2.6 eV to 3.5 eV was observed for the samples deposited at 40–100 W with lowest value for the 80 W thin film. I–V characteristics of all the CdO:ZnO thin films show an ohmic nature and resistance varies from 10^4 Ω to 10^9 Ω, suitable for resistive based gas sensor. The optimized thin film of CdO:ZnO deposited at 80 W was used for oxygen gas sensing applications 25–200°C operating temperatures and 25.4% sensor response was observed. The response and recovery times were found 10–20 s. Overall study reflects appreciable impact of RF sputtering power on different parameters under investigation.

Key words: RF sputtering, CdO, ZnO, oxygen sensing

INTRODUCTION

Nanocomposite materials open a door to developing more stable, efficient and cheaper nanoelectronic devices.[1–4] Metal oxide semiconductors have been continuously studied for various applications such as solar cells, IR detectors, photo-transistors, batteries, electrodes, gas sensors, humidity sensors and optoelectronic devices, and the research continues to improve favourable properties that are cost effective.[5–8] Metal oxide compound semiconductors such as ZnO, SnO_2, TiO_2, and CdO, ZrO_2 are being used due to their various promising properties viz, good transparency in the visible region, high electrical conductivity, stability and favourable microstructures.[9–12] Nanocomposite materials of a similar class offer better control to optimize desirable properties.

Zinc oxide (ZnO) has been studied for several applications and has become a favorite metal oxide, with optical band gap 3.2 eV and wurtzite crystal phase.[13,14] Cadmium oxide (CdO), another II–VI semiconductor similar to ZnO, was incorporated as a partner of ZnO for nanocomposites. The electrical conductivity of CdO is higher as compared to ZnO while its optical band gap is lower at 2.2 eV with a cubic phase[15,16] as compared to ZnO. The nanocomposites of ZnO:CdO have shown high electrical

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conductivity, better transparent thin films and mixed crystal phase, which is suitable to defect structure and high volume to surface ratio morphology[17,18] desired for gas sensing application.

An electronic nose is a requirement for the detection of several toxic and non-toxic gases for human beings and, therefore, various toxic gas sensors have been developed by several research groups.[19–25] However, sensors for non-toxic gases such as oxygen and nitrogen have few reports available and need further attention. Oxygen gas sensors have great importance in different applications such as automotive engines, industrial heating, purification, presence of oxygen in the environment, and also in various medical applications. Coban et al.[26] prepared a ZnO-based oxygen gas sensor by electrochemical deposition and tried to reduce the operating temperature. Peng et al.[27] have reported ZnO nanobelt-based oxygen gas sensors with Co dopant at low operating temperature, and similarly other researchers have also shown the importance of oxygen gas sensors.[28–30] The effects of different dopants in ZnO and CdO[27–29] synthesized by chemical method were also studied by several researchers.

Sputtering is a physical technique, which has a great significance in thin film technology for conducting and non-conducting materials that are thinner, have large area, are multi-layered and uniformly controlled thin films. The parameters such as distance between magnetron and target, argon and oxygen gas partial pressure, nature of substrates, substrate temperature, and sputtering time have affected growth and the properties of thin films. Sputtering power and argon-oxygen partial pressure have more influence on thin film properties such as structural, optical and morphological. Although there are several reports on effect of argon gas and oxygen gas partial pressure,[31–33] the effect of sputtering power has not been widely studied. The effect of sputtering power on thin films of CdO was studied by Dhivya et al.[34] who observed that the thickness increased with sputtering power due to an increase in their growth rate and energy of the sputtered atoms.

In the present work, a composite approach of physical and chemical methods was employed to deposit CdO:ZnO (3:1) thin films by RF sputtering, and the effect of RF sputtering power on crystal structure, surface morphology, optical and electrical properties have been investigated. The optimized CdO:ZnO thin film was employed for the oxygen gas sensing and good sensing response with fast reactive time for the oxygen gas has been observed.

THIN FILM PREPARATION

In the present work CdO:ZnO thin films were prepared by RF sputtering and the schematic diagram for the synthesis process is shown in Fig. 1. The sputtering target was prepared in our laboratory; firstly, the CdO:ZnO nanoparticles of 3:1 volume ratio were synthesized by sol–gel precipitation and annealed at 550°C. The target was compressed in pallet form and sintered at 450°C for 12 h

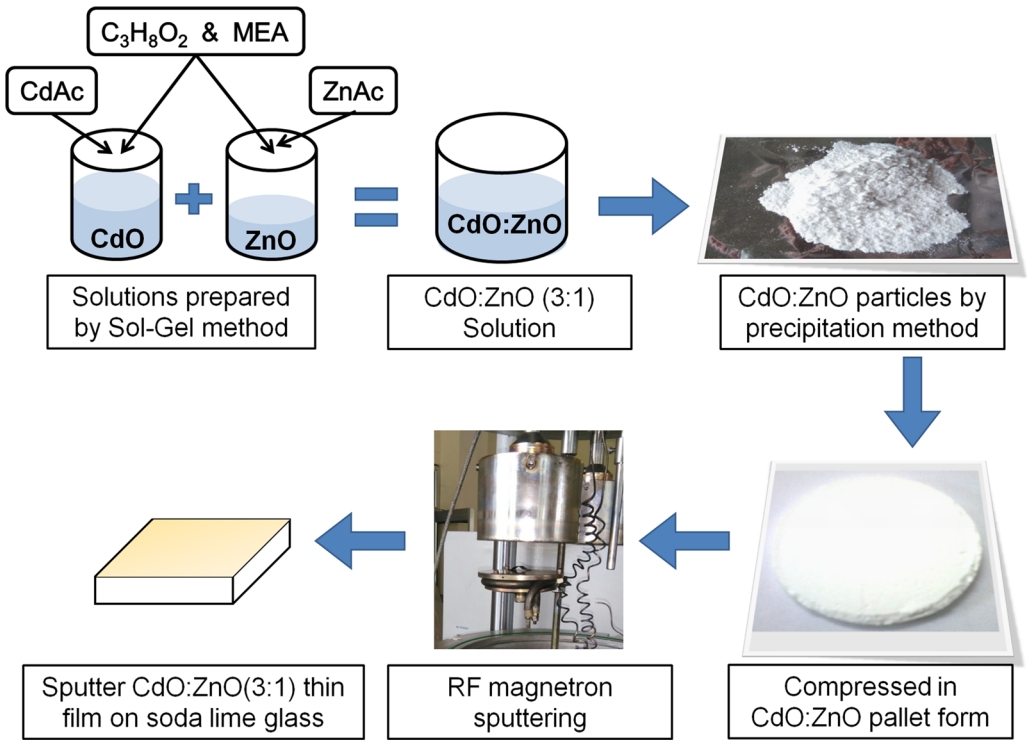

Fig. 1. The schematic diagram for complete synthesis process for preparation of CdO:ZnO thin films.

and then placed on target holder in sputtering chamber. Thereafter, the CdO:ZnO (3:1) thin films were deposited on the soda lime glass substrates by RF magnetron sputtering. The sputtering chamber was evacuated to a base pressure of 6.66×10^{-7} kPa using rotary pump and a diffusion pump; the distance between target and substrate was fixed at 5 cm. High-purity Ar gas was introduced as a sputtering gas into the chamber and monitored by mass flow controllers with fixed 80 SCCM (standard cubic centimeters per minute). The ultrasonically cleaned glass substrates were used for coating in sputtering chamber. When the pressure of the chamber reached $\sim 6.6 \times 10^{-3}$ kPa, RF sputtering was started and held to the fixed power for 40 min of sputtering. The four different thin film samples were prepared at 40 W, 60 W, 80 W and 100 W. The initial substrate temperature was 25°C and it increased up to 100°C during deposition due to the sputtering. The thin films so obtained were characterized and used for gas sensing application without further annealing. The experimental techniques and gas sensing measurement setup were similar, which were reported in our previous work.[15]

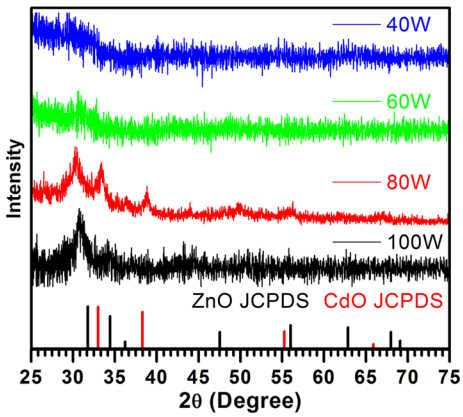

Fig. 2. X-ray diffraction patterns of CdO:ZnO nanocomposite thin films deposited at different RF sputtering power: 40 W, 60 W, 80 W and 100 W.

STRUCTURAL ANALYSIS

XRD patterns of CdO:ZnO thin films deposited at different powers in the 2θ range 25°–75° with step size 0.02° are shown in Fig. 2. It is clearly seen that good crystalline structure of nanocomposites are in the middle range of RF sputtering power. The XRD patterns for the lowest sputtering power of 40 W show amorphous structure, and crystallinity improved for higher sputtering power. The XRD pattern for 80 W shows peaks at different angles and confirms the crystalline nature of CdO:ZnO thin film. The intense peaks were observed at 30.55°, 33.44° and 38.78° corresponding to (100), (111) and (200), respectively.[35,36] Phase (100) was observed due to ZnO wurtzite structure, whereas (111) and (200) phases show cubic structure of CdO crystals. The small shifting in peak positions indicate the stress in thin films, which may be due to the interaction of Cd and Zn ions. The shifting of peaks also indicates that Zn ions were not replaced by Cd in the crystal lattice. The crystallinity further decreases for 100 W RF sputtering power and justifies that 80 W power is most suitable for good crystalline thin film.

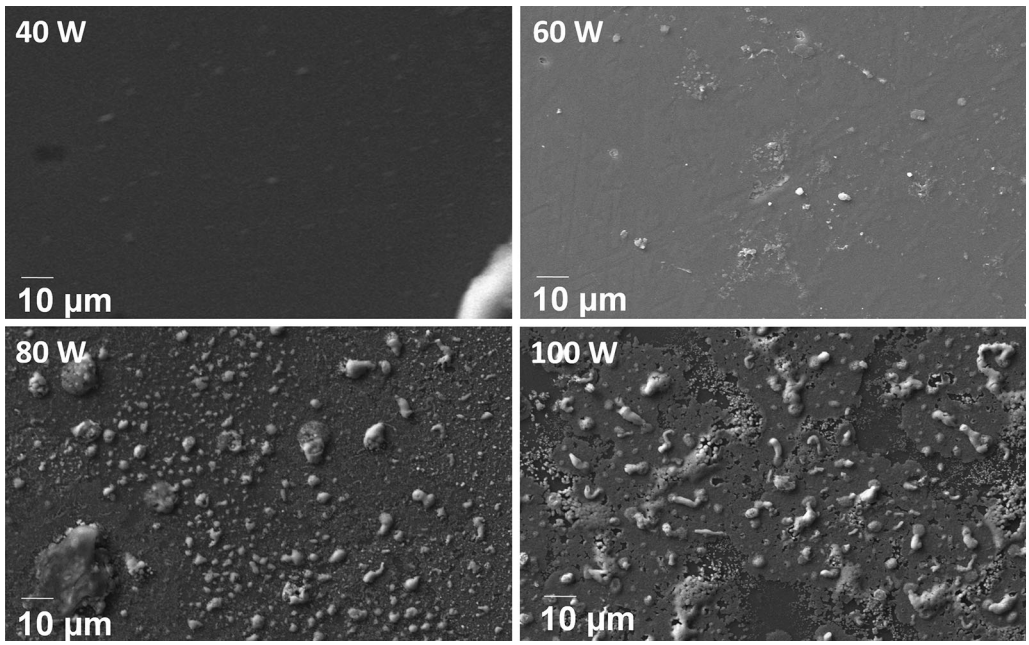

Fig. 3. Scanning electron microscopic images of CdO:ZnO thin films deposited at different sputtering powers 40 W, 60 W, 80 W and 100 W.

SURFACE ANALYSIS

The surface morphology of CdO:ZnO thin films was studied by scanning electron micrographs shown in Fig. 3 with a uniform scale 10 μm. The surface morphologies of the films change with different sputtering power and clearly show that the density of atoms increases at high sputtering power. CdO:ZnO thin film deposited at 40 W has a flat surface on which very small dot-like particles are seen, while the thin film deposited at 60 W also has a similar appearance, but is denser as compared to 40 W. The surface morphologies of thin films deposited at 80 W and 100 W clearly show the particles in different shapes and are much denser than the other two samples. However, the crystals of 80 W thin film are regular as compared to 100 W thin film. Similar results were also reported by Hsieh et al.[37] in their work for Al doped ZnO thin films at different sputtering powers. Ahn et al.[38] have reported that the higher power leads to plasma density and increases the flux of target material to the substrate and transfers more energy to the target particles to strike on the substrate. Therefore, higher power is suitable for growing good crystal, while on further increasing the sputtering power the morphology is rugged due to the excessive energy of sputter species. These species have a short time to diffuse within the growing film. The results revealed that the film deposited at 80 W shows regular morphology with dense albumen.

The elemental distribution on the surface was studied by energy-dispersive x-ray (EDX) spectrum

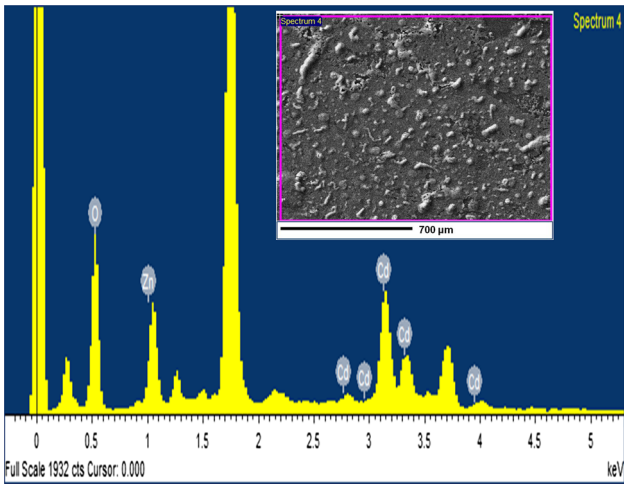

Fig. 4. Energy dispersive x-rays spectrum of the CdO:ZnO (3:1) thin film deposited at 100 W, and the SEM image of the sample of spectrum region shown in inset.

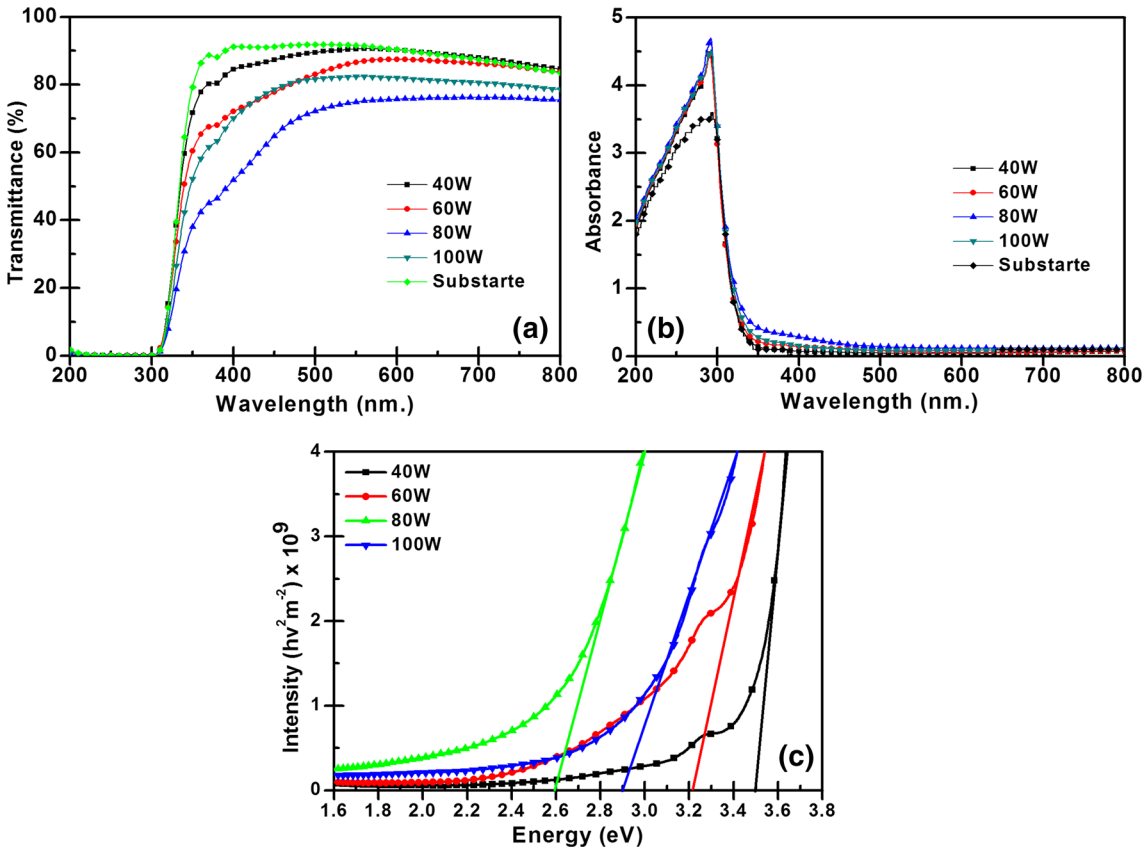

Fig. 5. The optical characterization of CdO:ZnO nanocomposites deposited at different sputtering power: 40 W, 60 W, 80 W and 100 W. (a) transmittance, (b) absorbance and (c) Tauc's plot for optical band gaps.

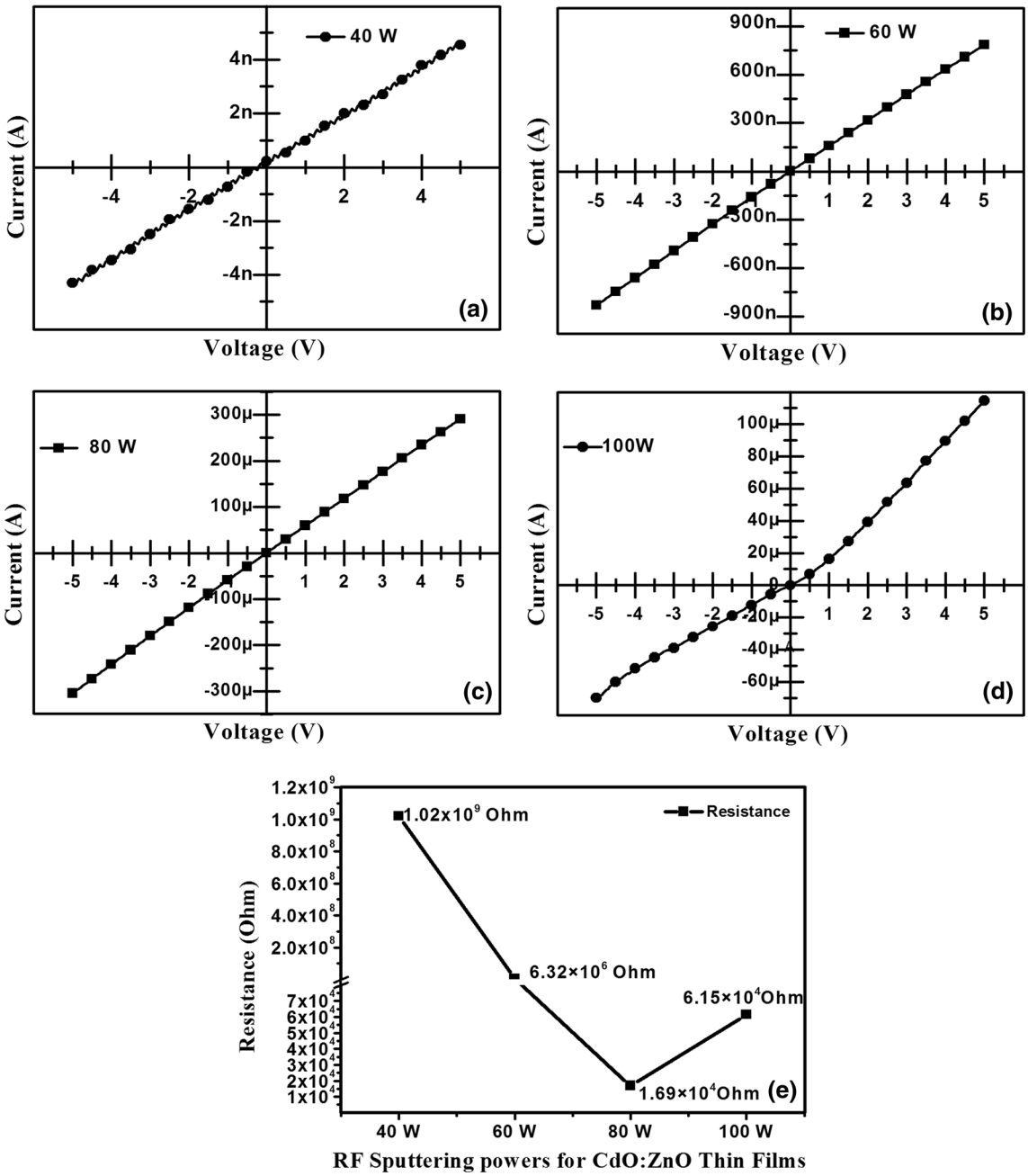

Fig. 6. The I–V characteristics of CdO:ZnO thin films deposited at (a) 40 W, (b) 60 W, (c) 80 W, (d) 100 W and (e) variation in resistance.

as shown in Fig. 4 and confirms the presence of zinc and cadmium atoms in the samples.

OPTICAL ANALYSIS

The optical properties of CdO:ZnO sputtered thin films were analyzed by transmittance and absorbance spectra in the wavelength range 200–800 nm as shown in Fig. 5. The transmittance of all thin films were found to be 70–85% in the visible region before the band edge and continuously decreases until the band edge becomes constant (zero) for 320–200 nm. The transmittance of 80 W and 40 W thin films show lowest and highest, respectively. The intermediate transmittance 82% was for film deposited at 60 W and 78% was for 100 W. The band edges show red shifting with increasing sputtering power for 80 W and were violet-shifted for 100 W. The absorbance spectrum was also recorded for better understanding the band edge position as shown in Fig. 5b. The absorbance of all the thin films were almost zero in visible region and rise in the wavelength 450–200 nm and was maximum at 310 nm. Similar transmittance results were observed by Saha et al.[39] for CdO thin film and reported 70% transmittance in visible region. The optical bandgaps of CdO:ZnO thin films were

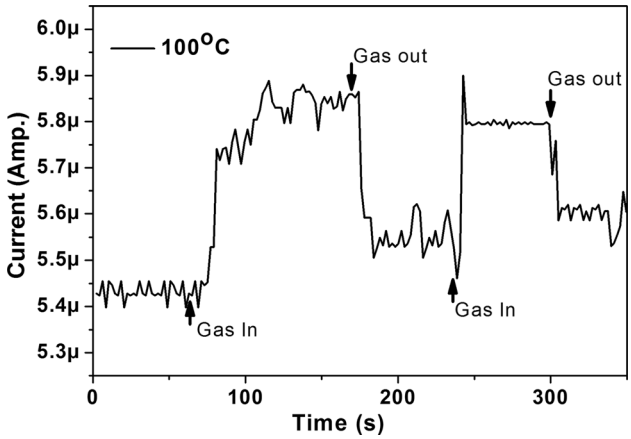

Fig. 7. Oxygen sensing response curve of CdO:ZnO thin film deposited at 80 W for operating temperature 100°C.

calculated by Tauc's plot method using transmittance spectra. The band gaps were found 2.6 eV, 2.9 eV, 3.2 eV and 3.5 eV for 80 W, 100 W, 60 W and 40 W thin films, respectively, as shown in Fig. 5c. Optical analysis has clearly indicated that optical properties of thin films strongly depend on RF sputtering power.

ELECTRICAL ANALYSIS

The DC electrical properties of all CdO:ZnO thin films of different powers were studied by I–V characteristic at room temperature as shown in Fig. 6a–e. The I–V characteristics were recorded by two probe method with silver electrode. All films show ohmic conduction in voltage range − 5 V to + 5 V. The electrical resistance of thin films were found to be $1.02 \times 10^9\ \Omega$, $6.32 \times 10^6\ \Omega$, $1.69 \times 10^4\ \Omega$ and $6.15 \times 10^4\ \Omega$ for thin films deposited at 40 W, 60 W, 80 W and 100 W, respectively, and the variation of resistance is shown in Fig. 6e. These results show that the thin film at 80 W RF sputtering power is suitable with highest electrical conductivity due to lowest electrical resistance, while the thin film deposited at 40 W shows lowest electrical conductivity. The electrical conductivity is related to the crystal grain size and optical band gap. The crystal grain of CdO:ZnO thin films deposited at 80 W were regular in size and the optical band gap was minimum, which may be the reason for better electrical conductivity.

OXYGEN SENSING ANALYSIS

The oxygen sensing properties of all the thin films were recorded by change in electrical resistance in gas environment with respect to base resistance in air. The resistances of thin films were recorded by two probe silver electrodes on top surface of thin films. The sensor response was recorded as a function of operating temperature because the metal oxide-based sensors are strong functions of operating temperatures. The thin films show high sensing response for oxygen gas, and sensor responses were recorded at fixed gas concentration 450 sccm. CdO:ZnO thin films deposited at 40 W and 60 W have not shown any change in resistance in vacuum to oxygen gas environment while the films deposited at 80 W and 100 W show response in presence of target gas. The sensor response curve for 80 W thin film at operating temperature 100°C and change in current in the presence of oxygen gas as compared to vacuum at a fixed voltage level of 0.5 V is shown in Fig. 7. The base resistance was recorded in air at corresponding operating temperature and had minimum resistance in the presence of oxygen gas. The sensor responses were calculated[15] and the maximum sensor response for CdO:ZnO thin film deposited at 80 W was 25.4% at 200°C. Thin film deposited at 80 W show 2–10% sensor responses at other temperatures. Sensor response of 100 W thin film varies form 5–31% and maximum at 200°C. The response time was increased with operating temperature and was found to be 20–30 s, while the recovery times were a little delayed 40-50 s. This sensing response has been explained by the oxygen ion sorption mechanism on the thin film surface. As thin films deposited at 80 W and 100 W have good morphology as compared to the other two, these two films have good sensing response.

CONCLUSION

The composite approach of physical and chemical methods to synthesize nanomaterial was found suitable for application in oxygen sensing. CdO:ZnO thin films were successfully prepared by RF sputtering at different RF sputtering powers. The 80 W RF sputtering power was found suitable to the growth of CdO:ZnO thin films. The surface morphologies of thin films for 80 W and 100 W were dense as compared to other films, and therefore, found suitable for gas sensor response. The optical transmittance for lower sputtering powers was higher as compared to higher powers. The highest conductivity of CdO:ZnO thin film was found for 80 W; therefore, oxygen gas sensing properties were observed for CdO:ZnO thin films deposited at 80 W as compared to other thin films. Overall, the study clearly shows that there is an impact of sputtering power on the properties of CdO:ZnO nanocomposites and 80 W sputtering power is the most suitable for depositing CdO:ZnO thin films for oxygen gas sensing.

REFERENCES

1. C. Ray and T. Pal, *J. Mater. Chem. A* 5, 9465 (2017).
2. Y. Li, F. Xu, Z. Lin, X. Sun, Q. Peng, Y. Yuan, S. Wang, Z. Yang, X. He, and Y. Li, *Nanoscale* 9, 14476 (2017).
3. S. Sikarwar, B.C. Yadav, G.I. Dzhardimalieva, N.D. Golubeva, and P. Srivastava, *RSC Adv.* 8, 20534 (2018).
4. J.K. Rajput and L.P. Purohit, *Nanosci. Technol.* 3, 1 (2016). https://doi.org/10.15226/2374-8141/3/2/00140.
5. H.B. Hassan and R.H. Tammam, *Solid State Ion* 320, 325 (2018).

6. B. Gerdes, M. Jehle, N. Lass, L. Riegger, A. Spribille, M. Linse, F. Clement, R. Zengerle, and P. Koltay, *Sol. Energy Mater. Sol. Cells* 180, 83 (2018). https://doi.org/10.1016/j.solmat.2018.02.022.
7. S. Sikarwar, S. Singh, R. Srivastava, B.C. Yadav, and V.V. Tyagi, *Smart Mater. Struct.* 26, 105047 (2017).
8. V.S. Rana, J.K. Rajput, T.K. Pathak, and L.P. Purohit, *J. Alloys Compd.* 764, 724 (2018).
9. D. Haridas and V. Gupta, *Sens. Actuators B Chem.* 182, 741 (2013).
10. S. Sikarwar, B.C. Yadav, S. Singh, G.I. Dzhardimalieva, S.I. Pomogailo, N.D. Golubeva, and A.D. Pomogailo, *Sens. Actuators B Chem.* 232, 283 (2016).
11. B. Bhowmik, P. Bhattacharyya, and I.E.E.E. Trans, *Nanotechnology* 16, 180 (2017).
12. J.K. Rajput, T.K. Pathak, V. Kumar, M. Kumar, and L.P. Purohit, *Surf. Interfaces* 6, 11 (2017).
13. D. Gedamu, I. Paulowicz, S. Kaps, O. Lupan, S. Wille, G. Haidarschin, Y.K. Mishra, and R. Adelung, *Adv. Mater.* 26, 1541 (2014).
14. Y.K. Mishra and R. Adelung, *Mater. Today* 21, 631 (2018).
15. J.K. Rajput, T.K. Pathak, V. Kumar, H.C. Swart, and L.P. Purohit, *Phys. B* 535, 314 (2018).
16. F.C. Eze, *Mater. Chem. Phys.* 89, 205 (2005).
17. T.K. Pathak, J.K. Rajput, V. Kumar, L.P. Purohit, H.C. Swart, and R.E. Kroon, *J. Colloid Interface Sci.* 487, 378 (2017).
18. C.V. Reddy and B.B.J. Shim, *J. Phys. Chem. Solids* 112, 20 (2018).
19. A. Sharma, M. Tomar, and V. Gupta, *Sens. Actuators B Chem.* 156, 743 (2011).
20. P.S. Shewale, G.L. Agawane, S.W. Shin, A.V. Moholkar, J.Y. Lee, J.H. Kim, and M.D. Uplane, *Sens. Actuators B Chem.* 177, 695 (2013).
21. P.H. Rai, Y.S. Kim, H.M. Song, M.K. Song, and Y.T. Yu, *Sens. Actuators B Chem.* 165, 133 (2012).
22. V.V. Ganbavle, S.K. Patil, S.I. Inamdar, S.S. Shinde, and K.Y. Rajpure, *Sens. Actuators A Phys.* 216, 328 (2014).
23. C.S. Park, D.B. Mahadik, and H.H. Park, *RSC Adv.* 5, 66384 (2015).
24. A.G. Imer, *Superlattices Microstruct.* 92, 278 (2016).
25. L. Yua, J. Wei, Y. Luo, Y. Tao, M. Lei, X. Fana, W. Yana, and P. Peng, *Sens. Actuators B Chem.* 204, 96 (2014).
26. Ö. Coban and S. Tekmen, *Sens. Actuators B Chem.* 186, 781 (2013).
27. L. Peng, Q. Zeng, H. Song, P. Qin, M. Lei, B. Tie, and T. Wang, *Appl. Phys. A Mater. Sci. Process.* 105, 392 (2011).
28. Y. Liu, T. Hang, Y. Xie, Z. Bao, J. Song, H. Zhang, and E. Xie, *Sens. Actuators B Chem.* 160, 266 (2011).
29. N. Al-Hardan, M.J. Abdullah, and A.A. Aziz, *Appl. Surf. Sci.* 257, 8993 (2011).
30. A. Yu, J. Qian, H. Pan, Y. Cui, M. Xu, L. Tu, Q. Chai, Q. Chai, and X. Zhou, *Sens. Actuators B Chem.* 158, 9 (2011).
31. Q. Zhou, Z. Ji, B. Hu, C. Chen, L. Zhao, and C. Wang, *Mater. Lett.* 61, 531 (2007).
32. T.K. Subramanyam, B.S. Naidu, and S. Uthanna, *Appl. Surf. Sci.* 169, 529 (2001).
33. C. Harish, K.S. Barshilia, and J. Rajam, *Nanosci. Nanotechnol. Lett.* 3, 300 (2011).
34. P. Dhivya, A.K. Prasad, and M. Sridharan, *J. Alloys Compd.* 620, 109 (2015).
35. Joint Committee Powder Diffraction Spectrum card no. 05-0640.
36. Joint Committee Powder Diffraction Spectrum card no. 14-3651.
37. P. Hsieh, T. Li, C. Chung, H. Peng, and J. Lin, *Adv. Mater. Res.* 579, 118 (2012).
38. K. Ahn, J. Park, B. Shin, W. Lee, G.Y. Yeom, and J. Myoung, *Appl. Surf. Sci.* 271, 216 (2013).
39. B. Saha, R. Thapa, and K.K. Chattopadhyay, *Solid State Commun.* 145, 33 (2008).