AGING EFFECT ON THE PROPERTIES OF CdO THIN FILMS

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Abstract :Nanostructured CdO thin films were prepared on glass substrates by spray pyrolysis technique using perfume atomizer from fresh and aged (1, 2, 3 and 4 days) precursor solutions. XRD studies confirm that all the films exhibit cubic crystal structure with a (1 1 1) preferential orientation. The 2θ value of the (1 1 1) plane shifts towards lower Bragg angles with aging inferring an expansion in the lattice volume of the aged films. Increased crystallite size is observed for the 3-days aged film for which minimum strain and dislocation density values are obtained. Optical transparency increases with increase in aging period of the precursor solution and the optical band gap exhibit a red shift from 2.48 eV to 2.32 eV. A minimum resistivity of 0.78×10^{-2} ohm-cm is observed for the CdO film prepared from 3-days aged solution. The obtained results infer that the CdO film prepared from 3-days aged solution exhibit better physical properties.

INTRODUCTION

Thin film can be defined as a thin layer of material created experimentally by an atom (or ion or molecule) by atom (or ion or molecule) by condensed process. The thickness of thin films may be ranging from fraction of a few nano meters to a few micrometers. The beginning of "Thin film science" can possibly be traced to the observations of Grove who noted that metal films were formed by sputtering of cathodes with high energy positive ions. Since then it has come a long way and today it is no longer a subject of some casual academic interest but has become a full-fledged discipline. The phenomenal rise in thin film researches is, no doubt, due to their extensive application in the diverse fields of electronics, optics, space science, aircrafts, defense and other industries. These investigations have led to numerous inventions in the forms of active devices and passive components, piezo-electric devices, micro-miniaturization of power supply rectification and amplification, sensor elements, storage of solar energy and its conversion to other forms, magnetic memories, superconducting films, interference filters, reflecting and antireflection coatings and many others. The present developmental trend is towards newer types of devises, monolithic and hybrid circuits, field effect transistors (FET), metal oxide semiconductor transistors (MOST), sensors for different applications, switching devices, cryogenic applications, high density memory systems for computers, etc. Further, because of compactness, better performance and reliability coupled with the low cost of production and low package weight, thin film devices and components are preferred over their bulk counterparts. There has been a phenomenal increase in their applications which have outpaced the technology of production, development of newer types of materials and better processes for semiconducting dielectric and other films needed by various industries intensive investigations are going on not only in the field of basic thin film physics, but also in materials science, thin film circuit designs, production engineering concerning thin films, etc., to cope up the demand of industries. Film properties are also sensitive not only to their structures but also to many other parameters including their thickness especially in the thin film regions. Hence a control of the latter is imperative for reproducible electronic, dielectric, optical and other properties.

SPRAY PYROLYSIS TECHNIQUE

EXPERIMENTAL DETAILS

CdO thin films were prepared on glass substrates maintained at 400°C by spray pyrolysis technique using perfume atomizer by spraying 50 ml of aqueous solution containing 0.05 M of cadmium acetate, $Cd(CH_3COO)_2$. To study the aging effect of the precursor solution, CdO thin films were prepared i) using fresh solution and ii) using solutions having different aging periods (1, 2, 3 and 4 days). The CdO thin films prepared from precursor solutions having aging periods of 1, 2, 3 and 4 days will hereafter throughout the manuscript be called as first day film, second day film, third day film and fourth day film, respectively. The thicknesses of the films measured using a stylus type profilometer (Surftest SJ 301) were found to be equal to 678, 689, 697, 706 and 714 nm for the films prepared from fresh solution, first, second, third and fourth day films respectively. The crystal structure morphology, optical and electrical studies were performed using X-ray diffractometer (PANalytical –PW 340/60 X" pert PRO) with CuK_α radiation (λ = 1.5406 Å) X-ray source, scanning electron microscope (HITACHI S – 3000H),probe setup respectively.

RESULTS AND DISCUSSION
CRYSTAL STRUCTURE

Fig. 4.1 shows the XRD patterns of CdO thin films prepared from a) fresh, b) 1-day aged, c) 2-days aged, d) 3-days aged and e) 4-days aged precursor solutions.

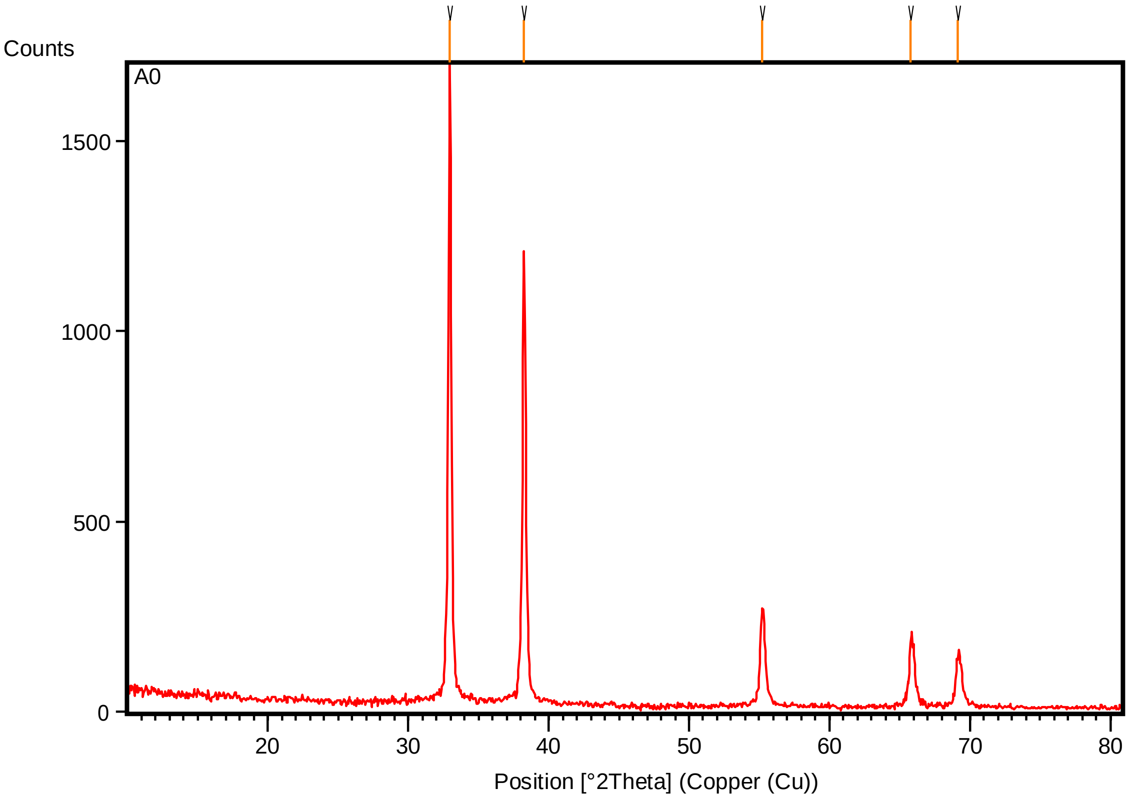


Fig. 4.1(a) shows the XRD patterns of the CdO thin films prepared from fresh

Peak list

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
32.9735	1687.01	0.1968	2.71654	100.00
38.2547	1209.44	0.2460	2.35279	71.69
55.2144	259.05	0.3444	1.66363	15.36
65.8009	184.69	0.2460	1.41930	10.95
69.0881	131.63	0.2952	1.35958	7.80

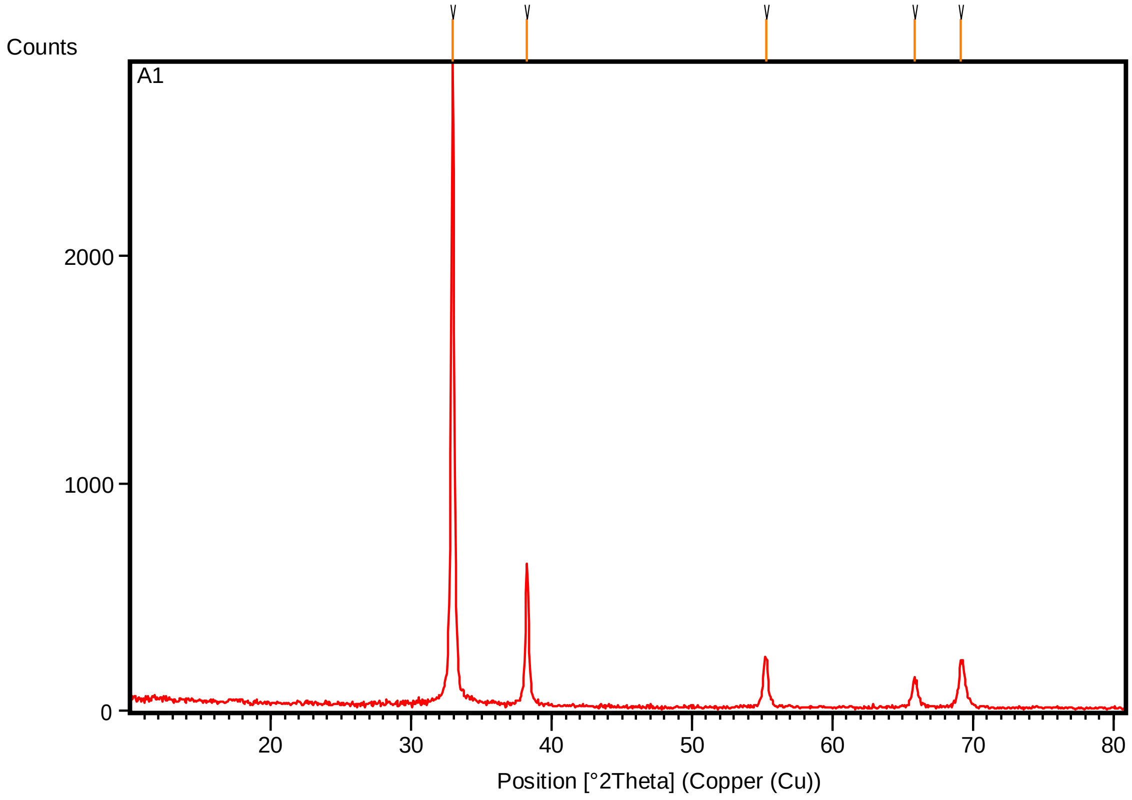


Fig. 4.1(b) shows the XRD patterns of the CdO thin films prepared form day 1

Peak list

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
32.9646	2842.88	0.1968	2.71725	100.00
38.2504	636.36	0.2460	2.35305	22.38
55.2439	223.92	0.3444	1.66281	7.88
65.8739	134.53	0.2952	1.41790	4.73
69.1199	207.83	0.3936	1.35903	7.31

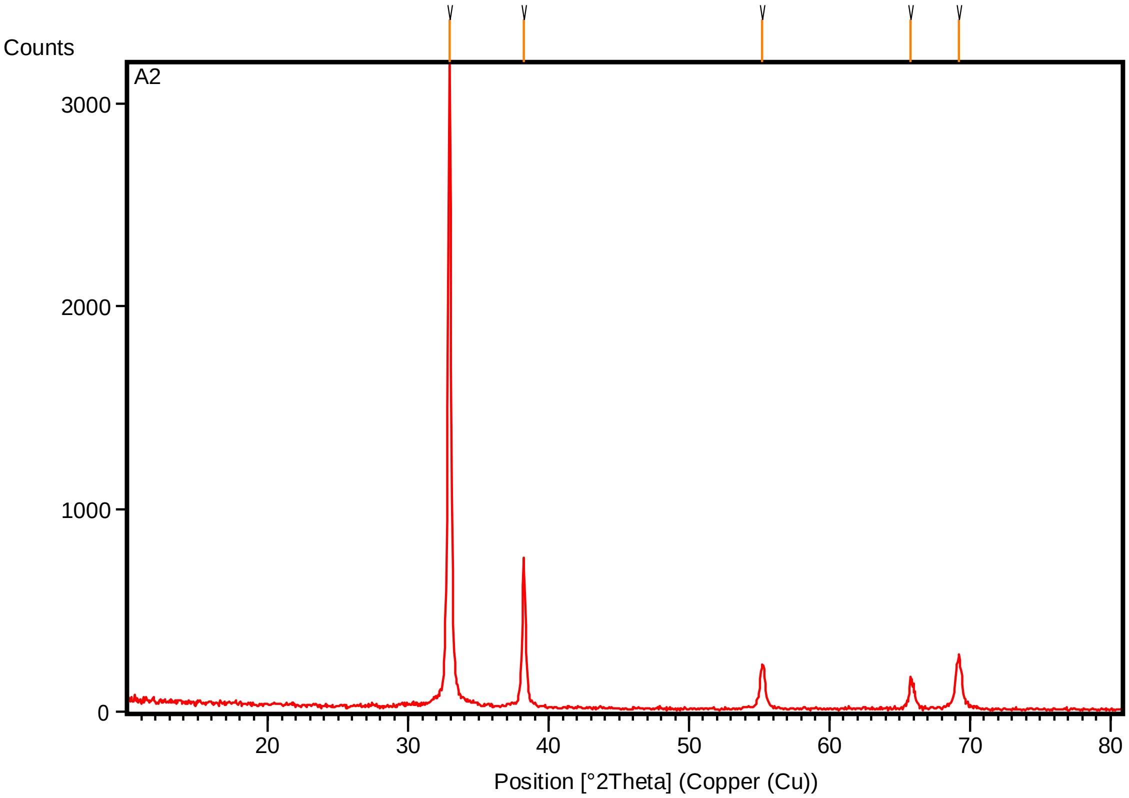


Fig. 4.1(c) shows the XRD patterns of the CdO thin films prepared form day 2

Peak list

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
32.9531	3260.08	0.2460	2.71818	100.00
38.2345	742.66	0.2460	2.35399	22.78
55.2213	217.41	0.3444	1.66344	6.67
65.7803	157.54	0.2460	1.41970	4.83
69.2173	273.60	0.4920	1.35736	8.39

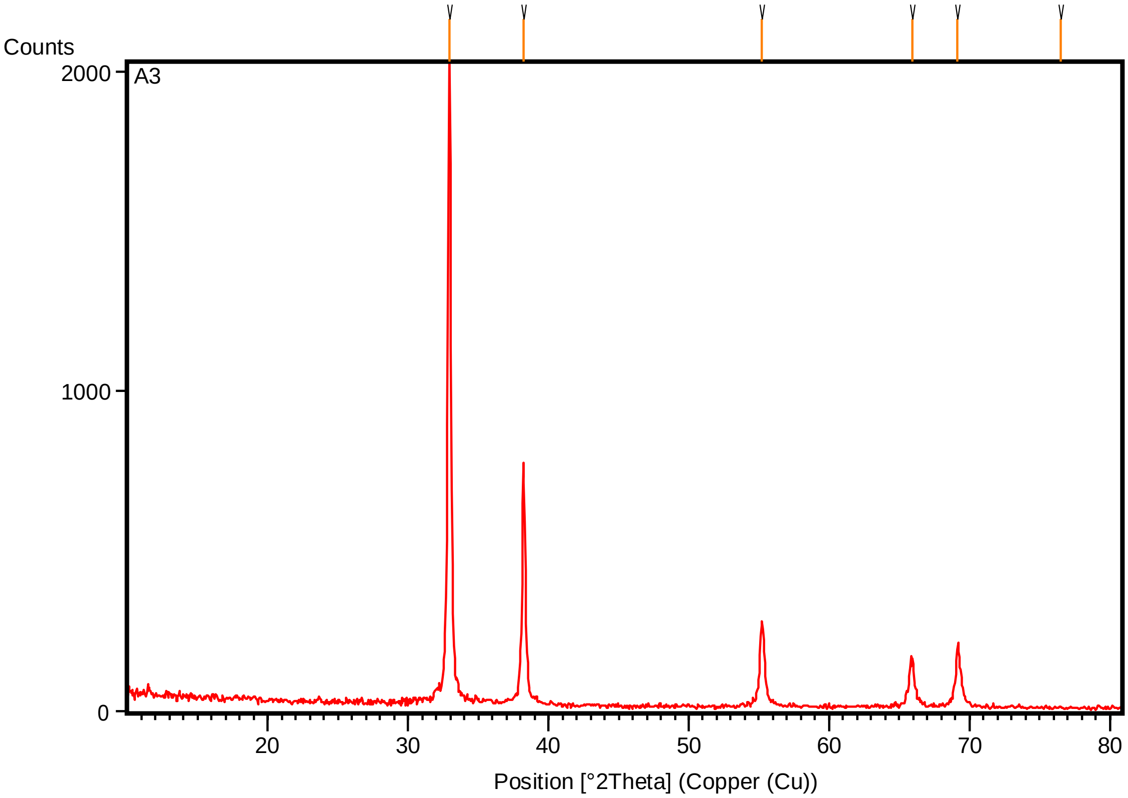


Fig. 4.1(d) shows the XRD patterns of the CdO thin films prepared form day 3

Peak list

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
32.9563	2044.06	0.2460	2.71792	100.00
38.2416	755.12	0.2460	2.35357	36.94
55.1884	259.42	0.3444	1.66435	12.69
65.9078	150.06	0.2952	1.41726	7.34
69.1577	202.83	0.2952	1.35838	9.92
76.5108	3.05	0.6888	1.24512	0.15

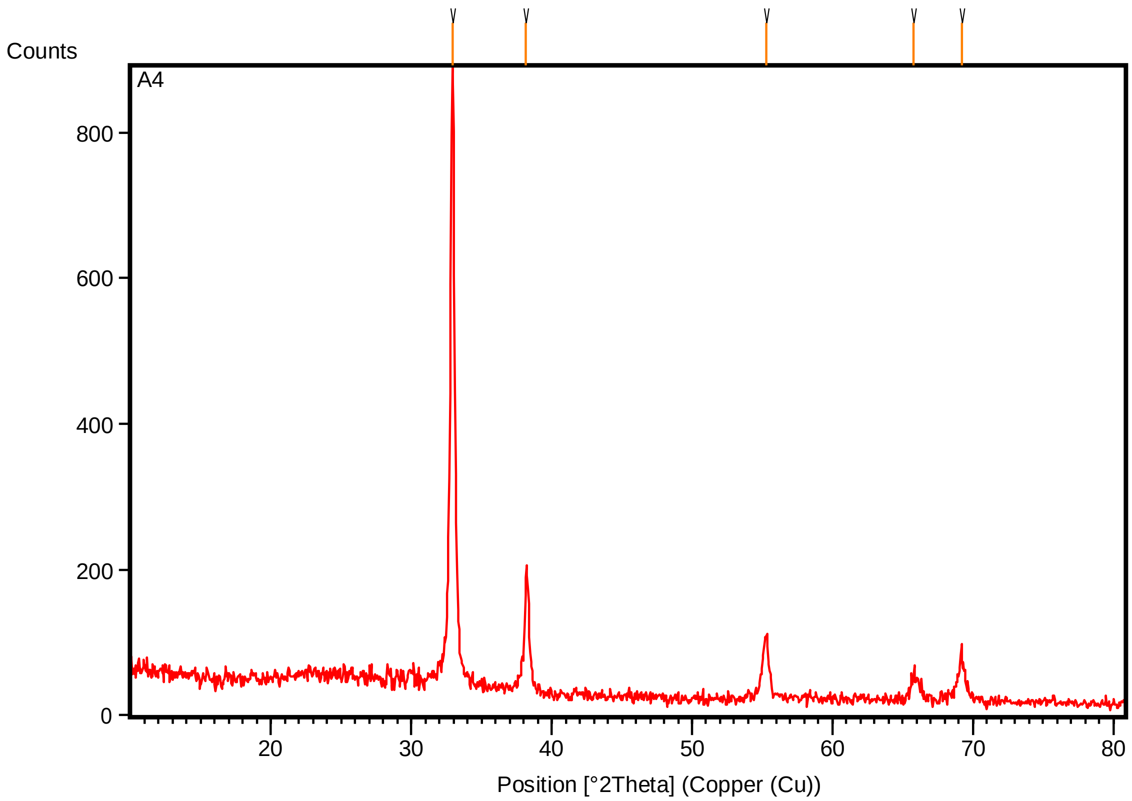


Fig. 4.1(e) shows the XRD patterns of the CdO thin films prepared form day 1

Peak list

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
32.9496	853.27	0.2460	2.71846	100.00
38.1917	163.22	0.2460	2.35653	19.13
55.2762	87.96	0.2952	1.66191	10.31
65.7459	36.19	0.4920	1.42035	4.24
69.2069	63.42	0.2952	1.35754	7.43

The presence of diffraction peaks at 2θ values approximately equal to 32.974°, 38.255°, 55.214°, 65.801° and 69.088° indexed to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes of cubic CdO (JCPDS Card No. 73-2245) confirm its polycrystalline nature. It is observed that all the films exhibit a (1 1 1) preferential orientation irrespective of aging period of the starting solution. The preferential orientation along the (1 1 1) plane observed here exactly matches with the results reported by Manjula et al. [11] and Usharani et al. [14] for undoped and doped CdO thin films prepared using perfume atomizer. A close examination of the XRD patterns clearly show that the 2θ value of the (1 1 1) plane shift towards lower Bragg angle (Table 1) for the aged films inferring an expansion in their lattice volume. The lattice parameter values calculated for the (1 1 1) plane are compiled in Table 1.

Table 1 Structural parameters, optical band gap and electrical resistivity values of CdO films prepared from precursor solutions having different aging periods.

Aging period of the precursor solution [days]	$2\theta_{(1\,1\,1)}$	Lattice parameter*, a [Å]	Optical band gap, E_g [eV]	Electrical resistivity, $\rho \times 10^{-2}$ ohm-cm
0	32.974°	4.7051	2.48	4.27
1	32.953°	4.7081	2.42	3.09
2	32.965°	4.7065	2.4	1.94
3	32.950°	4.7086	2.35	0.78
4	32.956°	4.7075	2.32	0.92

*Standard a = 4.699 Å (JCPDS Card No. 73-2245)

As expected the lattice parameter values increases with increase in aging period of the precursor solution, which might be due to a change in the crystal strain with aging. The deviation in the lattice parameter values from the bulk value observed here clearly suggests that the grains in the films are under stress. This deviation can be attributed to the change of nature, deposition conditions and the concentration of the native imperfections [16].

The microstructural parameters such as crystallite size (D), strain (ε) and dislocation density (δ) were calculated using the formulae [17]:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \quad (1)$$

$$\varepsilon = \frac{\beta\, cot\theta}{4} \quad (2)$$

$$\delta = \frac{1}{D^2} \quad (3)$$

where λ is the wavelength of the X-rays used (1.5406 Å), β is the full width at half maximum of the strongest diffraction peak ((1 1 1) in this case) measured in radians and θ is the Bragg angle. It is observed that the crystallite size increases with increase in aging period of the precursor solution, attaining a maximum value for the third day film confirming its improved crystallinity which was well supported from the minimum values of strain and dislocation density obtained for this film.

SURFACE MORPHOLOGY ANALYSIS

Fig. 4.2(a-e) shows the SEM images of CdO thin films prepared from precursor solutions having different aging periods.

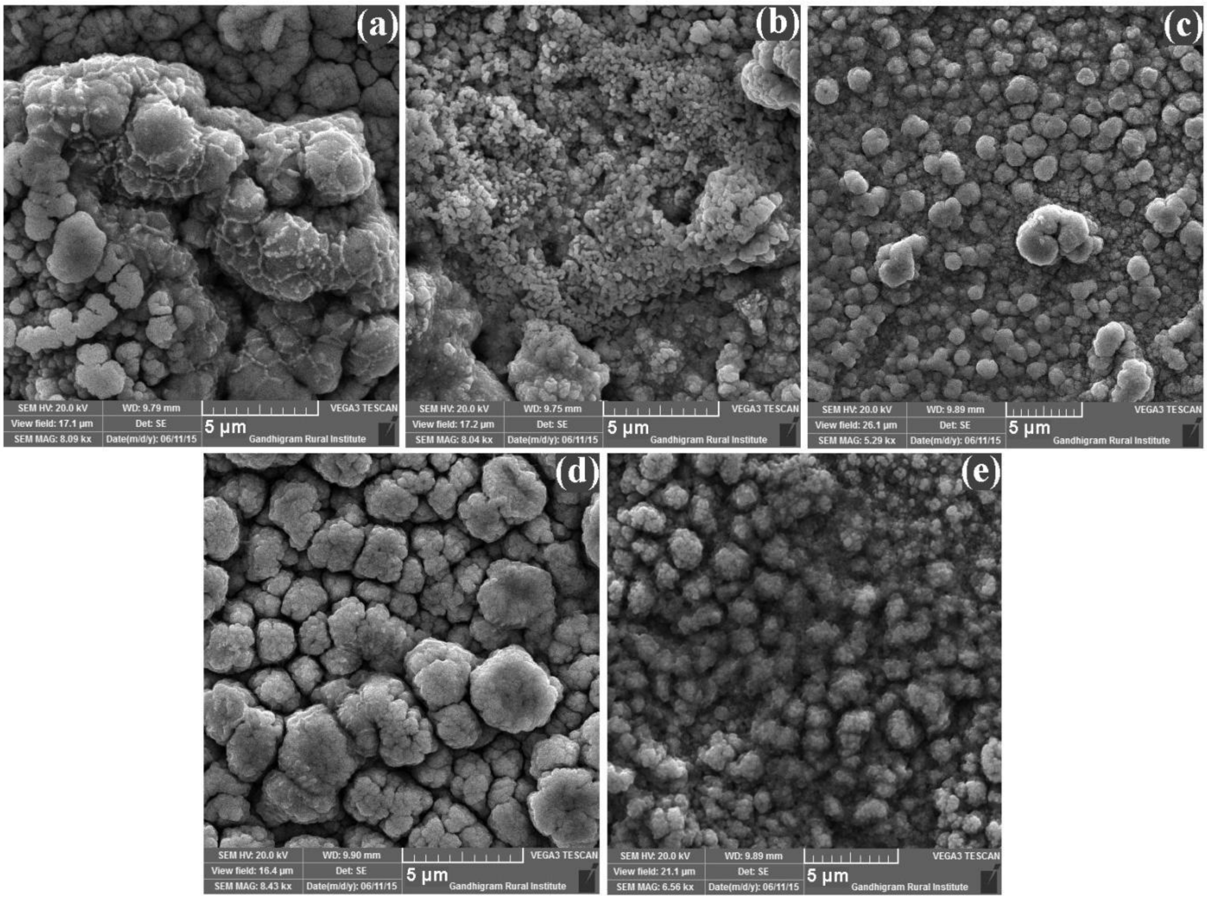
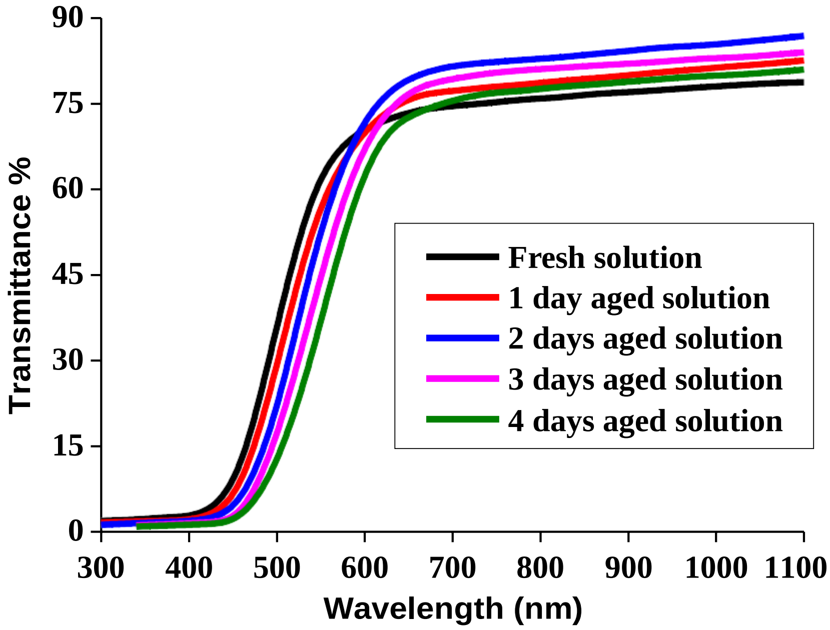


Fig. 4.2(a-e) shows the SEM images of aging effect of CdO thin films

The surfaces of all the films appear to be uniform and tightly packed. Caterpillar shaped grains along with cauliflower shaped nanostructures are visible for the CdO film prepared from fresh solution (Fig. 4.2(a)). The surface gets modified with unequal sized tiny cauliflower shaped grains for the film prepared from 1-day aged solution (Fig. 4.2(b)). As the aging period of the precursor solution increases, the surface gets composed with equal sized cauliflower shaped grains for the CdO film coated with 2-days aged solution (Fig. 4.2(c)). For the third day film, the surface gets modified with perfectly shaped cauliflower structures. The surface appears to be smoother without any holes or cracks (Fig. 4(d)). The film surface appear to be slightly deteriorated with unequal sized cauliflower shaped grains for the CdO film coated for the fourth day film (Fig. 4(e)). From the obtained results it is observed that among the aged films, the CdO film coated with 3-days aged precursor solution exhibited better surface morphology which very well acknowledged the results obtained in XRD analysis (Section 3.1).

OPTICAL STUDIES

Fig. 4.3 shows the transmittance spectra of CdO films prepared from precursor solutions having different aging periods.



It is observed that the transparency of the CdO films increases with increase in aging period of the starting solution, which might have been resulted from enhanced diffusion of chemical species in the precursor solution with aging. Moreover, all the films have the same absorption edge and the absorbance increases with increase in aging period of the solution. It can also be seen that the absorption edge shift towards higher wavelength side with aging period of the starting solution indirectly suggesting a decrement in their band gap values. The optical band gap energy (E_g) was calculated from the absorption spectra using the dependence of the absorption coefficient (α) on the photon energy (hυ) by the relation [18]:

$$\alpha hv = A\, hv - E_g^{\;1/2} \qquad (4)$$

where A is a constant.

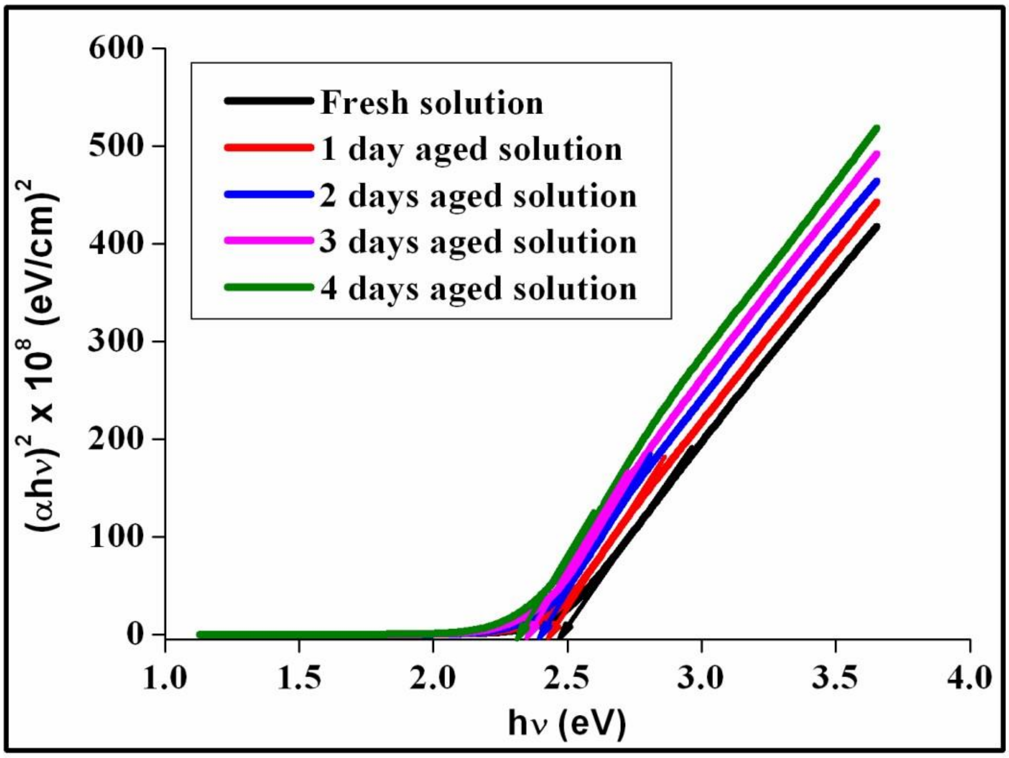


Fig. 4.4(a-e) shows the plots of $(\alpha h\upsilon)^2$ vs. (hυ) for the aging effect of CdO thin films

Fig. 6 shows the plots of $(\alpha h\upsilon)^2$ vs. (hυ) for the films and from the extrapolation of the linear portion of the plots onto the energy axis at $\alpha = 0$ the band gap values of the films are calculated and the obtained values are compiled in Table 1. The band gap value of the CdO film prepared from fresh precursor solution (2.48 eV) is found to be slightly lower than that of bulk CdO (2.42 eV) and this blue shift could be attributed to quantum confinement effect. This is in accordance with the results reported by Usharani et al. [19] for Cl-doped ZMCO thin films. It is observed that the band gap energy decreased from 2.48 eV to 2.32 eV with increase in aging period of the starting solution. This red shift in the optical band gap with aging may be due to the influence of various factors such as grain size, structural parameters, carrier concentration, deviation from stoichiometry of the films and lattice strain [20].

CONCLUSIONS

Precursor solutions with different aging periods are used to prepare CdO thin films by spray technique using perfume atomizer. The films were characterized structurally, morphologically, optically and electrically to study the influence of aging period of the precursor solution on the physical properties of CdO thin films. Structural studies confirmed the polycrystalline nature of the films. All the films exhibited cubic crystal structure with preferential orientation along the (1 1 1) plane. Crystallite size estimated using the Scherrer formula increased from 33.68 nm to 50.64 nm with increase in aging period of the solution. An increased crystallite size of 50.64 nm, decreased strain and dislocation density values of 0.685×10^{-3} and 390×10^{15} lines/m^2 respectively are observed for the CdO film prepared from 3 days aged solution. Optical transparency is found to be increased with increase in aging period of the precursor solution. Electrical resistivity decreased with increase in aging period of the starting solution and the third day film exhibited a minimum resistivity value of 0.78×10^{-2} ohm-cm. The obtained results infer that among the aged films, CdO film prepared from 3 days aged precursor solution exhibited better physical properties.

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