



## Temperature dependent structural, luminescent and XPS studies of CdO:Ga thin films deposited by spray pyrolysis

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### ABSTRACT

The structural, compositional, photoluminescent and XPS properties of CdO:Ga thin films deposited at temperatures ranging from 275 to 350 °C, using spray pyrolysis are reported. X-ray diffraction characterization of as-deposited GCO thin films reveals that films are of cubic structure with a (200) preferred orientation. The crystalline quality of the GCO films improves and the grain size increases with deposition temperature. The EDS analyses confirm oxygen deficiency present in the film and are responsible for n-type conductivity. The photoluminescence spectra demonstrated that the green emission peaks of CdO thin films are centered at 482 nm. The relative intensity of these peaks is strongly dependent on the deposition temperature. Oxygen vacancies are dominant luminescent centers for green emission in CdO thin films. The XPS measurement shows the presence of Cd, Ga, O and C elements and confirms that CdO:Ga films are cadmium-rich.

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### 1. Introduction

Among different TCO materials like tin oxide, indium oxide, zinc oxide, cadmium oxide and these oxides doped with different and appropriate doping elements attracted the attention of researchers over the globe due to their fascinating characteristics such as high electrical conductivity and optical transmittance in visible spectral region, required for various optoelectronic devices such as photo-detectors, solar cells, gas sensors, and antireflection coatings [1–3]. In particular, developing reliable luminescent materials for flat panel displays has been produced considerable research interests. These efforts have been promoted for the search on different thin film deposition techniques as well as different types of materials and dopants which can be used as active components in many photoluminescent devices [4].

Cadmium oxide (CdO) is a n-type semiconductor with nearly metallic conductivity and has a direct band gap of 2.3 eV with two indirect transitions at lower energies. The n-type conductivity is

attributed to its native oxygen vacancies and cadmium interstitials; which can be further increased by controlling these native defects or by doping with different metallic ions. The optical transmission, the band gap values, carrier concentration and mobility are found to be dependent on the defect/dopant concentration and are attributed to the Burstein-Moss effect [5]. The varieties of techniques have been used for the deposition of pure and doped cadmium oxide thin films which includes ultrasonic spray [6], spray pyrolysis technique [3,7–9], metal organic chemical vapor deposition [10], sol-gel [11], vacuum evaporation [12], chemical bath deposition [13], low-pressure chemical vapor deposition [14] electrochemical method [15], R.F. Sputtering [16], electro-spinning [17] and thermal oxidation [18]. The sputtering, evaporation and other physical processes are expensive from industrial point of view especially for photovoltaic applications. The chemical spraying offers a competitive alternative for the large area deposition and massive production of different coatings. The spray pyrolysis method presents some noticeable advantages, such as: simplicity in operation, a wide possibility of varying the films properties by changing the composition of the starting solution (introduction of dopants and change the film microstructure) and cost effectiveness required for large-scale production.

Concerning the specific applications different dopants like Gd [2], Ti [19], Sn [14], F [7–9], In [6,10], Al [12,17], Mn [20], Zn [3,21] and Ga [22] have been proposed, studied and employed in CdO thin films. Among these dopants, gallium (Ga) is frequently used in CdO

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and ZnO thin films. Recently the effect of Ga composition and the deposition temperature on ZnO thin film is reported [23]. In case of CdO:Ga (GCO) thin films the Cd<sup>2+</sup> ions are replaced by Ga<sup>3+</sup> ions in the CdO host lattice [10,24]. Bazargan et al. [17] have studied the detailed optical properties of cadmium oxide nanofibers based on the photoluminescence (PL) spectrum using electro-spinning technique. Lefebvre et al. [24] have reported on the temperature dependent photoluminescence of single-walled carbon nanotubes grown on the silicon substrates. Hoang et al. [25] have studied the temperature dependent PL to explain the electronic properties of single CdS nanowires.

The literature survey shows that until now, not much attention have been paid for the preparation of CdO thin films using spray pyrolysis technique. Previously the effect of appropriate [Ga] concentration of on the properties of sprayed GCO thin films have been reported [23]. Since this material show the possibility as an alternative to the traditional TCO members used in various photovoltaic applications, to inspect the effect of deposition temperature on GCO films with respect to the structural, compositional, luminescent and XPS studies using cost effective spray technique, seems to be quite interesting and motivating one.

## 2. Experimental

The spray pyrolysis technique using air as a carrier gas at atmospheric pressure has been described previously in detail [3]. In this technique, a mist of a spraying solution is driven to the surface of a heated substrate where a pyrolytic reaction takes place, leaving a solid film plus some volatile compounds. It involved the spraying of a precursor solution of 0.1 M cadmium acetate ((CH<sub>3</sub>COO)<sub>2</sub>Cd·2H<sub>2</sub>O, 99.99%, A.R. grade, Aldrich) and the required amount of gallium nitrate (Ga(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O, 99.9%, A.R. grade, Aldrich) to have optimum [Ga]/[Cd] = 0.015, through a pneumatic nozzle onto a substrate located on a temperature controlled heating plate. The substrates used in this work were soda lime glass slides supplied by Blue star, Mumbai. The preparative parameters like spray rate (5 cm<sup>3</sup> min<sup>-1</sup>), nozzle to substrate distance (32 cm) and quantity of the spraying solution (50 ml) were kept constant for all experiments. Compressed air was used as a carrier gas. The gas regulator valve was used to control the pressure of the carrier gas flowing through the gas tube of the spray nozzle. The temperature of the substrate during deposition was varied from 275 to 375 °C. Chromel–alumel thermocouple was used to measure the temperature of the substrates which was fixed at the center of the hot plate. The temperature of the hot plate was monitored with temperature controller model, 9601 (Aplab make). Hazardous fumes were expelled out from deposition chamber using an exhaust system attached to the spray pyrolysis unit. After deposition, the heater was switched off and these films were allowed to cool at room temperature. All the films were yellowish, pinhole free, well adherent to the substrates. No post-deposition annealing was given to these films and the as-deposited GCO thin films were further used for structural, elemental, photoluminescence and XPS characterizations.

The cross-sectional morphology of the films was observed by using field emission scanning electron microscope (FE-SEM, Model: JSM-6701F) for estimating the thickness of GCO thin films. The crystallinity of the samples was determined with a commercial high-resolution X-ray diffraction patterns obtained using XRD machine (XRD, X'Pert PRO, Philips, Eindhoven, Netherlands) using Cu K $\alpha$  radiation. The elemental composition was determined using an energy dispersive spectrometer (EDS) system attached to FE-SEM (JEOL, JSM-7500F, Japan). Photoluminescence (PL) spectra were obtained using a closed-cycle liquid helium cry generator (APD, SH-4, USA), spectrometer ( $f = 0.5$  m, Acton Research Co., Spectrograph 500, USA) and intensified photodiode array detector (Princeton Instrument Co., IRY1024, USA). All spectra were measured at room temperature with an argon ion laser as a light source using an excitation wavelength of 325 nm. The chemical composition and the valence states of constituent elements were analyzed by X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5400, USA) with monochromatic Mg K $\alpha$  (1254 eV) radiation source.

## 3. Results and discussion

Previously we have reported on the sprayed ITO thin films that there is a critical value of the substrate temperature which decides the quality of the TCO films [26]. In spray pyrolysis, homogeneous and/or heterogeneous reactions that occur near substrate surface and droplet size decide the crystalline nature and crystallinity of the deposited films. At lower substrate temperatures, for instance, at 275 °C in present case, due to relatively higher droplet size het-

erogeneous reaction occurs at substrate surface leading to slower decomposition rates of the ingredients. As substrate temperature increases, homogeneous and heterogeneous reactions occur at and just above the substrate surface, respectively due to decreased droplet size leading to increased decomposition rate. At relatively higher substrate temperatures ( $T_s \geq 375$  °C), homogeneous reaction occurs above substrate surface resulting into declination of decomposition rate. So there is an optimum temperature where the decomposition occurs at an optimum rate. The thickness of GCO thin films varies from 350 to  $770 \pm 10$  nm (Fig. 1). The uniformity in film thickness is verified from various cross-sectional parts of GCO films. The films have sharp interface between the film and substrate. The film thickness increases with increasing deposition temperature up to 350 °C and thereafter it decreases. Such kind of temperature dependence on the crystalline quality and the film thickness for sprayed thin films has been reported earlier [26].

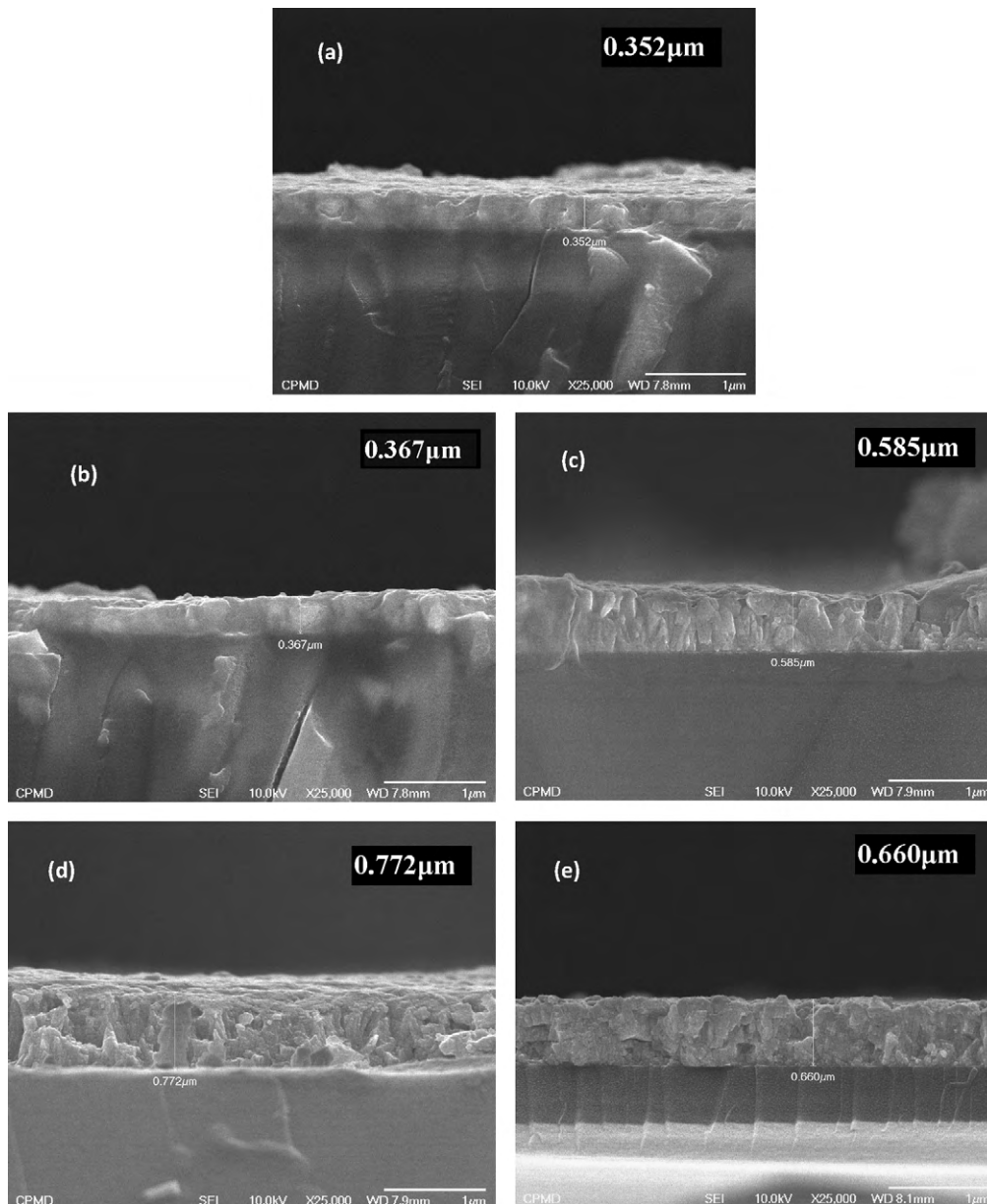
### 3.1. X-ray diffraction analysis

Fig. 2 shows the XRD patterns of as-deposited GCO thin film as function of deposition temperatures. The relatively stronger intensity of the peak at  $2\theta = 33.09^\circ$  indicating preferential (1 1 1) orientation of the films, has been reported previously [3,17]. In the present case the well defined (2 0 0) diffraction peak indicating the formation of cubic CdO phase is observed at  $2\theta \sim 38^\circ$ . All the patterns exhibit a preferential growth along (2 0 0) plane. The change in the crystalline volume due to Ga entering in the crystalline structure of CdO is of the order of  $-1.5\%$ . The average lattice constant of GCO films is 0.468 nm, and it is almost identical with the reported values [27]. The decrease in lattice constant in CdO films due to Ga incorporation is 0.019 nm. The intense peak (1 1 1) of GCO films is found to be shifted by  $-0.1^\circ$  due to a strain of about  $-1.38 \times 10^{-3}$  due to Ga incorporation. The small change in lattice parameter and thereby lattice volume is attributed to the smaller ionic radii of adsorbed Ga<sup>3+</sup> ions into the crystalline structure of CdO. The comparison of standard and observed 'd' values for GCO thin films shows that they are in well agreement with each other [28]. As the deposition temperature increased (2 0 0) peak intensity increased dramatically, indicating improvement in crystalline nature and preferred orientation. The other weak intensity peaks corresponding to (1 1 1), (2 2 0), (3 1 1) and (4 0 0) planes are also observed. The increased peak intensity as well as number of peaks with the deposition temperature can be attributed to the improved crystallinity of GCO thin films. The preferential growth along (1 1 1) plane for undoped CdO [3,14,16,17], and doped CdO thin films with In [6] and Ga [12] is already reported. In the present study, the films are found to be oriented along (2 0 0) direction. The preferred orientation along (2 0 0) direction for undoped CdO and sprayed CdO:F thin films is also reported [9]. Further it is also reported that at high substrate temperature, the mobility of the ad-atoms is high which promotes the diffusion of ad-atoms. To conclude, the favoured growth depends upon the nature of impurities incorporated and the appropriate temperature required for perfect decomposition of the solution, which decides the plane to be favoured. It is believed that the plane having minimum surface energy is always favoured, which is (2 0 0) plane, in the present case.

The size of the crystallites oriented along (2 0 0) plane is calculated using well-known Scherrer's formula [29]:

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

where  $D$  is the size of crystallite,  $\beta$  is the broadening of diffraction line measured at half its maximum intensity (FWHM) in radians. It is found that the crystallite size of GCO films increases with an increase in film thickness, which increases due to increase in



**Fig. 1.** Cross-sectional scanning electron micrographs showing thickness estimation of sprayed GCO thin films prepared at different deposition temperatures: (a) 275 °C, (b) 300 °C, (c) 325 °C, (d) 350 °C and (e) 375 °C.

deposition temperature (Fig. 2). This indicates that the film thickness contributes to the improvement in crystallinity. The maximum crystallite size of 146 Å is observed for the GCO film deposited with 350 °C. At higher temperature, due to high evaporation rate of the spraying solution the film with smaller crystallite size of 124 Å is resulted.

The texture coefficient (TC) is estimated using the following formula [30]:

$$TC_{(hkl)} = \frac{I_{(hkl)}/I_0}{(1/N) \sum I_{(hkl)}/I_0} \quad (2)$$

where  $TC_{(hkl)}$  is the corresponding texture coefficient of the  $(hkl)$  plane,  $I_{(hkl)}$ , and  $I_0$  denotes the measured and standard intensities in the X-ray spectra [28], respectively, and  $N$  is the total number of diffraction peaks and here  $N=5$ . From this definition it is clear that the deviation of the texture coefficient of a particular plane from unity implies the preferred orientation along that plane. The higher is the deviation of TC from unity the higher is preferred

orientation of the film. This preferred growth is always favoured by a high substrate temperature and specific interaction of the nucleus with the substrate surface. The surface energy of interaction determines the plane of orientation to be preferred; such as the orientation having low surface energy of interaction is favoured. In the present case the (200) plane has been observed to have minimum surface energy of interaction [31]. Further, with increase in deposition temperature from 275 to 350 °C, the  $TC_{(200)}$  varies from 2.04 and becomes a maximum of 3.85 and then it reduces to 3.26 for further deposition temperature (Fig. 3). This is attributed to the increase in extent of preferred orientation associated with the increased number of grains along (200) direction. The grains may coalesce and rotation of a preferred growth in (200) direction may take place where the interfacial energy is minimum one. Due to increased coalescence of the grains, its size and film thickness increases as the deposition temperature increases. The typical GCO thin film of 772 nm thickness, deposited with 350 °C indicates highly oriented growth along (200) direction due to perfect

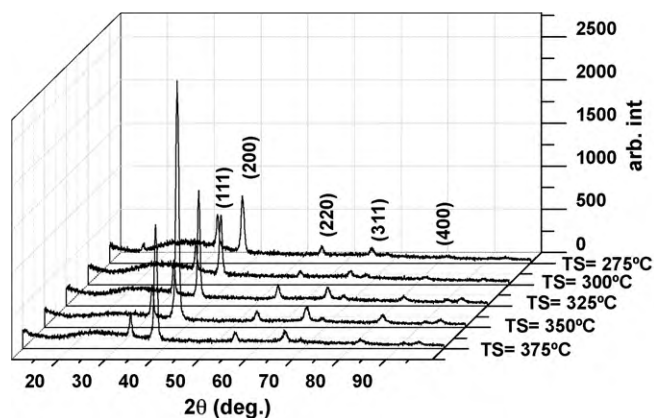


Fig. 2. XRD spectra of sprayed GCO thin films prepared at various deposition temperatures.

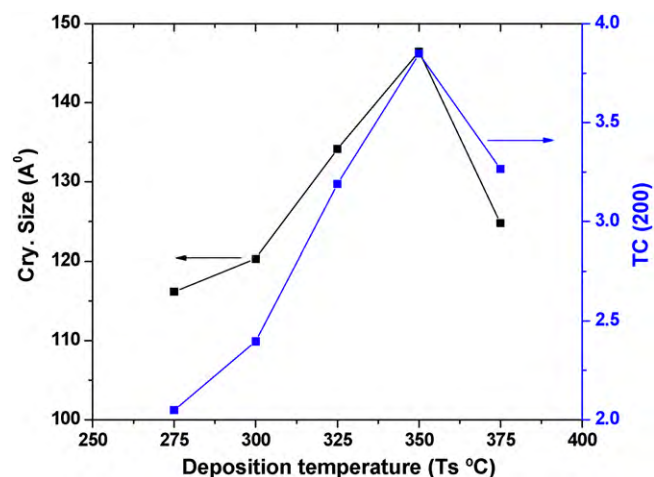


Fig. 3. The dependence of crystallite size for the sprayed GCO thin films prepared at various deposition temperatures.

decomposition of the spraying solution. The TC(1 1 1), TC(2 0 0) and TC(2 2 0) have been calculated. But since value of TC(2 2 0) is found to be very much less than one as observed from the peak intensity (Fig. 2) it has been ignored. The values of TC(1 1 1) plane for the GCO films prepared at different temperatures from 275 to 375 °C, are 1.19, 1.07, 0.96, 0.47 and 0.37, respectively. Thus from texture coefficient calculations, the (2 0 0) peak prevails over the rest, as the corresponding TC(200) is higher than 1 while TC values for other planes are lower than 1. This indicates the occurrence of very small crystal reorientation effect due to the change in deposition temperature.

### 3.2. Compositional analysis

Fig. 4 shows the typical EDS pattern of GCO thin films prepared at deposition temperature of 350 °C. An EDS spectrum normally displays peaks corresponding to the energy levels for which the most X-rays have been received. The highest peak in a spectrum corresponds to more concentrated element present in the specimen. The intensity of [Ga], [O] and [Cd] is in increasing order and the highest peak intensity has been observed for [Cd]. The fact that the [O]/[Cd] ratio is smaller than unity confirms the presence of oxygen deficiency in GCO films, which serves as donors and are responsible for n-type conductivity of GCO thin films.

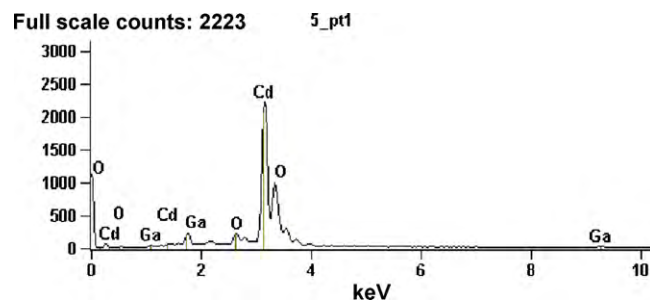


Fig. 4. Typical EDS pattern of the CdO:Ga thin films prepared at optimized deposition temperature of 350 °C.

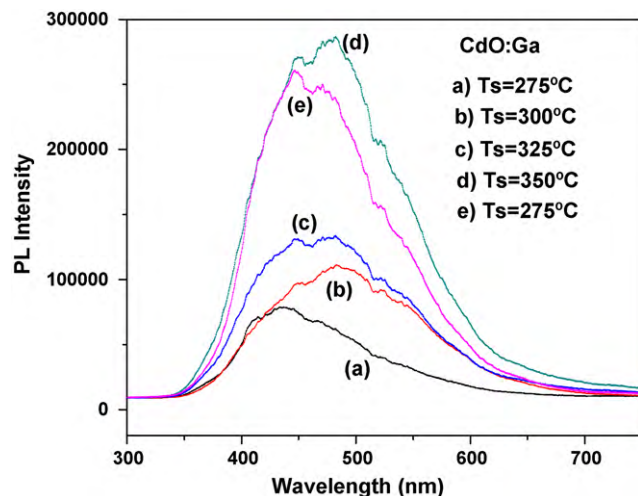


Fig. 5. Photoluminescence emission spectra of sprayed GCO thin films prepared at various deposition temperatures.

### 3.3. Photoluminescence

Fig. 5 shows the room temperature luminescent spectra measured in the visible region for GCO films prepared at different deposition temperatures. For the GCO film deposited at 275 °C only one luminescent peak is observed at 437.26 nm. This peak position has been found to be shifted to higher wavelength side, for  $T_s = 300$  °C, it is 482.96 nm; while for other deposition temperatures, i.e. 275, 325, 350 and 375 °C it is almost at 482.31 nm. For deposition temperature greater than 275 °C, one more additional weak peak has been observed. As the deposition temperature is increased, the luminescence of the GCO films is increased, up to the deposition temperature of 350 °C, due to increase in film thickness. But above 350 °C, the intensity of the peak decreases. The green emission is mainly due to concentrations of free electrons, and the existence of various point defects identified as  $V_o$ . These defects are due to heating treatments associated with the deposition process that forms the recombination centers [32]. In our earlier report the shift in position of PL intensity to lower wavelength side with increasing [Ga]/[Cd] ratio is reported wherein the green emission to average wavelength of 470 nm has been observed. Here, it is found that the PL intensity increases with increase in deposition temperature along with the shift in wavelengths corresponding to 437.3, 482.1, 482.3, 482.3 and 446.4 nm, respectively. The possible reason may be the difference in film thickness. The observed green emission around  $470 \pm 2$  nm in our previous report may be due GCO film having thickness from 0.5 to 0.6  $\mu\text{m}$  [23]. Since there is not much noticeable change in film thickness, relatively small change in the wavelength of green emission is observed. The varied deposition temperatures in the present case have resulted into GCO films with different thicknesses. The

lowest thickness is about 350 nm while the highest thickness is 770 nm. So the increased thickness may be the possible reason for the observed green emission shift to higher wavelength. For the GCO films deposited with moderate temperature (excluding low and high 275 and 375 °C) using 300–350 °C, the green emission around 482 nm is observed. Shaleev et al. [33] have reported on the PL shift to higher energy side with increase in growth temperature and is attributed to increase in the offset of valence band at the interface between the island and the deposited layer. This PL peak shift is disregarded to the effects of quantum confinement on the position of the energy levels of holes. Further the morphological changes of the surface due different growth temperatures are also responsible for the observed PL shifting to higher energy side [34]. For CdO cadmium oxide nanofibers two emission peaks at 493 and 528 nm are reported. The first peak is attributed to the excitonic transitions which are size-dependent and the second peak is due the deep trap emission that is less size-dependent [18,35].

The dependence of the luminescent spectra with increase in deposition temperature is consistent with the crystallinity nature and the electrical properties as well. The resistivity, carrier concentration and mobility values of the GCO thin films are calculated using Hall effect in Van der Pauw configuration. The main source of experimental error is being due to the technique itself, i.e. due to the sample size and the contact spot size, which estimated to be about 5% [12]. It is found that when the deposition temperature is varied from 275 to 350 °C, the electrical resistivity decreased from  $5.2 \times 10^{-4}$  to  $1.9 \times 10^{-4} \Omega \text{ cm}$ . The decrease in resistivity can be explained by the fact that the grain size increases significantly with increase in deposition temperature, reducing grain boundary scattering, and increasing conductivity. The decrease in resistivity can be also associated with (i) the observed increase in carrier concentration from  $9.25 \times 10^{21}$  to  $11.7 \times 10^{21} \text{ cm}^{-3}$  and

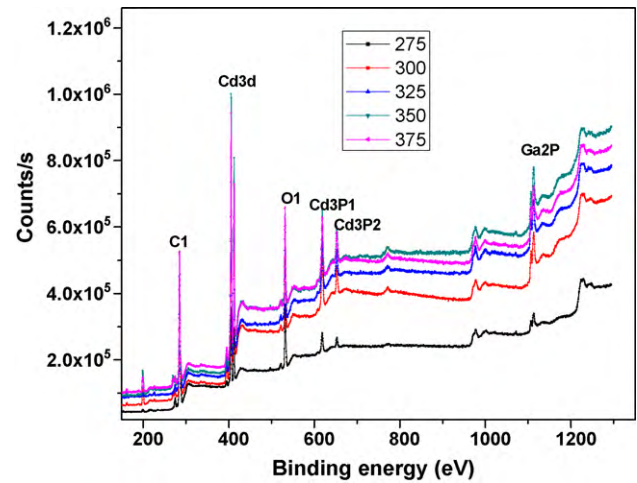


Fig. 6. XPS survey scan spectrum of sprayed GCO thin films prepared with various deposition temperatures, recorded with monochromatic Mg K $\alpha$  (1254 eV) radiation source

(ii) this change may be partially due to the mobility change from  $13$  to  $27.64 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Above 350 °C, the resistivity increases to  $3.1 \times 10^{-4} \Omega \text{ cm}$ , as a consequence of stoichiometric deviations which signify the decrease of dislocations and grain boundaries. Hence it is related to an improvement in crystallinity leading to decrease of donor sites trapped at the dislocations and grain boundaries. Such a behavior with respect to substrate temperature has been reported [14,36,37]. The minimum resistivity value  $1.9 \times 10^{-4} \Omega \text{ cm}$  obtained in the present case is lower than the reported for GCO thin films using evaporation method [14].

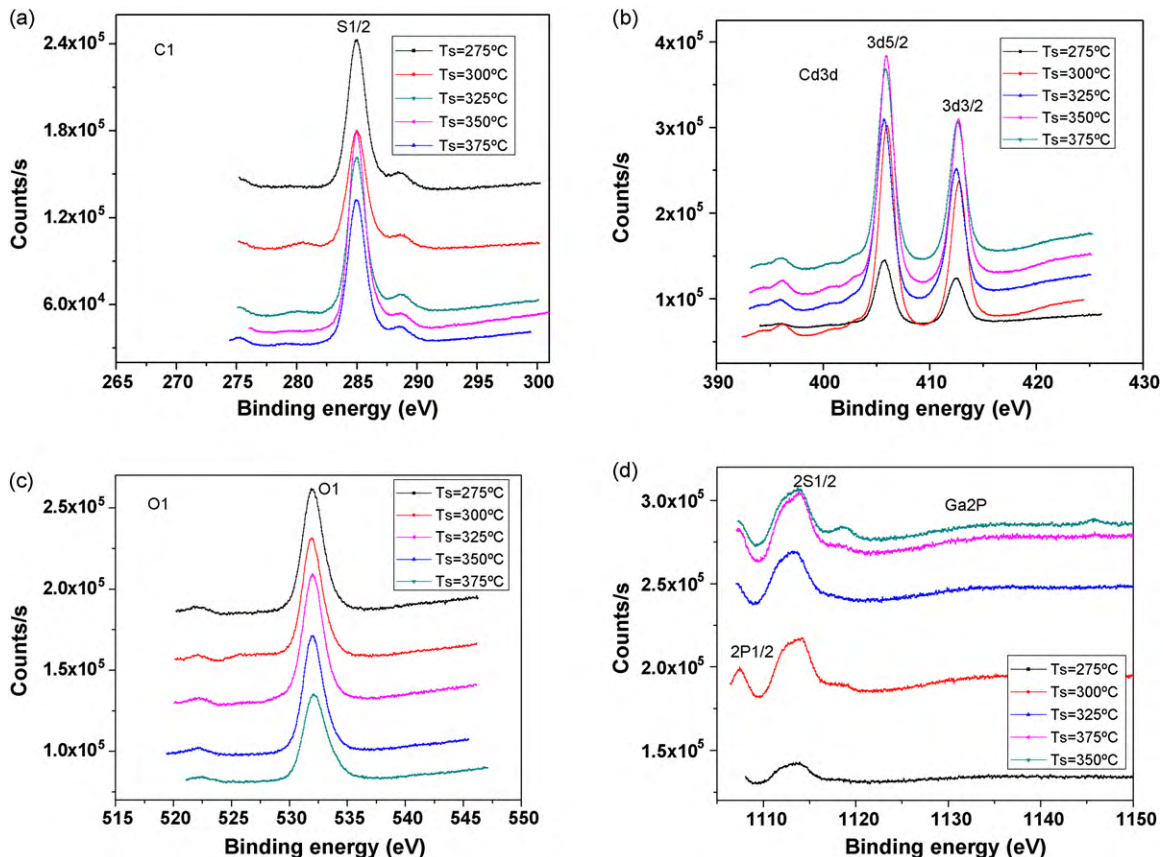


Fig. 7. XPS narrow scans for (a) C1, (b) O1, (c) Cd3d and (d) Ga2P of CdO:Ga thin films prepared at various deposition temperatures.

### 3.4. XPS analysis

Fig. 6 shows XPS survey scan spectra consisting of Cd, Ga, O and traces of C elements for GCO thin film prepared at different deposition temperatures. It shows two components for C1 peak; of course the intensities are quite different, as first one is relatively very stronger than the second one, whose binding energy is 275 eV for all the films. From the narrow scan of C1 peak (Fig. 7(a)), the binding energies are found to be 285.05, 285.1, 285.75, 285 and 285 eV, for the films prepared with 275, 300, 325, 350 and 375 °C, respectively. The presence of C1 peak observed at around 285 eV is assigned to C1s<sub>1/2</sub> due to some surface contamination resulted due to exposure to air before the XPS measurements [16].

Narrow scan XPS spectra of Cd3d for GCO films as a function of deposition temperatures are shown in Fig. 7(b). The Cd 3d features consist of the main 3d<sub>5/2</sub> and 3d<sub>3/2</sub> spin-orbit components. The binding energies of 405.85, 405.95, 406, 405.9, 405.7 and 412.6, 412.75, 412.75, 412.54 and 415.5 eV, respectively, have been noticed for 3d<sub>5/2</sub> and 3d<sub>3/2</sub> components. The binding energy of Cd3d<sub>5/2</sub> is attributed to the Cd<sup>2+</sup> bonding state, which agrees well with the previous report [38]. In addition, some other peaks corresponding to Cd3P1 and Cd3P3 centered at 618 and 675 eV are also observed.

Two O1s peaks are evident from survey of the GCO thin films prepared as a function of deposition temperature, which is common for oxides containing oxygen in multiple valence states. The peak on the low binding energy side of the O1s spectrum can be attributed to the Cd–O bonds [39]. The component having the medium binding energy of O1s peak is associated with O<sup>2-</sup> ions that are in oxygen deficient regions. From the narrow scans of varied temperatures (Fig. 7(c)), the binding energies for major peak O1s are found to be 531.9, 531.95, 532.05, 532.01 and 532 eV, respectively. These features are identical to those which are already reported for related CdO systems and are due to the presence of hydroxide species on the surface, which are ubiquitous in air-exposed CdO materials. In particular, it has been reported that when atomically clean CdO surface is exposed for a few minutes in air, the characteristic double XPS O1s peak is observed [40].

The binding energies corresponding to the peaks Ga 2P<sub>1/2</sub> (observed in survey scan), Ga 2S<sub>1/2</sub> as obtained from XPS analysis are 1113 and 1117 eV, respectively (Fig. 7(d)). Further the GCO film deposited at 275 °C have 48.28 atom% O and 51.71 atom% Cd, yielding an O:Cd ratio of 0.93. When the deposition temperature is increased to 350 °C, the oxygen concentration decreased to 43.18 atom% and the cadmium concentration increased to 56.81 atom%, resulting in an O:Cd ratio of 0.76. The XPS measurements indicate that the GCO films are cadmium-rich throughout the investigated deposition temperature range.

### 4. Conclusions

The structural, compositional, photoluminescent and XPS properties of n-type GCO thin films prepared using cost effective spray pyrolysis method are found to be influenced by the deposition temperature. The thickness of deposited GCO thin films varies from 350 to 770 ± 10 nm. X-ray diffraction studies showed that the films are polycrystalline and the peaks fit well to the cubic structure with a preferred orientation along the (200) direction. The crystalline quality of the films gets better and the grain size increases with increase in deposition temperature. The EDS analysis confirms the oxygen deficiency present in the deposited films, showing [O]/[Cd] ratio is less than unity. These oxygen vacancies work as donors, and are responsible for n-type conductivity of the GCO films. The values of minimum resistivity, highest carrier concentration and

high mobility for the best film deposited at optimized deposition temperature of 350 °C are of 1.9 × 10<sup>-4</sup> Ω cm, 11.7 × 10<sup>21</sup> cm<sup>-3</sup> and 27.64 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively. Oxygen vacancies are dominant luminescent centers for the green emission in GCO thin films. The best GCO film deposited with 350 °C, has the oxygen concentration (43.18 atom%) and the cadmium concentration (56.81 atom%) resulting in an O:Cd ratio of 0.76. The XPS measurements indicate that the all GCO films are cadmium-rich.

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