Chapter

Structural, Morphological and Optical Properties of Perfume Atomizer Spray Pyrolysis CdO Thin Films: Effect of Solution Volume

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Abstract

CdO films have been deposited on glass substrates with different solution volume (30, 40 and 50 mL) at 200°C using perfume atomizers spray pyrolysis method. X-ray diffraction studies shows that the prepared thin film had cubic and polycrystalline nature. Scanning electron microscope shows the influence of solution volume on surface morphology of the CdO thin film. Optical studies show that in these films the electronic transition is of the direct transition type. The optical energy gap for the films of as deposited are vary from 2.12 to 2.00 eV with solution volume. Photoluminescence results analysis confirmed that the dependence of optical energy gap on solution volume. The Hall measurements were carried out and the results were discussed.

Keywords: Thin films, X-ray diffraction, Thickness, Transmittance, Photoluminescence

1. Introduction

Cadmium oxide (CdO) thin films are one of the transparent conducting oxide (TCO) materials and have been fascinated the investigators for their remarkable properties such as tunable band structure, high extinction coefficient, possible multiple exciton generation, electronic and transport properties [1–4]. CdO is a degenerate n-type semiconductor with a wide energy gap and high electrical conductivity [5]. Its high electrical conductivity is due to the increased grain size at high substrate temperature, moderate electron mobility, and high carrier concentration. The properties of CdO can be controlled to a suitable value to for the suit particular applications by controlling some of the process parameters viz. film thickness, the temperature of the substrate, pH value of the solution, Wt.% and solution flow rate etc. Though CdO is a first transparent conducting oxide film studied by Bedekar in 1907, not many investigations have been done for quite a long time. During last few years CdO is being extensively investigated in bulk and thin film form. CdO has interesting properties like large band gap, low electrical resistivity and high transmission in the visible region etc. These characteristics make it suitable for a variety of applications, including photodiodes, phototransistors, photovoltaic transparent electrodes, liquid crystal displays, IR detectors, and anti-reflection coatings [6–10].

For the last few decades various techniques such as chemical vapor deposition, sputtering, chemical bath deposition, sol–gel, SILAR, thermal evaporation, layer by layer assembly, spin coating, activated reactive evaporation, metal organic chemical vapor deposition (MOCVD), pulsed laser deposition and spray pyrolysis techniques are employed for the preparation of CdO thin film [11–29]. Among these routes, spray pyrolysis technique is a simple and low cost chemical method for the preparation of thin films with large area of coating. In this work the simplified perfume atomizer spray pyrolysis homemade setup is used for prepare a CdO thin films. The usage of a perfume atomizer offers a number of advantages over traditional spray gun assembly: low cost, no need for carrier gas, fine atomization, better wettability between sprayed micro particles, and nearly no loss of the precursor to the environment. We recently demonstrated that by effectively synthesizing CdO films, this simplified spray process can be a desirable alternative to the standard spray technique. The structure, morphology and optical behavior of the film depend on molarity, solution pH, substrate temperature, age of solution and solution volume. The precursor solution pH affects the hydrolysis and condensation behavior of the solution, which, in turn, influences the structure of the resultant film, morphological and optical behavior of the films. The role of the solution aging on the properties of thin films and interesting photo luminescent characteristics had been already reported [30–32]. In general, the properties of coated film depend on pH of the precursor solution, substrate temperature, molarity of the starting solution and solution volume. In this chapter, the effect of volume of solution on the structural, morphological and optical properties of CdO films prepared by perfume atomizer spray pyrolysis deposition method were investigated and reported in detail (Section 2).

2. Experimental

CdO films have been prepared by using cadmium acetate dihydrate as a source material of Cd and double distilled water was used as solvent. The glass substrates of 1.5 cm × 1.5 cm were used for the CdO deposition. The substrates were cleaned following a well-established methodology consisting on an initial washing step with soap and water followed by a washing procedure using acetone and isopropyl alcohol in an ultrasonically bath and a final rinsing step with distilled water [33]. For the implementation of the perfume atomizer spray pyrolysis method, homemade system was designed and implemented (**Figure 1**).

The system consists on a perfume atomizer, a power supply and a heating plate. The optimized deposition parameters such as substrate – spray nozzle distance (25 cm), spray angle (about 45°), spray time (5 s) and spray interval (30 s) were kept constant. The precursor solution was prepared at room temperature and kept on a container attached to the atomizer. Once the precursor solution was prepared, cleaned glass substrates were positioned onto the heating plate and heated until the temperature of the substrates reached to the desired value. The glass substrates were positioned at a horizontal separation distance of 25 cm from the perfume atomizer. The CdO thin films have been prepared by spraying a solution (30, 40 and 50 mL) composed of cadmium acetate dissolved in double distilled water and when the droplets of sprayed solution reached the preheated substrate, owing to the

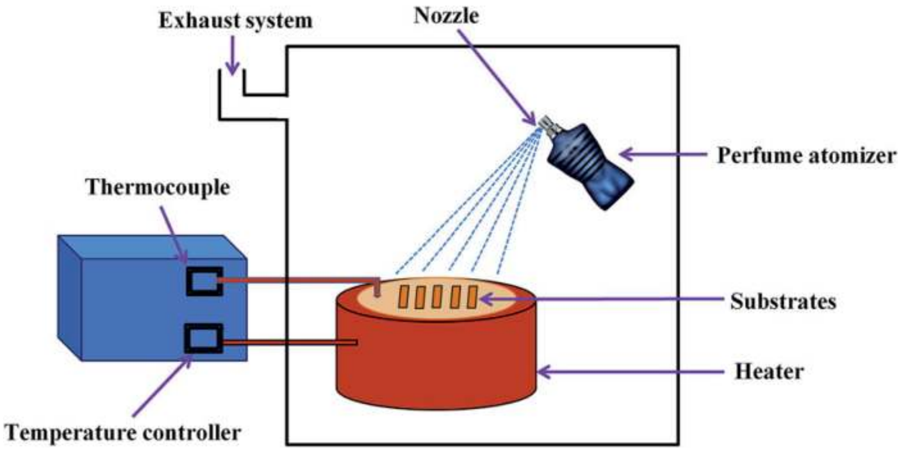

Figure 1.
Perfume atomizer spray setup.

pyrolytic decomposition of solution, a well adherent, pinhole free, uniform yellowish colored films of cadmium oxide are formed on the substrate surface according to the following reaction [34, 35].

$$Cd(CH_3COO)_2 + 3H_2O \rightarrow CdO\downarrow + CH_4\uparrow + 4H_2\uparrow + 3CO_2\uparrow \tag{1}$$

After the CdO deposition on the glass substrate, the samples were cooled down at room temperature and stored in dry conditions for further characterization. For the present study, the appropriate chemical and physical parameters were changed to study the effect of solution volume such as 30, 40 and 50 mL on structural, morphological and optical properties of CdO thin film.

3. Results and discussions

3.1 X-ray diffraction analysis

X-ray diffraction (XRD) is a versatile, non-destructive analytical technique for identification and quantitative determination of the various crystalline compounds, known as ‘phases’, present in solid materials and powders [36–38]. X-ray diffraction spectra were recorded using Philips X Pert PRO X-ray diffraction system (Cu $K\alpha$ radiation; K = 1.54056 Å). The average crystallite size (D) of the CdO film was calculated from Scherer’s equation for the (111) plane [39].

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{2}$$

Where, λ is the X-ray wavelength, β is the full-width at half-maximum of the peak and θ is the reflection angle. Dislocation density (δ) and strain (ε) for (111) plane was evaluated using the relations [40, 41].

$$\varepsilon = \frac{\beta\cot\theta}{4} \tag{3}$$

$$\delta = \frac{1}{D^2} \tag{4}$$

The number of crystallites per unit area is calculated from the following relation:

$$n_c = \frac{t}{D^3} \tag{5}$$

The lattice constant '*a*' of the cubic phase of CdO films was determined by the following relations [42].

$$\frac{1}{d^2} = \left\{ \frac{h^2 + k^2 + l^2}{a^2} \right\} \tag{6}$$

where (*hkl*) and *d* have the same meaning as before. **Table 1** shows the estimated lattice constants, which are in good agreement with the conventional lattice constant (*a*) value.

Different sets of starting solutions were prepared by dissolving 0.2 M cadmium acetate with different volumes such as 30, 40 and 50 mL in doubly deionized water. The solutions thus got are sprayed manually by a perfume atomizer on preheated glass substrates at 200°C. The recorded XRD spectra of CdO thin film grown from different solvent volumes are shown in **Figure 2** and show sharp and narrow diffraction peaks at (111), (200), (220), (311) and (222) planes confirms that the films coated have good crystallinity and also it reveals that the films are polycrystalline in nature with cubic structure. It is also observed that all the films have preferential orientation along the (111) plane irrespective of the solvent volume. The intensity of the peaks (111), (200) and (220) increases as the solvent volume increases, showing the crystalline nature of the samples. The other prominent peaks are also obtained in the XRD pattern corresponds to the planes (200), (220), (311) and (222) according to the JCPDS Card No. 75-0591. The findings demonstrate that as the solution volume increased the intensity of the (111) peak is also increased significantly.

The calculated crystallite size and other crystal parameters are presented in **Table 1**. It is observed that the crystallite size increases with an increase in solution volume. This is because a low solution volume allows for the formation of a dense film structure with small crystals, whereas a high solution volume allows for a slower nucleation process, high agglomeration, and the formation of larger crystals. The deviation in the lattice parameter values of the films coated with solutions having solvent volumes 30 and 40 mL suggest that the films were under strain. The strain may be because of the oxygen vacancies and the interstitial Cd atoms incorporated in the CdO lattice. Film coated with 50 mL solvent volume has the minimum value of strain and dislocation density (δ) which strongly favors for the improved crystallinity of this film. The lesser value of δ obtained for the film coated with 50 mL solvent volume shows the degree of crystallization of the film.

Volume of the solution (mL)	Lattice constant '*a*' (Å)	Film thickness (nm)	Crystallite size (nm)	Dislocation density ($\times 10^{15}$) lines.m^{-2}	Strain ($\times 10^{-3}$)	Number of crystallites ($\times 10^{16}$ m^{-2})
30	5.049	850	34	0.8800	3.59	2.2192
40	4.666	880	42	0.5633	2.88	1.1767
50	4.670	920	43	0.5633	2.88	1.2304

Table 1.
Structural parameters of CdO thin films at different solution volume.

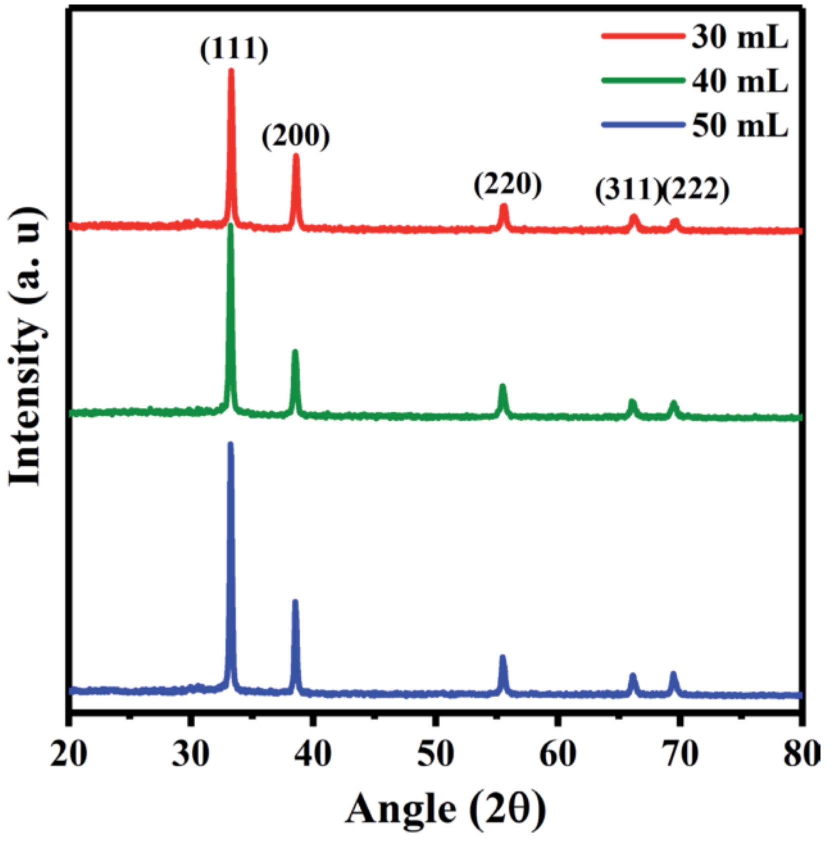

Figure 2.
XRD spectra of CdO thin film at different solution volume.

3.2 SEM and EDAX analysis

Scanning electron microscopy (SEM) is a widely used tool for surface analysis of thin films. SEM, accompanied by X-ray analysis, is considered a relatively rapid, inexpensive and basically nondestructive approach for surface analysis [43]. High resolution images of surface topography, with excellent depth of field are produced using a highly-focused, scanning (primary) electron beam [43–46]. Elemental composition of a specimen can be analyzed using energy dispersive X-ray (EDAX) technique. Other than preliminary insight peak of the examined sample, EDAX also offers quick and efficient characterization technique that acquires elemental information of the prepared samples at high resolutions [47, 48].

Figure 3(a–c) shows the SEM image of CdO thin film deposited with different solution volumes such as 30, 40 and 50 mL. The surfaces of the coated films are and densely packed and homogeneous. It is seen that there are well defined grains and it confirms the crystalline nature of the coated film. From the microscope, as the solution volume increases small sized grains are fused together and begin to for a patch of grain for 40 mL solution volume. The SEM image for 50 mL solution volume reveals that the spherically shaped grains with different size are found scattered throughout the substrate surface uniformly as reported earlier [49]. This study confirms that as solution volume increases, grain size increases, and these findings are well consistent with XRD tests. **Figure 3(d)** show the EDAX spectra and it confirms the presence of expected element in the prepared CdO films. It is found that the weight percentage of Cd and O atoms are 77.99 and 26.01% respectively.

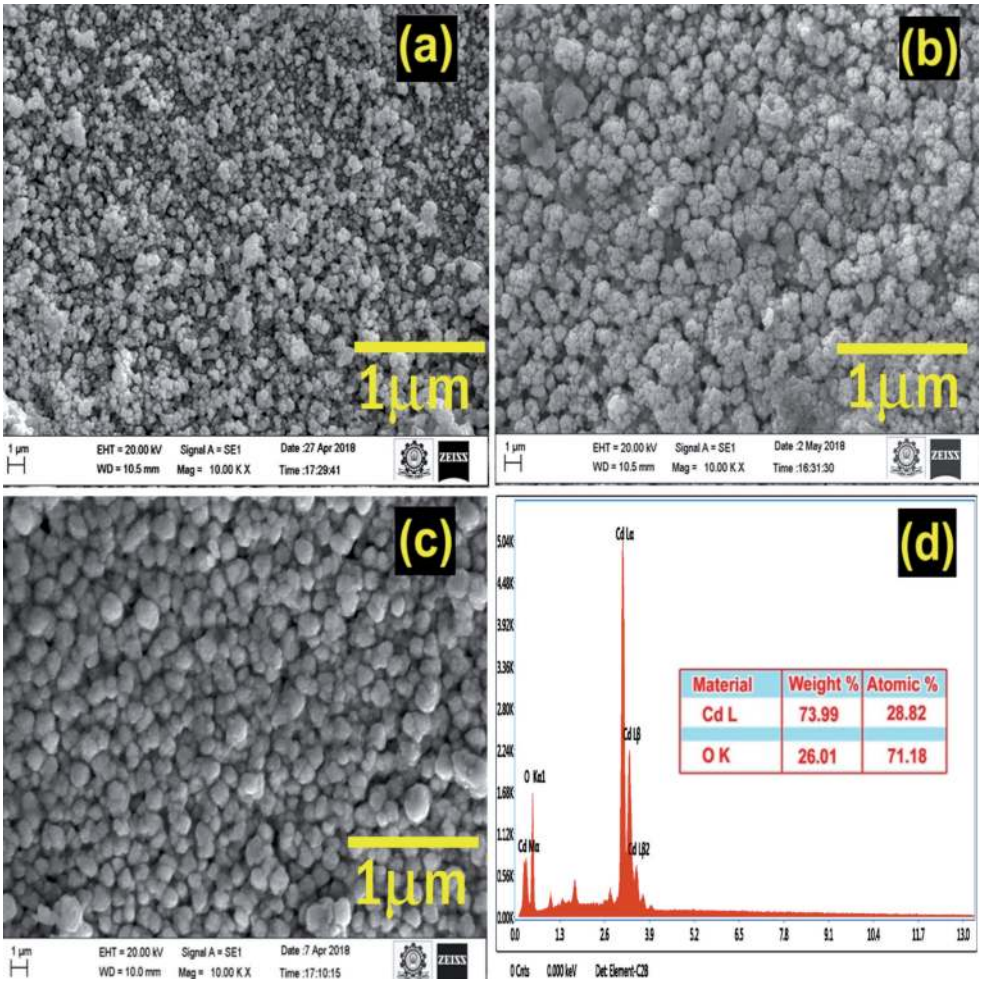

Figure 3.
SEM image of CdO thin film: (a) 30 mL, (b) 40 mL, (c) 50 mL, and (d) EDAX spectrum.

3.3 UV–Visible spectroscopic analysis

The optical transmittance spectrum in the wavelength region 300–800 nm was recorded using UV–Vis spectrometer. **Figure 4** shows the optical transmittance spectra of the CdO film deposited at different solvent volume. The variations in the solvent volume affect evidently the optical properties. Film coated with 30 mL solvent volume show a high transmittance of 68%. The transmittance decreases for the films with increase in solvent volume from 40 to 50 mL. The high thickness of the films and the optical scattering at the increased number of grain boundaries cause the decrease of transmittance. Usually in transparent metal oxides, metal or oxygen ratio in the film decides the percentage of optical transmittance. Metal rich film usually shows less transparency [50]. Also the optical transmittance is known to strongly depend on the grain size of the films. A smaller grain size marks to the high transmittance for the films coated with less solvent volume. When the grain size increases, the grain boundary scattering reduces, which causes a decrement in the transmittance. The sharp absorption edges obtained in the spectrum for all volumes clearly show the good crystallinity of the films.

The optical band gap (E_g) of the films was estimated from the transmittance data where the photon energy ($h\upsilon$) and absorption coefficient (α) are related by the equation [51].

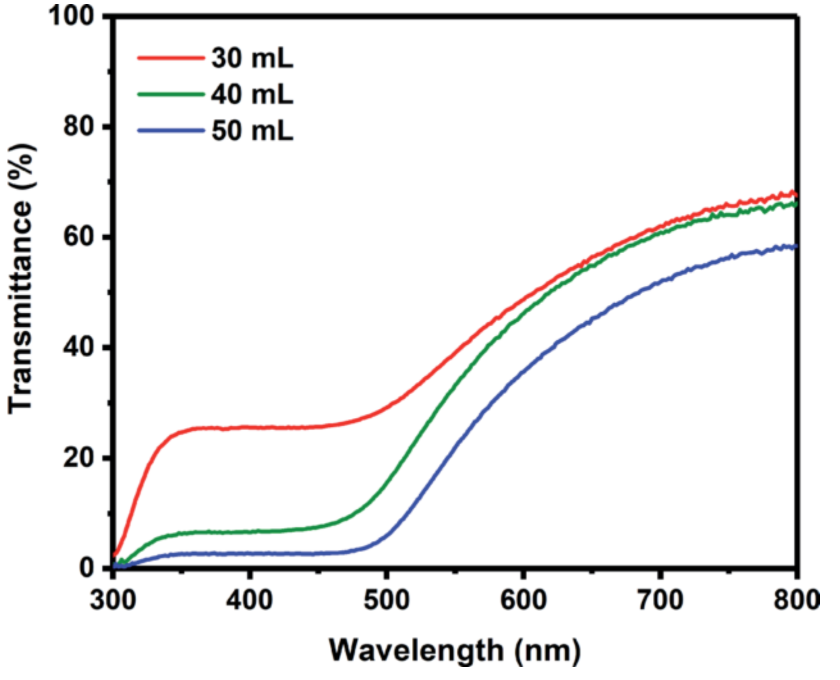

Figure 4.
Optical transmittance spectra of CdO thin film at different volume of solution.

$$\alpha h\nu = B\left(h\upsilon - E_g\right)^n \tag{7}$$

For allowed direct transition, the value of n = 1/2 and B is constant. Tauc graph is plotted between $(\alpha h\upsilon)^2$ against $h\upsilon$ to calculate the band gap of prepared CdO films. The fundamental absorption which clearly shows itself by a rapid fall in the transmittance can be used to find out the band gap of the as deposited samples to decide whether the CdO film deposited using the simplified spray technique have direct band gap $(\alpha h\nu)^2$ vs. $(h\nu)$ plot are drawn. Since better linearity is obtained in the $(\alpha h\nu)^2$ vs. $(h\nu)$ plot, the direct band gap values are determined by extrapolating the linear portion of this plot to the energy axis shown in **Figure 5**. The optical band gap (E_g) is found to be in the range of 2.12–2.00 eV for the coated films. As the solvent volume increases, the optical band gap is red shifted from 2.12 to 2.00 eV. Thus increased solvent volume reduces the optical band gap. This decreasing band gap is due Moss–Burstein effect. The Moss–Burstein effect is associated with lifting the Fermi level into the conduction band of degenerate semiconductors, which leads to decrease the band gap.

Furthermore, using the following relationships, we were able to determine the refractive index (n) and optical extinction coefficient (k) of cadmium oxide thin films [52, 53].

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \tag{8}$$

$$k = \frac{\alpha\lambda}{4\pi} \tag{9}$$

where each sign has its own meaning. In general, film transmittance is inversely proportional to refractive index (n) and extinction coefficient (k) at the same

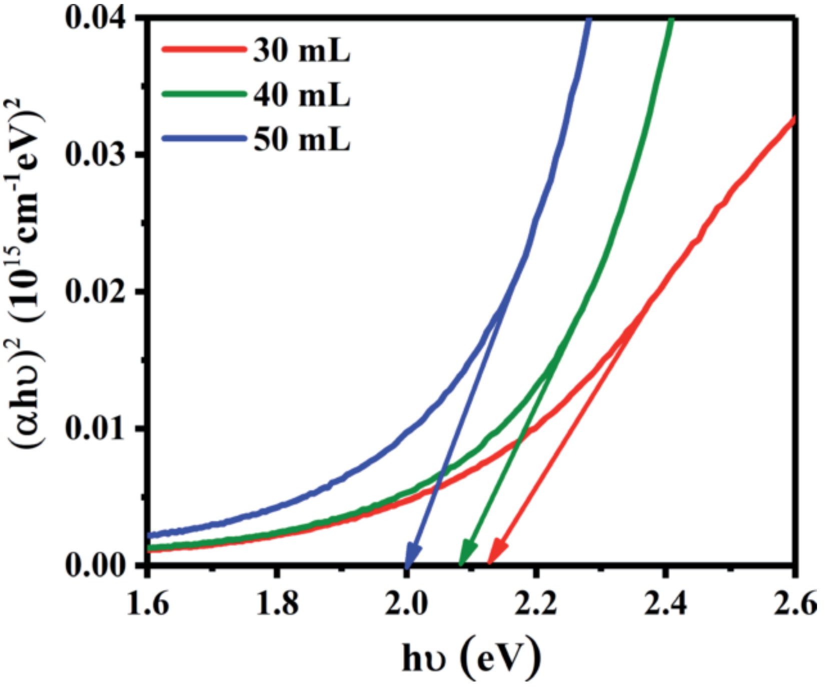

Figure 5.
Tauc plot of the CdO thin film at different volume of solution.

wavelength. Similarly, in both (n) and (k) values, we have seen an increase in parallel variation. **Table 2** shows the predicted (n) and (k) values. This data value clearly shows that both (k) and (n) values are low in all wavelength ranges, indicating that all films have good transparency and smooth surface roughness. When the solvent volume was increased from 30 mL to 50 mL, the refractive index and extinction coefficient both increased. This is due to a decrease in the optical energy gap.

Dielectric nature of CdO films were also quantified using the following equation [54].

$$\varepsilon_r = n^2 - k^2 \tag{10}$$

$$\varepsilon_i = 2nk \tag{11}$$

3.4 Photoluminescence spectroscopic analysis

PL spectroscopy is used to determine the optical quality of CdO semiconductor films and the common radiative transition in the semiconductor occurs between the states at the bottom of the conduction band and the top of the valence band in the prepared CdO thin film. Room temperature luminescence spectrum was recorded using (SHIMADZU-5301) spectrofluorometer. The PL spectra of different solution volume produced CdO thin films obtained at room temperature under the excitation of 325 nm are shown in **Figure 6**. The peak (ultraviolet light emission) about 360 nm was caused by free exciton recombination. The blue emission due to the passage of electrons from oxygen vacancies to the valence band is attributed to the peak centred at 458 nm. The blue emission peak at 494 nm is generally attributed to the radiative recombination of a photo-generated hole with an electron occupying the oxygen vacancy. This peak is attributed to the excitonic transitions which are size-dependent and excitation wavelength independent of

Volume of the solution (mL)	Transmittance (%)	Band gap (eV)	Refractive index (n)	Extinction coefficient (k)	Dielectric constant (ε_r)	Dielectric constant (ε_i)
30	68	2.12	2.130	0.08	4.56	0.32
40	66	2.08	2.134	0.06	4.55	0.56
50	58	2.00	2.136	0.05	4.55	0.81

Table 2.
Optical and dielectrical properties of CdO thin films.

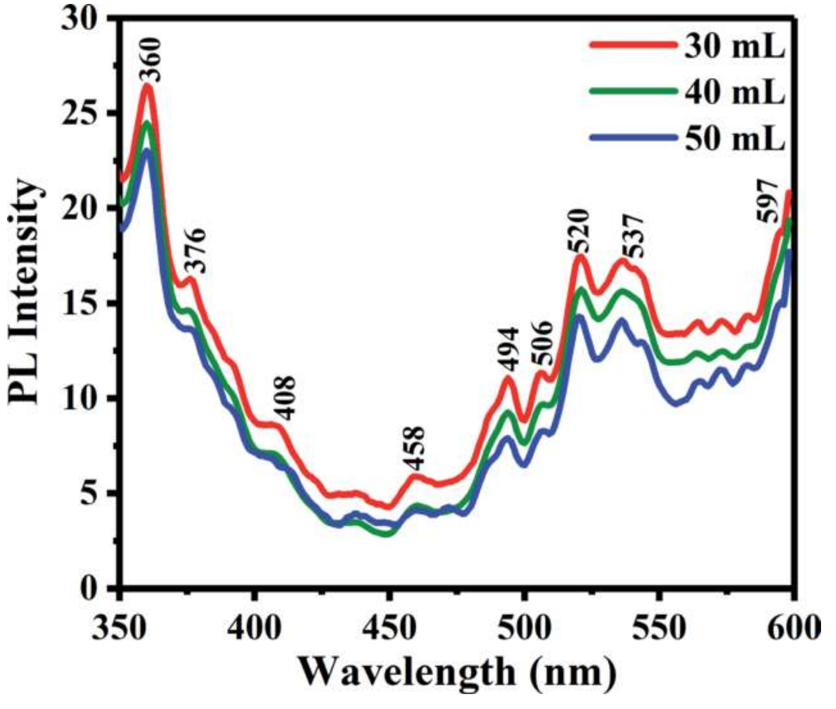

Figure 6.
Photoluminescence spectra of CdO thin film at different solution volume.

the certain wavelength range [55]. The peak at 506 nm arises from the combination of holes from the valence band and electrons from the conduction band. This peak might also be attributed to the electronic transitions from cadmium interstitial and oxygen vacancies to the top of the valence band [56]. The green emission peak at 520 nm might have originated from the electronic transitions of ionized oxygen vacancies from the deep level donor to the valence band [57]. The low intensity of this peak indicates a low concentration of surface defects in the prepared CdO thin film. The green emission peak at 595 nm might have originated from the oxygen vacancies on the surface of CdO. The intensity of the principal emission peaks likewise decreases as the solution volume increases, which could be due to the creation of more Cd and O vacancies as well as an increase in charge carrier recombination.

3.5 Electrical studies

Hall Effect measurements were carried out in a van der Pauw configuration (Ecopia HMS-3000) at room temperature. The negative sign of the Hall coefficient confirms that the conduction is n-type. The electrical parameters in the CdO films were clearly influenced by the solution volume. By increasing the volume of precursor solution, the carrier concentration (n) was increased. For 50 mL of solution, the resistivity (ρ) (0.552×10^{-3} Ω cm) is lower and the carrier concentration (6.165×10^{-3} Ω cm) is higher. Resistivity (ρ) for different solution volumes is 0.835×10^{-3}, 0.665×10^{-3}, and 0.552×10^{3} cm, carrier concentration (n) is 3.547×10^{20}, 4.448×10^{20}, and 5.369×10^{20} cm^{-3}, and carrier mobility (μ) is 21.11, 17.51, and 16.51, cm^2 V^{-1} s^{-1}.

4. Conclusion

Cadmium oxide thin films have been deposited by perfume atomizer spray pyrolysis technique on glass substrate at different solution volume. In this study, the effect of volume of solution on structure, morphology and optical properties of prepared CdO thin film were reported. X-Ray diffraction studies shows that the preferred growth orientation along (111) plane with cubic crystal structure for all solution volume. It is evident that the microstructural parameters vary with volume of solution and may be useful to enhance the properties of CdO thin film for various applications. An average optical transmittance about 55% in the wavelength range 480–800 nm, was obtained. The Tauc graphs were plotted and revealed that the band gap of the CdO thin films can be altered by changing the appropriate solution volume. Intense PL emission peaks were observed at different wavelengths confirms that the presence of oxygen vacancies, defect centre and recombination of electron hole.

Conflict of interest

The authors declare no conflict of interest.

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