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SYNTHESIS AND CHARACTERIZATIONS OF ZNO-CDO LAYERS AND ITS THEORETICAL APPLICATIONS OF SOLAR CELLS BY SPIN COATING TECHNIQUE

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Abstract

In this paper, the detailed investigation on related to the structure, morphological and optical properties of Solgel spin coated ZnO-CdO thinflim films is carried out. Solgel spin coating was used to create potential Zinc Oxide (ZnO) and Cadmium Oxide (CdO) alloy (ZnO-CdO) films for solar applications. X-ray diffraction (XRD), UV-vis, and Raman spectroscopy were used to carefully study the characteristics of these films. And the thickness of the prepared thin flim were measured mechanical stylus profilometer. Theoretical properties of prepared ZnO-CdO thinflimare calculated Bruggmen's method and transfer matrix method and compared with experimental result. These investigations indicate that Solgel spin coated ZnO-CdO thin films have an appropriate band gap, a low defect density, and low strain. These findings will aid in the development of highly efficient photovoltaic devices by helping to narrow the ZnO band gap to a stoichiometric concentration and causing it to shift from the red to the green area with longer wavelengths.

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1. Introduction

Window layers, heat mirrors, light-transparent electrodes, photovoltaic cells, gas and semiconductor sensors, conductive devices, ultraviolet lasers and the context emitters, liquid crystal devices, and other opto-electronic devices are a few examples of materials with reasonably good conducting metal oxides that are used in energy-efficient applications.

One of the most promising materials is zinc oxide (ZnO), which has good electrical, optical, and piezoelectric properties as well as inexpensive, toxic-free,harmless, and non-flammable and remarkable stability of chemicals. It possesses a wurtzite-like hexagonal structure, a direct band gap of 3.3 eV, and a 60 meV excitonic coupling energy. CdO is a more important material than ZnO because of its applications, particularly in the realm of opto-electronic devices. It exhibits low resistance, an irregular structure, and a direct band gap of 2.2–2.5 eV. It is possible to create composite coatings with improved optical, magnetic, catalytic, and other properties by carefully selecting the metal matrix and inserted particles. Chemical composition influences microstructure, morphology, and other factors. It can be customised to obtain different physical, chemical, and optical qualities. Nanostructured Zn and Cd oxide mixture films' optical properties can vary depending on the ratio of oxides present [1]. According to Caglar et al. [2], utilising the sol-gel technique to make CdZnO films with various compositional ratios, the optical transmission increased as the Zn concentration raised.

Due to their predicted band gap modulation and transitional physical properties among clean CdO and ZnO, these two unusual materials can be a possibility for usage as buffer layers on solar cells. For the fabrication of CdO-ZnO films, a number of techniques have been documented, including electrodeposition, the molecular beam epitaxial approach, the sol-gel process, spray pyrolysis, and many more. The most straightforward and economical of them is spray pyrolysis. The current article focuses on the synthesis of ZnO and CdO doped ZnO utilizing a locally constructed spin coater that is controlled by a microcontroller [3]. Analysis methods such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), elemental dispersive X-ray analysis (EDAX), ultraviolet-visible spectroscopy (UV-Vis), and others are used to look into the effects of composition variation of CdO and ZnO on the structural and morphological characteristics of ZnO and CdO-ZnO thin films. Furthermore, a profile metre was used to study the thickness of CdO doped ZnOthinflim. Using Bruggemen's approach and the Transfer matrix method, a thorough analysis of optical studies and selectivity at the operating wavelength is conducted. The findings will be used to improve and build CdO-ZnO optical coating and window layers for solar cells [4].

2. Experimental analysis

The spin coater for the current study's CdO doped with ZnO thin films is a locally developed microcontroller-based spin coater that was used for the sol-gel-spin coating process. To make the precursor solution for making the sol-gel, 2.5 gm of zinc chloride ($ZnCl_3$) was dissolved in 100 ml of ethanol, 5 ml of hydrochloric acid (HCl), and 0.5 gm of cadmium chloride ($CdCl_2$) were added. This produced the desired amount of the precursor salt.

For one hour, the solution is refluxed at 60 oC. The sol is now prepared. For gelation, it is stored in an open beaker. Sol-gel is utilised for coating after three days of gelation. On the same glass substrate, successive coatings have been applied to achieve a sizeable film thickness. To prevent cracking, each coating is heat treated independently after it has been air dried [5]. These films were made by modifying process variables to get the optimum results, such as the solute concentration, gelation duration, turn table spin rate, number of coatings (i.e., film thickness), and the procedure temperature (i.e., the heat treatment temperature).

The precursor salt concentration (solute) must be optimised to produce high-quality films because it strongly affects the development of the film, as well as its transparency and quality. Initially, the thin film of zinc oxide doped with cadmium oxide had a powdery coating on top that could be gently wiped off when 2.5 g of zinc chloride (ZnCl2) and 0.5 g of cadmium chloride were employed in the sol-gel synthesis. To raise the thickness of the thin films, all these variables were held constant and the operations were carried out nine times. A hazy, lusterless coating with a thick 280 nm layer and a high resistance of 0.30 cm has been created [6].

2.1 Characterization

Use of an X-ray diffractometer (XPERT-PRO diffractometer) with Cu-K radiation (= 1.5405980A^0), room-temperature ultraviolet-visible (UV-Vis) spectroscopy in the wavelength range of 300 to 700 nm, and EDX, respectively, were used to characterise the samples' structural and optical properties**.** To examine the structure and quality of generated films, The Lab Ram HR-800 System, which stimulated a laser's 532 nm line at an incident power of 10 mW Ar, was employed to capture Raman spectra. These spectra had a resolution of 3.5 cm1.The thickness of the thin film was determined using a mechanical stylus profilometer.

2.2 Theoretical analysis

The experimentally analysedZnO and CdO-ZnO thin films optical properties are theoretically inveticated and compared with empirical results. The effective permittivity and optical properties of CdO-ZnO composite were calculated using Bruggmen method and transfer matrix method (TMM) with Matlab software respectively. The effective permittivity of a CdO-ZnO composite is calculated using the effective medium theory and the Bruggeman approximation [7].

The Bruggeman approximation formula is

$$f_1 \frac{\varepsilon_1 - \varepsilon_{eff}}{\varepsilon_1 + 2\varepsilon_{eff}} + (1 - f_2)\frac{\varepsilon_2 - \varepsilon_{eff}}{\varepsilon_2 + 2\varepsilon_{eff}} + f_3 = 0$$

where fi (i = 1; 2) is the volume filling percent of the ith component of the combination and where $\varepsilon_1$and ε_2 permittivity of CdO and ZnO composites obey the following evident relation:

$$f_1 + f_2 = 1 \qquad (3)$$

.

It is obvious that the solutions to Eq. (2) represent the effective permittivity values for the mixture.

2.3 Numerical Technique -Transfer matrix method

To calculate transmission coefficients based on wavelength, angle of incidence, and number of periods, transverse matrix method (TMM) is used. [8–9]. In this sketch, one-layer acts as the substrate, and another layer is a CdO-ZnO composite coating. Each layer's transfer matrix is unique, and the combined transfer matrix is the sum of all the individual transfer matrices. [10-11]

$$M_i = \begin{bmatrix} \cos\delta & \frac{-i}{n_l}\sin\delta \\ -in\sin\delta & \cos\delta \end{bmatrix} \qquad (4)$$

i here stands for either the H or L layer. The expression for the phase δ_l is

$$\delta_i = \frac{2n_i d_i * \cos\theta_i}{\lambda_0} \qquad (5)$$

Where i=1, 2 ……

$d_{1,2}$ are thickness of substrate and CdO-ZnO composite coating

The refractive indices of the substrate and CdO-ZnO composite coating are $n_{1,2}$ respectively.

for the entire structure Air

The total transfer matrix method is given by

$$T = (M_s M_{CdO-ZnO})^N \qquad (6)$$

Using the single-period matrix as a basis, we can determine the transmission coefficient for tunneling through such a structure if N has the values 1 and 2. [12]

$$T = \frac{4}{(T_{11} + T_{22}) + (T_{12} + T_{21})} \qquad (7)$$

3. Result and Discussion

3.1 Crystal Structure and Phase analysis

Figure 1 displays the observed XRD patterns for pure ZnO and CdO-ZnO thin films with diffraction angles (2h) ranging from 25° to 80. This demonstrates that pure ZnO film has a prominent, polycrystalline wurtzite peak at 34.38. Peaks from (100), (110), and (103) were visible in the XRD pattern for the CdO-ZnO doped structure (JCPDS no. 64-3411), while (111), (200), and (220) were seen in the ZnO hexagonal wurtzite (JCPDS no. (65-2880)) accordingly. As a result of the increasing structural disorder and density of point defects in the CdO-ZnO doped sample, the FWHM widens and the crystallinity decreases, contributing to peak broadening [13].

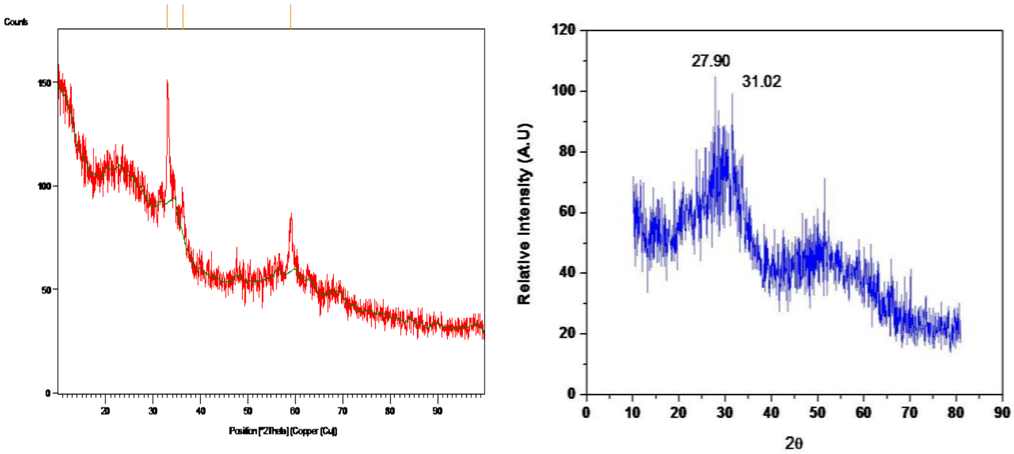

Fig.1. XRD Analysis of (a) ZnO(65-2880) (b) CdO doped with ZnO on glass substrate by Spin coating technique (65-3411)

Table.1. XRD Analysis of ZnOCdO -ZnO composite on glass substrate by Spin coating technique

	Pos. [°2Th.] Obs	hkl planes	FWHM [°2Th.]	d-spacing [Å] Obs	Rel. Int. [%]	Crystalline Size (nm)
ZnO	33.0453	111	0.4015	2.71080	100.00	21.56
CdO-ZnO	31.8117	100	04015	2.81305	73.58	21.87

3.2 SEM and EDAX mapping

The results of a SEM analysis that was done to look at the surface morphology of pure ZnO and CdO-ZnO thin films are shown in Figures 2(a) and (b).The figure shows that smooth, elliptical-sized, and cluster-like films were used to create pure ZnO thin films. The grains get agglomerated and bigger grains of spherical shape are formed. The figure of doped CdO-ZnO thin film revealed cluster structure are slightly scattered as well particle size slightly decreased. The SEM images show that the grains are agglomerated and uniformly spread over the substrate.

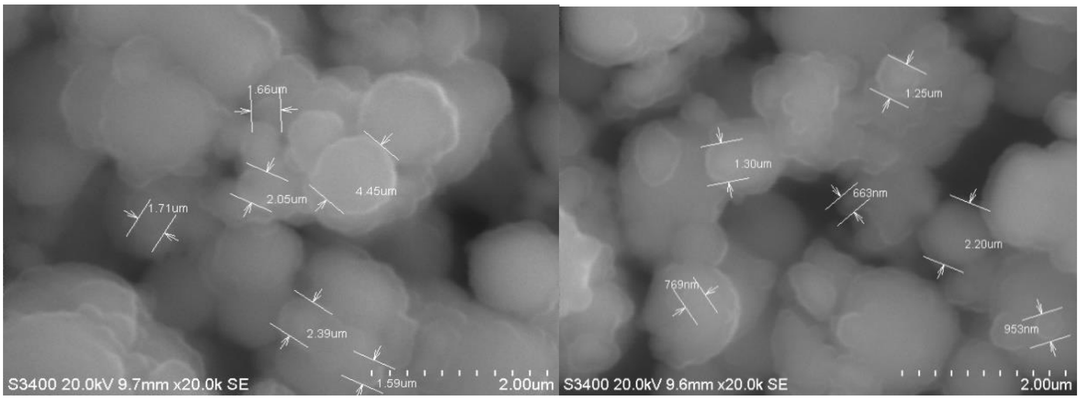

Fig.2. SEM Analysis of (a) ZnO (b) CdO-ZnOcomposite on glass substrate by Spin coating technique

To ensure the prepared sample's stoichiometry, see Figure 3; EDX analysis. Figures 3(a) and (b) from the deposited films demonstrate that the EDX analysis verified the existence of Zn, O elements and Zn, O Cd elements there. Figure 3(a) depicts how the Cd peak appears in the EDX spectrum of the Cd:ZnO film, confirming the inclusion of Cd in the film. The EDX pattern does not show any further impurities.

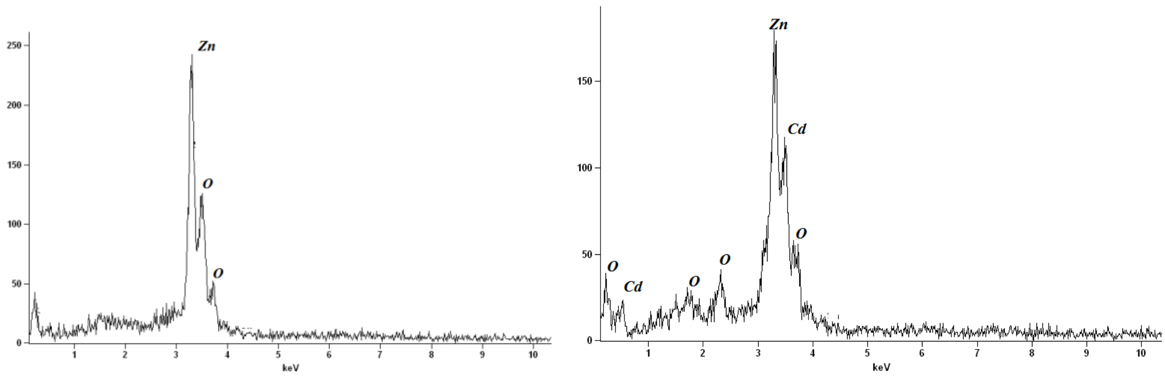

Fig.3. EDX Analysis of (a) ZnO (b) CdO-ZnOcomposite on glass substrate by Spin coating technique

Table.2. EDX Analysis of ZnOCdO -ZnO composite on glass substrate by Spin coating technique

Element Line	*Net Counts*	*Net Counts Error*		*Weight %*	*Atom %*	*Formula*
Zn L	5268	+/-	145	94.34	94.52	Zn
Zn M	0	+/-	24	---	---	
O L	305	+/-	121	5.66	5.48	O
O M	0	+/-	21	---	---	
Total				100.00	100.00	

Element Line	*Net Counts*	*Net Counts Error*		*Weight %*	*Atom %*	*Formula*
O K	137	+/-	16	26.21S	61.38	O
O K	291	+/-	55	5.99	7.00	O
O L	0	+/-	13	---	---	
Cd K	735	+/-	124	15.91	15.25	Cd
Cd L	0	+/-	18	---	---	
Zn L	1396	+/-	124	51.89	16.38	Zn
Zn M	0	+/-	16	---	---	
Total				100.00	100.00	

Figure 6(a) and (b) display the EDAX images of the nanocomposite ZnO and CdO-ZnO. CdO and ZnO were present in the composite arrangement, which was corroborated by the presence of Cd, Zn, and O. The table 2 displays the estimated atomic percentage compositions of Cd, Zn, and O based on the EDAX graphical depiction of various compositions. These results matched the amount of material used as a precursor very well.

3.4 FTIR-Analysis

Figure 4 displays the nanocomposite samples' IR reflection spectra between 500 and 4500 cm^{-1}. Several well-defined peak bending was observed at 398,564, 1155, 1277 and 2339 cm^{-1}. The metal oxide peak is centered at 564 cm-1 in pure ZnO, actually the peak Centre corresponding to ZnO present between 450 cm–1to 500 cm^{-1}, for ZnO-CdO composite material the peak is slightly shifted towards higher wavelength side this is expected due to defects present in the material. In nanocomposite samples that were taken from the air, a broad absorption peak at 1277 cm-1 coincides with the H-O-H bond of stretching vibrations [24] associated to the presence of water, and the other absorbance peaks at 2339 cm^{-1} provide an estimate of the C-O-C existence of a CdO-ZnO composite coating. No additional absorption bands were observed having a different functional group which indicates that the synthesized CdO–ZnO was in its purest form [15].

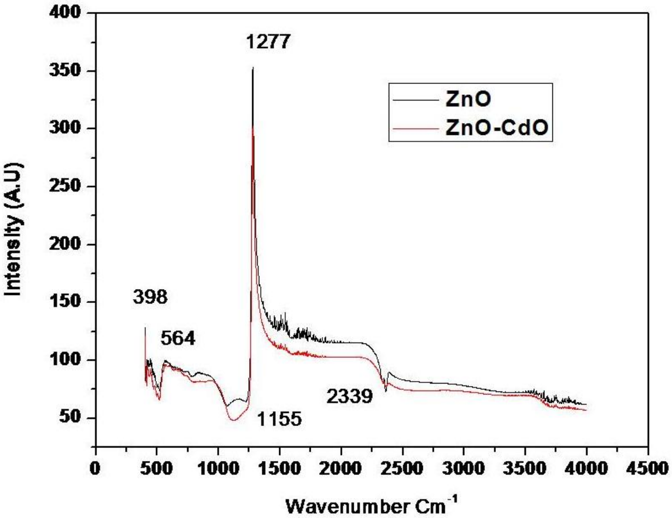

Fig.4. FTIR Analysis of (i) ZnO and (ii) CdO-ZnO composite on glass substrate by Spin coating technique

3.5 Optical Properties

Figure 5 displays the absorption spectra of spin coated ZnO and CdO doped with ZnO thin films in the 300–1000 nm range. Figure 5(a) makes it abundantly evident that the transmission occurs in the UV-VIS range and steadily rises by 80–90% until it reaches 900 nm.It is clear that the transmittance increases with the amount of ZnO to reach its maximum value compared to the amount of CdO (ZnO 2.5gm:CdO 0.5gm).This can be explained by the pure CdO thin film's increased surface roughness, which results from more light being incident on the film's uneven surface and scattering optically [16]. With the addition of CdO to the samples, the transmittance is reduced, which may be caused by the CdO's narrower bandgap than ZnO, which causes band-to-band absorption.This may be due to the fact that additional crystalline defects caused by higher doping concentrations, As oxygen vacancies and cadmium and zinc interstices scatter light, optical transmittance decreases.

As illustrated in figure 5(b), spin-coated ZnO and CdO thin films doped with ZnO exhibit an increase in absorbance at 330 nm. In spin coated ZnO and CdO doped with ZnO thin films, band gap absorption may be the cause.Using the well-known equation, it is possible to estimate the optical transition type and the optical band gap (Eg) based on the optical spectrum absorption.

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

A constant is A, and hv is the photon energy. The value of n depends on the type of band transition; it is equal to 1/2 for direct transitions and equal to 2 for indirect transitions. In Figure 5(c), we show plots of (h) 2 vs. h for spin-coated ZnO and CdO doped with ZnO thin films. By extrapolating the straight-line component of the curve at = 0, the optical band gap is discovered. The fact that both graphs are linear at the absorption edge indicates that the film's substance has a direct band gap. For spin coated ZnO and CdO doped with ZnO thin films, the band gap is calculated from the graph to be 2.65 and 2.79 eV, which roughly coincides with the values previously reported. The range of 2.65 to 2.79 eV is the tuned composite band gap. Thus, nanocomposite is created as Cd^{2+} ions take the place of Zn^{2+} ions.

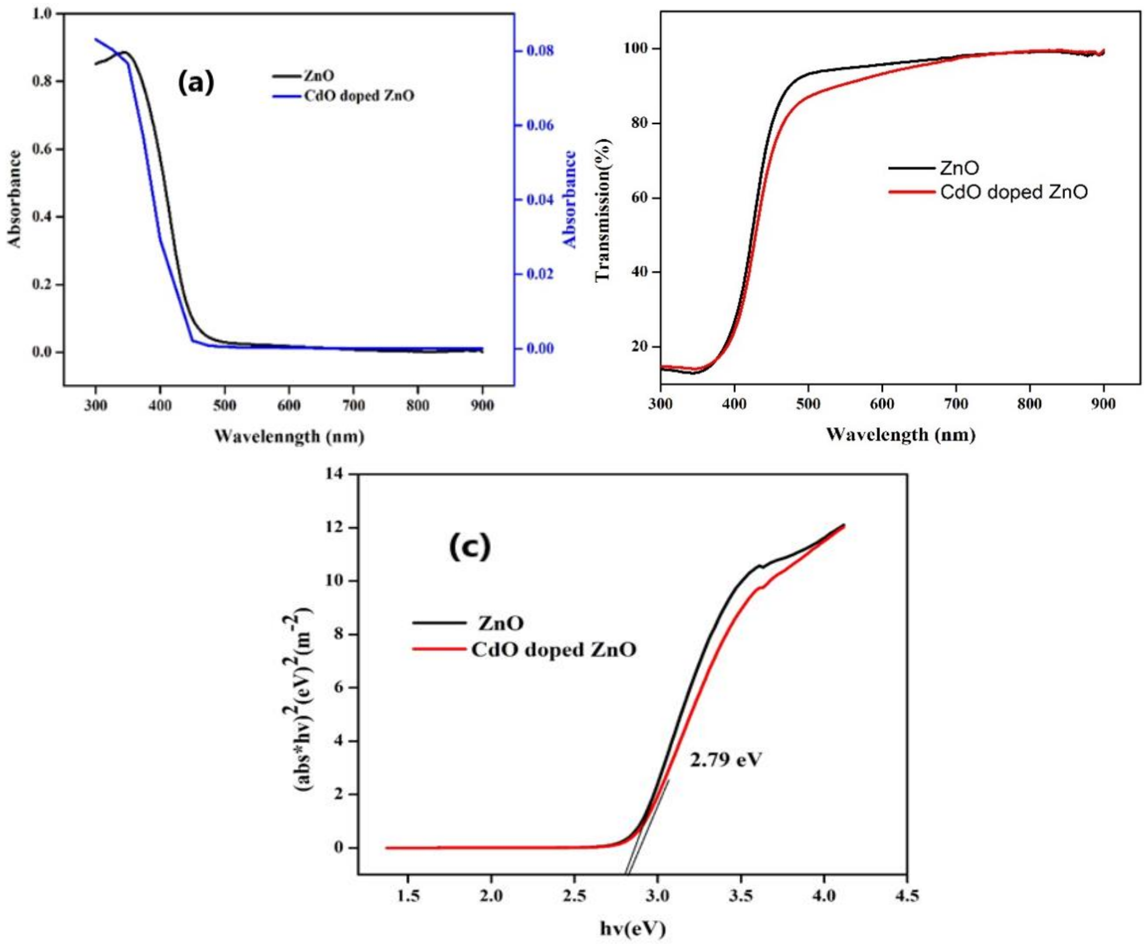

Fig.5. UV-Vis Analysis (a) Absorbance (b) Transmittance and (c) Bandgap of ZnOand ZnO -CdO composite thinfilm coated on glass substrate by using Spin coating technique

3.6 Thickness measurement:

The thickness of the prepared thin flim were measured mechanical stylus profilometer. Thus, the thicknesses of the samples were below 0.21 and 0.19 µm respectively as measured with profilometry.

Rp is the highest profile peak height over the evaluation length and the mean of the profile peak height for each sampling length.

$$\mathbf{R_p} = \left[\frac{R_{p1} + R_{p2} + R_{p3} + R_{p4} + R_{p5}}{5}\right]$$

Rv is the maximum profile valley depth over the length and the mean of the profile valley depth over the assessment length.

$$\mathbf{R_v} = \left[\frac{R_{v1} + R_{v2} + R_{v3} + R_{v4} + R_{v5}}{5}\right]$$

The value R_t is formed by adding the highest profile peak height and the deepest profile valley over the assessment length. The arithmetic mean roughness is known as Ra.Rz maximum height of profile, Rq root mean square deviation, and Ry root mean square of valley depth [17].

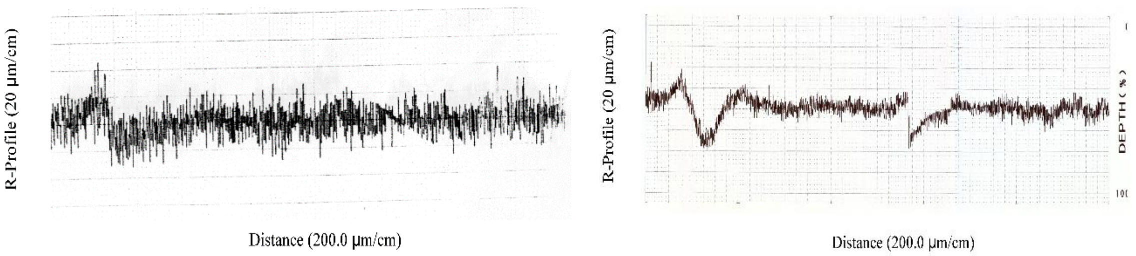

Fig.6. Stylus Profilometer Analysis of (i) ZnO and (ii) CdO-ZnO composite on glass substrate by Spin coating technique

Table.3, Spin coating technique thickness measurement of ZnO and ZnO -CdO composite thinfilm deposited on glass substrate

Temperature (in RT °C)	**Profile Parameters (inµm)**						
	Ra	**Ry**	**Rq**	**Rz**	**Rp**	**Rv**	**Rt**
ZnO	0.091	0.34	0.09	0.19	0.15	0.12	0.26
ZnO-CdO	0.052	0.35	0.07	0.14	0.11	0.09	0.19

The profile meter's calculations are shown in Table 3 as profile peak height Rp, profile valley depth R_v, and the total of maximum profile height R_t. It demonstrates that the limited interactions created by the narrow dispersion and thin coatings of big particles lead to a relatively direct transmission of force to the substrate. The thin ZnO film on the glass substrate measured 0.26 m in thickness, whereas the CdO-ZnO composite thin films with the same chemical composition on both and the glass substrate measured about 0.19 m in thickness. During the process of creating thin films, it was found that the thickness of the finished product could be altered Reduced coating time on substrate may result from controlling thickness in the nm range [18].

3.7 Theoretical analysis

Using the effective medium theory and the Bruggeman approximation, the refractive index of the CdO-ZnO composite coating is estimated in the 400 nm–900 nm wavelength range. CdO and ZnO have dielectric constants of 2.49 and 2, respectively. The figure shows 7 that the effective permittivity and refractive index of composite coating was calculated uing the equation 2 and for various filling fraction values consider the equation 3(0.05 to 1). The figure exhibits refractive index decreases with increases fill fraction of ZnO . It shows that the mixture or fill fraction values effectively act on refractive index of CdO-ZnO oxide coating. The optimized refractive index value improve the optical properties of composite coating

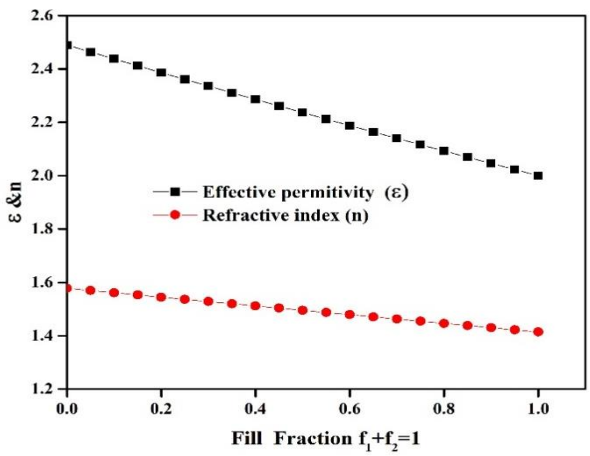

Fig.7 Bruggmen Theoretical measurement of Effective permittivity and Refractive index of CdO-ZnO composite on glass substrate

The figure 8 (a) and (b) shows that the experimental and theoretical comparison of CdO-ZnO composite. The numerical analysis of CdO-ZnO composite's optical properties are carried out by transfer matrix method equation 4 to 7 and compared with experimental results.The thickness of CdO-ZnO is 50nm on glass substrate and refractive index value taken from equation 2 in 0.5:0.5 mixture ratio. The figure illustrates how gearbox qualities vary significantly between 300 and 400 nm and just little between 450 and 900 nm. According to the findings, composite coating also has the highest transmission value (90%) of pure ZnO and Additionally, nanocomposite coatings have up to two times the hardness of amorphous oxide coatings, as well as improved crack resistance.It is important to remember that mechanical characteristics of nanocomposite coatings remain unchanged during thermal annealing as long as the coating's grain structure and the proportion of the two phases remain constant. Thermally stable oxide-based composite coatings are possible. [19].

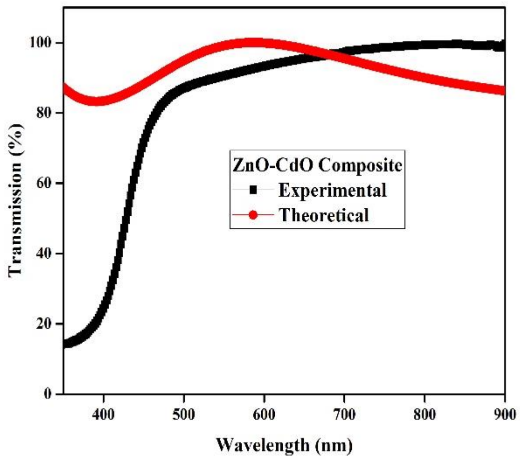

Fig.8 Theoretical and experimental transmission comparison of CdO-ZnO composite on glass substrate

Conclusion

Structure, morphology, and optical characteristics features of solgel spin-coated ZnO-CdO thinflim films are investigated in detail experimentally in this study, along with a numerical analysis of the films' optical characteristics. According to the XRD data, the peak broadening in the ZnO-CdO doped sample may be brought on by an increase in structural disorder and a density of point defects. The estimated optical parameter of ZnO-CdOthinflim composites have better than the pure ZnO coating. The raman spectroscopy result shows, no additional absorption bands were observed having a different functional group which indicates that the synthesized ZnO-CdOwas in its purest form. The thickness of coated film are 0.19 μm and 0.21 μm for ZnO-CdOand pure ZnO which shows composite coating thickness can be controlled by reduce time of growing process on substrate. The numerical analysis of ZnO-CdOcomposite optical properties slightly varies with experimental result composite coating enhances the optical absorbtion also have good mechanical properties, thermal stability, resistance to cracking than the pure oxide coating such ZnO, CdO. These investigations will aid in developing reasonably priced photovoltaic devices that are free of optical losses.

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