Temperature dependence of general properties of CdO thin films prepared by nebulized spray pyrolysis technique

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Abstract:*Polycrystalline transparent conducting cadmium oxide thin films were synthesized by inexpensive method of nebulized spray pyrolysis technique at five different substrate temperatures (150, 175, 200, 225 and 250˚C) on amorphous glass substrates with precursor Polycrystalline transparent conducting cadmium oxide thin films were synthesized by inexpensive method of nebulized spray solution of cadmium acetate dihydrates. These thin films had a preferential orientation along the (111) plane having face centered cubic structure. Surface morphology of these thin films changed from closely packed cauliflower structure to well defind grain the substrate temperature had increased. Transparency of these samples had increasedfrom 75% to 90% at longer wavelengths (900 nm -1100 nm) with increase in substrate temperature. Optical band gap decreased from 2.4eV to 2.25eV belonging to direct transition with increase in substrate temperature. Presence of vibration band at 675 cm^{-1} corresponding to Cd-O bondwas confirmed by FTIR spectrum. A minimum resistivity of 97□ cm was determined for the film coated at 150˚C with activation energy of 0.01 eV***.**

Keywords:*Cdo, Electrical, Nebulized spray pyrolysis, Optical and structural properties, Thin films.*

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1. INTRODUCTION

TCO thin films have been used in a wide range of application such as heating elements on aircraft windows for de-icing and defogging, antistatic coatings on instrument panels, electrical contacts in liquid crystals and electroluminescent displays. The high reflection in the infrared region, along with high transparency in the visible region, has been exploited to make heat reflecting mirrors. In recent years, the renewed research interest in these films arises from cadmium oxide thin films (CdO), an n-type semiconductor with band gap of 2.5 eVariesfor various applications such as solar cells and photodiodes, due to its low electrical resistivity, high carrier concentration and high optical transmittance in the visible region of the solar spectrum [1]. It also finds applications in phototransistors, liquid crystal displays and IR detectors due to its low band gap [2]. CdO thin films had been deposited by various techniques such as dc magnetron sputtering [3], spray pyrolysis [4], chemical bath deposition [5], SILAR [6], pulsed laser deposition [7], sol-gel dip coating [8], etc. In the present work , a new technique called nebulized spray pyrolysis is adopted which to method simple and inexpensive. Nebulizer is an instrument for converting a liquid into an aerosol. An aerosol is a suspension of small particles of liquid or solid in a gas, where the size of the particle fall within the range of 1-5 micrometer in diameter. Examples of aerosol include dusts, bacteria, water and smoke[9**]**. The substrate temperature is varied from 150 - 250°C in steps of 25°C while preparing CdO thin films. In this paper the effect of substrate temperature of the general properties of the thin films were investigated.

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2. EXPERIMENTAL DETAILS

Thin films of cadmium oxide were prepared by spraying (20ml volume) 0.20 M cadmium acetate dehydrate aqueous solution [Cd(CH3COO)2].2H2O(sigma Aldrich) on to amorphous glass substrates at different substrate temperatures varying from 150˚C to 250˚C insteps of 25˚C. Other deposition parameters are kept constant as shown in Table 1.

The crystal structure of the crystallites in these thin films were examined by the XPERT PRO diffractometer using Cu Kα radiation (k= 1.5406 A°). The scanning angle 2θ was varied in the range of 20-70 degree in steps of 0.05 degree.The thickness of the thin films was measured by stylus profilometer. The surface morphological studies were recorded with TESCAN VEGA-III scanning electron microscope, magnification had 25,000... The absorption spectrum of thesefilms was recorded in the wavelength range 200 to 1100 nm using Shimadzu-UV 1800 model double beam spectrophotometer. The absorption spectral data was used to determine the type of optical transition and the band gap present in the sample.IR spectra for these samples were recorded using IRAFFINITY-1 FTIR spectrometer. The electrical conducting studied using four-point probe method.

Table No 1: "Deposition parameter applied in this work"

Substrate temperature	150˚C to 250˚C in steps of 25˚C
Carrier gas pressure	1.5 kg/cm^{-1}
Precursor molor concentration	0.20 M
Volume of the solution	20 ml
Distance between glass tube and substrate	1 cm
Precursor	$[Cd(CH_3COO)_2].2H_2O$
Solution ratio	Deionised water : isopropylalchohal 1 : 1

3. RESULT AND DISCUSSION

3.1 FILM FORMATION PROCESS

In the Nebulized Spray pyrolysis method, starting materials required to form the desired semiconducting compound are in the form of solution, which are sprayed onto preheated glass substrates, resulting in the formation of thin films on the upper surface of the substrates. The depositions are carried out at substrate temperature between 150˚C to 250˚C using 0.2M solution. The samples were uniform, well adherent and yellow colored.

3.2 X-RAY DIFFRACTION PATTERN OF CdO THIN FILM

The XRD pattern of CdOthin films prepared at different substrate temperatures are shown in fig 1. The diffroctrograms were obtained for the thin films grown on amorphous glass substrate. All the five thin films have polycrystalline nature. If exhibit a strong peak at around 33.03 degree corresponding to (111) plane face centered cubic structure. The other peaks are (200), (220), (311) and (222). The first threetemperature 150,175and 200 the crystaline nature increased and the abovetemperature 225,250decreased thecrystanality. All the CdO thin films diffraction peaks compared to the JCPDS value [file no. 65-2908]. K.Usharani et al also reported a similar cubic structure for CdO thin films synthesized by spray pyrolysis technique [10][11].The crystallite size (D) value is calculated using thedebyeScherrer formula

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

Where λ is the wavelength of the X-ray used (1.5406 Å), β is the full-width at half-maximum of the peak which has maximum intensity and ϴ is the Bragg angle.

The lattice constants 'a' , volume 'v', dislocation density 'δ', and strain 'ε' and number of crystallites 'N'using the formula's:

$$\frac{1}{d2} = \frac{h2+k2+l2}{a2} \quad ; \quad v = a^3 \quad (2)$$

$$\delta = \frac{1}{D2}; \quad N = \frac{t}{D3} \quad ; \varepsilon = \frac{\beta\, COS}{4} (3)$$

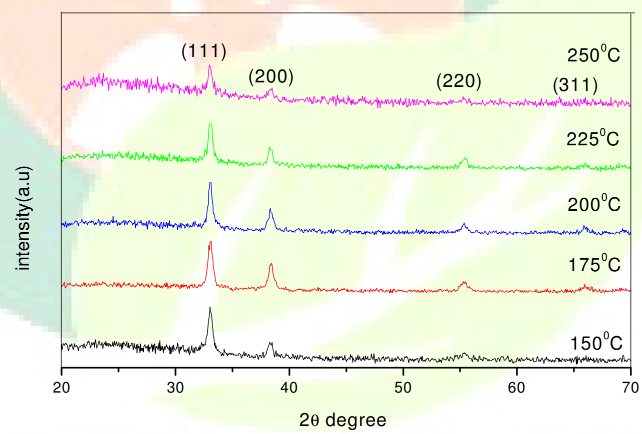

Fig 1: XRD patterns of Cdo thin films coated at different substrate temperatures.

XRD patterns also revealed that the growth temperature induces variation of CdO film growth texture. The texture of a particular plane can be represented by the texture coefficient TC(h k l), which can be calculated from X-ray data using the formula

$$\mathrm{TC(hkl)} = \left[\frac{I(hkl)}{Io(hkl)}\right] / \{1/N \sum_N [\mathrm{I(hkl)/Io(hkl)}]\} \ (4)$$

\Where I(hkl) is the measured relative intensity of the plane (hkl), I_0 (hkl) is the standard intensity of the plane (hkl) taken from the JCPDS data, and N is the reflection number. Any deviation of the calculated Tc value from unity implies preferred growth. The variation of the texture coefficient of CdO thin films with different substrate temperature for the diffraction peak (111) shown in table 2.

Fig 2 shows the variation of crystallite size along the (111) plane with different substrate temperature. The intensity of(111) plane has been found to be increased with substrate temperature up to200˚C and then decreases for higher temperature.

The crystallite size was found to (111) direction increase from 22 nm to a maximum of about 35.19 nm for CdO film coated with 200˚C. Above the substrate temperature, the crystallite size decreased which might be due to the decreased intensity of (111) plane obtained for the film coated with 250˚C. The deviation in the lattice parameter values of the CdO films coated with different substrate temperature might be due to the small shift in 2Θ in (111) diffraction towards higher Bragg angle.

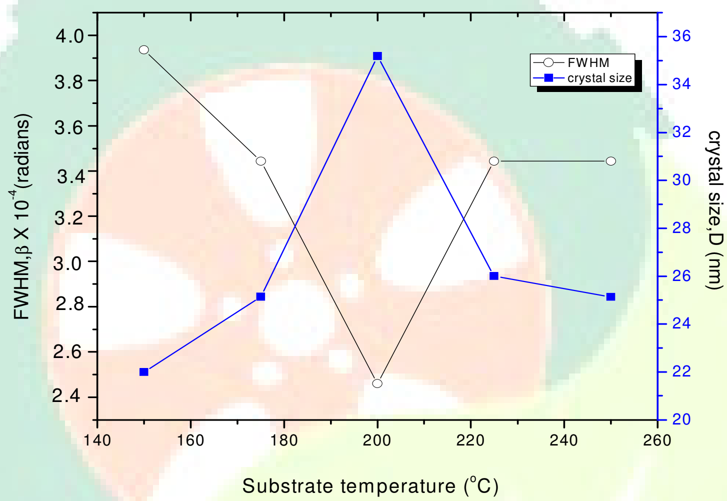

Fig. 2The variation of FWHM and Crystallite size of CdO films with different substrate temperature

. The calculated values of microstructural parameters such as lattice constant 'a', strain 'ε', dislocation density 'δ', texture coefficient 'TC', volume 'v'and the number of crystallites per unit area'N' of (111) plane of the CdO films are presentend in Table 2. Thethickness (t) is observed from stylus profilometer.

Table.2 Effect of substrate temperature on the structural properties of CdO thin films

Substrate Temperature (˚C)	Observed 2Θ(deg) (111)	Lattice Constant Å	Thickness (µm)	volume	Dislocation Density(10^{15}) (lines/m^2)	Strain (10^{-3})	Number of crystallites (10^{17}) (m^{-2})	TC(111)
150	33.1140	4.6858	1.63	103.0	2.066	1.645	1.531	1.98
175	33.0859	4.6896	1.65	103.14	1.582	1.440	1.038	1.78
200	33.0376	4.696	1.60	103.56	0.808	1.029	0.367	1.77
225	33.1071	4.686	1.56	103.0	1.479	1.399	0.888	2.02
250	32.9888	4.703	1.39	104	1.583	1.440	0.876	1.89

3.3 SURFACE MORPHOLOGY AND COMPOSITIONAL ANALYSIS

Surface morphology of CdO thin films coated with different substrate temperatures shown in fig 3.These SEM photographs were recorded with a magnification of 25000 x. The scanning electron micrographdifferent forms with increase in substrate temperatures.The shapes ofcauliflower with well defind grain boundries for the film coated with 150˚C [12]. The temperature is increased then the surface modifies tightly packed

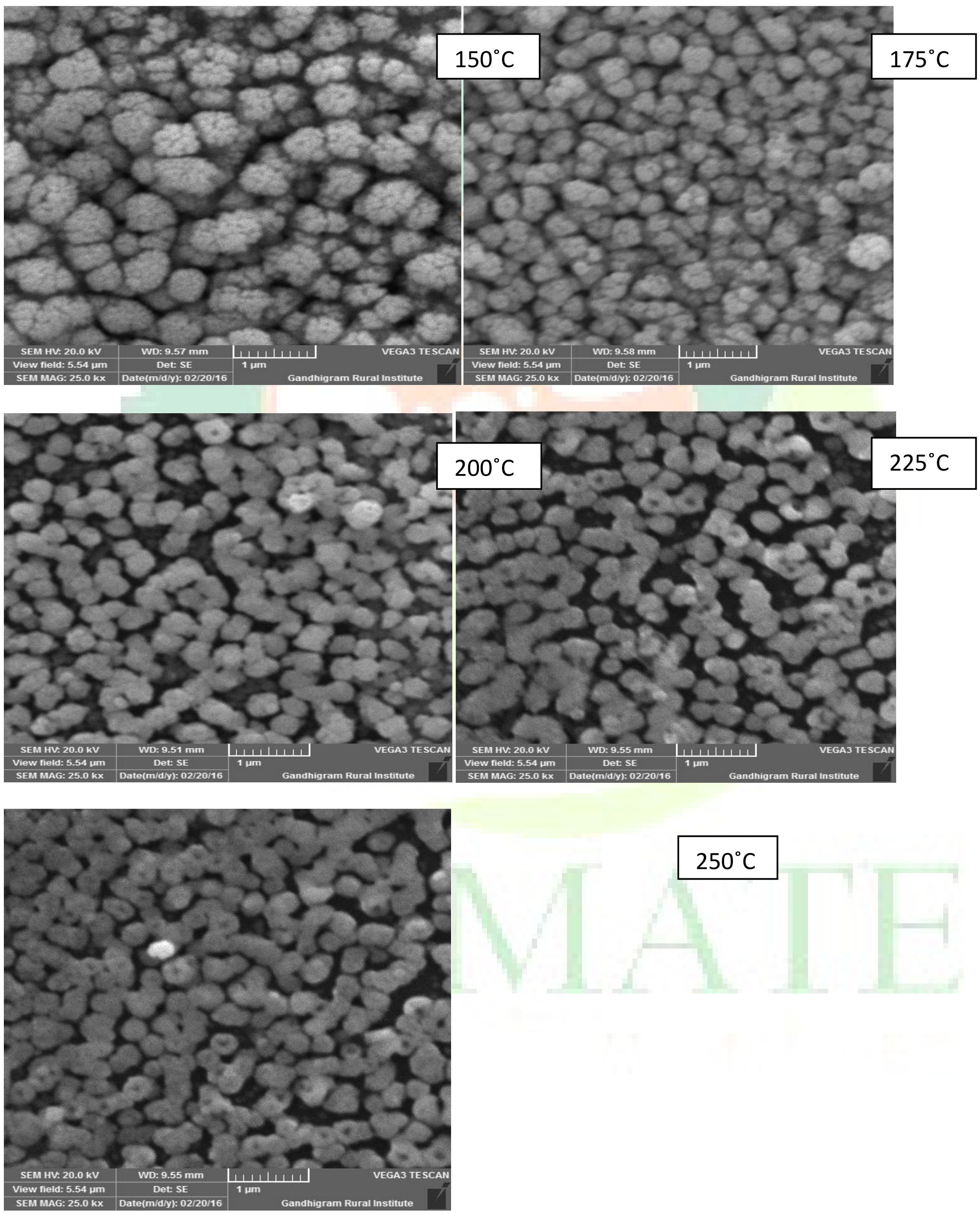

Fig. 3 SEM images of Cdo thin films at different substrate temperatures

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spherical grains with pin holes well defind boundaries and uniform distribution throughout the surface.

Energy dispersive analysis of X-ray spectrum of CdO thin film deposited on the amorphous glass substrate at 200˚C temperature reprasents by fig 4. EDAX spectrum recorded the binding energy region 0-10 eV. Analysis shows the presence of only Cd and O elements and Si peak which corresponds to the glass substrate. EDAX analysis confirms the presence of Cd and O elements without any other impurity , pure nature of the thin film [13].

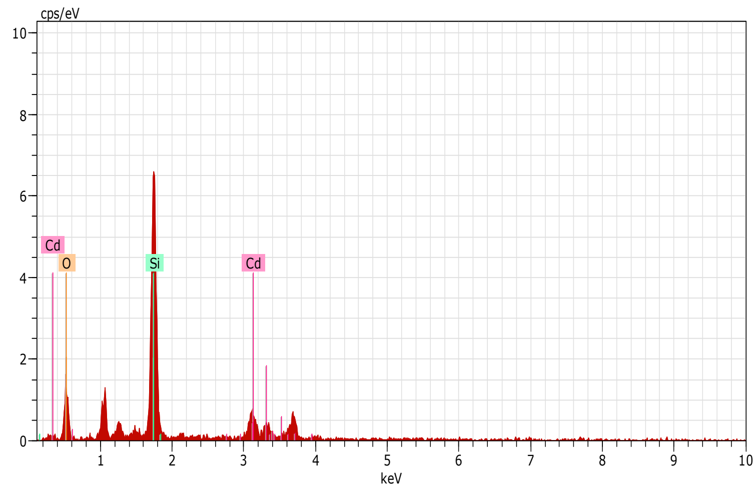

Fig. 4 Elemental analysis of Cdo thin film at 200˚C substrate temperatures

3.4 OPTICAL ANALYSIS

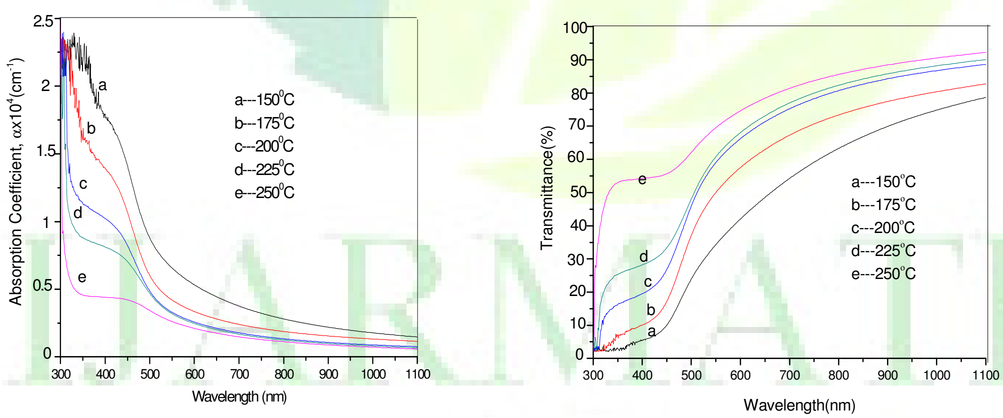

Fig. 5 Absorption Coefficient&Transmittance spectra of Cdo thin films prepared at different substrate temperatures

Absorption coefficient and Transmission spectra of the deposited Cdo thin films at different substrate temperatures shown in fig 5. The highest absorbance of Cdo thin films were in the UV region about 350nm wavelength. The fundamental absorption edge shifted towards the longer wavelengths and lower energies, this shift may be attribute to the improvement of the crystallinity of the films and to the changes of the quality of the Cdo film with increasing the temperature .

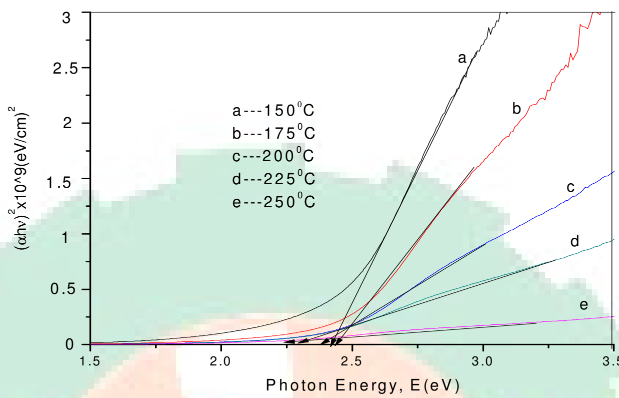

Fig. 6 Energy band gap of CdO thin films prepared at a different substrate temperature

The optical transmissions of thesesamples were about 75% to 90% in the wavelength range from 300-1100 nm. At wavelengths around 450 nm for all samples transmittance shows a minimum. Above the wavelength for all samples (900 nm – 1100 nm) the transmittance increased. The lower substrate temperature has a less transmittance in the visible region in comparison with the films at higher substrate temperature. The increase in transmittance may be attributed to the increase in crystallinity and the structural homogeneity of the thin films with the increase in substrate temperature.

The energy gap of CdO thin films ploted at different substrate temperatures shown in fig 6. The direct energy gaps were calculated from the plots $(\alpha h\nu)^2$ versus hν. All these films the electron transition was direct. The energy gap value decreased from 2.4 eV -2.25 eV with increased in substrate temperatures, this changes may to attribute to red – shift The energy gap value matched with the value obtained by Hassan H.Afify et al [11]. The variation of optical energy gap with substrate temperature is shown in fig 7.

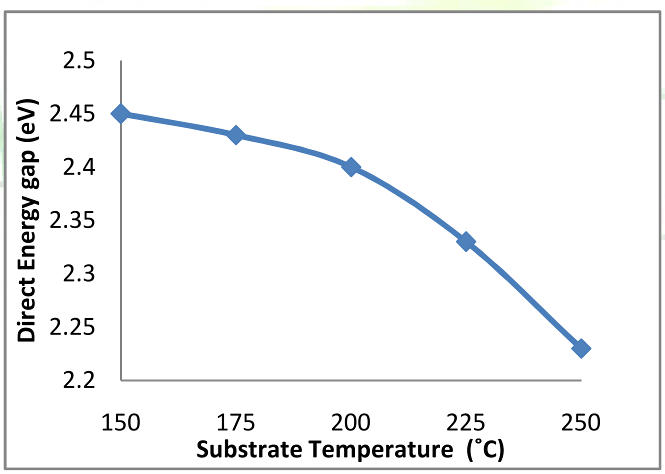

Fig. 7 Variation of Energy gap with Substrate temperature for CdO thin films

3.5 FTIR ANALYSIS

The Fourier transform infrared (FTIR) spectroscopy of the CdO thin films at different substrate temperatures were shown in fig 8. The broad absorption peak at around 3522.02 cm^{-1} is attributed to O-H stretching vibration of H_2O in CdO lattice. The weak absorption peak at around 2941.40 cm^{-1} is assigned to C-H stretching vibration in CdO lattice. The peaks at 675 cm^{-1} is assigned to CdO [14].

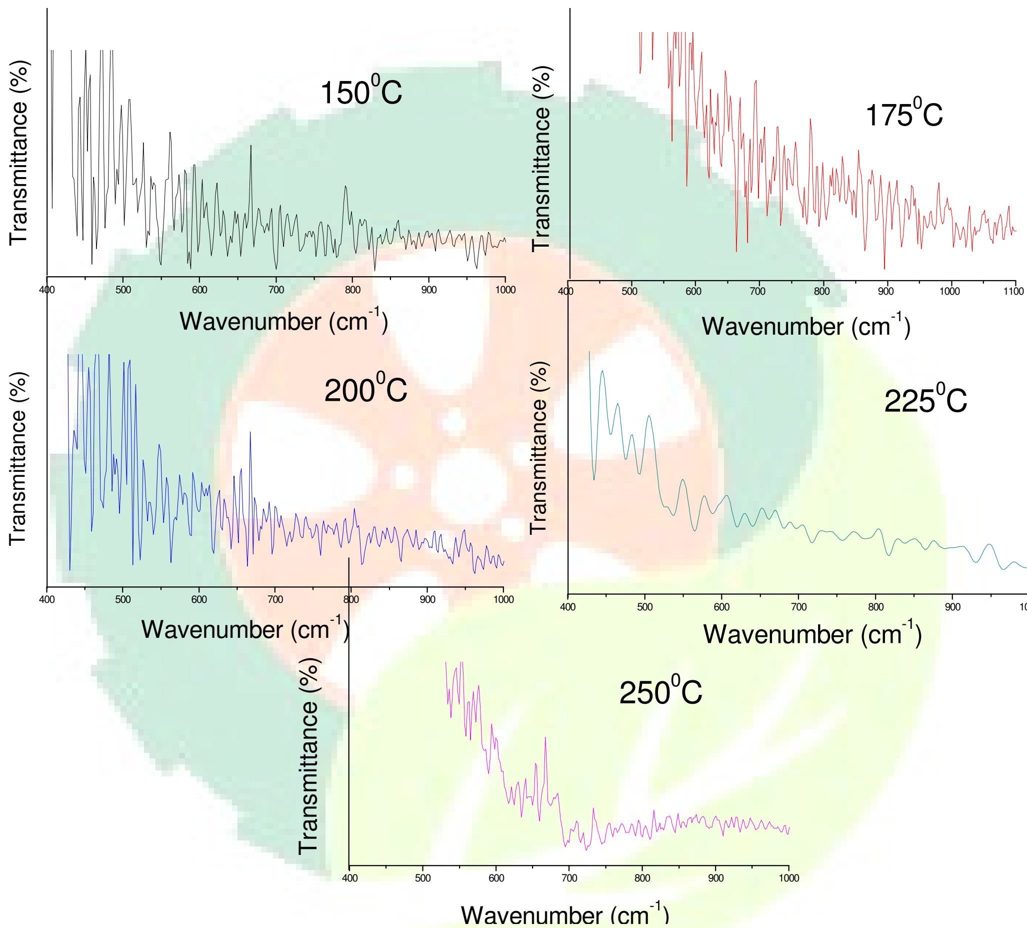

Fig. 8 FTIR analysis of CdO thin films prepared at different substrate temperature

3.6 ELECTRICAL PROPERTIES

Pure CdO is an n-type degenerate semiconductor with high electrical conductivity without any extrinsic doping. The electrical measurements were calculated by four probe measurement system. The electrical resistance R at room temperature was calculated by using the equation R=K(V/I) Where k is a constant found to be 1.53, V is the applied voltage and I is the intensity of dc current. Fig 9 shows the variation of electrical resistivity and activation energy of the thin films with different substrate temperature. The resistivity value increases from 97.37 ohm-cm to 241.28 ohm-cm as the increase of different substrate temperature from 150˚C to 225˚C. The variation of logρ versus 1000/T for CdO thin films. For all the samples it is observed that the resistivity decreases with increase in temperature, confirming the semiconducting nature of the films. The activation energy values E_a are calculated by using the relation

$$\rho = \rho_0 \exp(-E_a / Kt) \quad (5)$$

Where "k" the Boltzmann constant, "ρ_0" is a constant and "T" the temperature in Kelvin. The values of activation energy E_a is decreased for increased in substrate temperature. The activation energy of the CdO thin films prepared with the substrate temperature 150˚C almost agreement with Usharani .K et al [15]

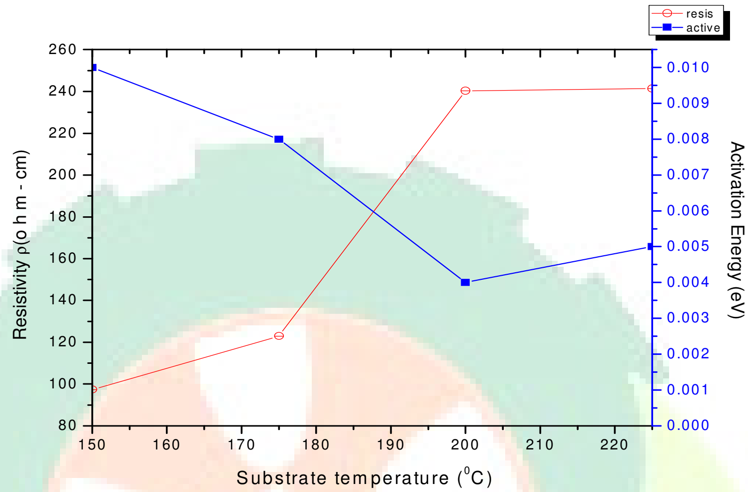

Fig. 9 Variation of resistivity and activation energy with different substrate temperature

4. CONCLUSION

Yellow colored thin films ofcadmium oxide prepared on amorphous glass substrate via nebulized spray pyrolysis technique by using cadmium acetate dehydrate as starting material. The thin films were prepared at different substrate temperature. The effect of substrate temperature on the crystal structure, morphology, optical band gap, bonding confirmation and electrical resistivity of the films was investigated. XRD patterns suggested that all films were polycrystalline in nature with face centered cubic crystal structure with a preferential orientation along the (111) plane irrespective of the substrate temperature. Optical studies revealed that the optical transparency increases and band gap value decreases from 2.4 eV to 2.15 eV with increase in substrate temperature. The presents of functionalgroups and chemical bonding were confirmed by FTIR analysis. The low electrical resistivity was found to be in the range of 97 □ cm in the substrate temperature 150˚C.

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