Chapter 5

Transparent and Conductive Fe Doped CdO Thin Films and its Ethanol Sensing Applications
5.1 Introduction

As one of the wide-band-gap oxides, CdO has attracted a great deal of attention due to its wide range of technological applications. By an appropriate impurity doping such as Al and In, CdO thin films can be highly conductive as well as exhibiting high optical transparency in the visible range applicable for transparent electrodes, thin film transistors in solar cells, gas sensor and flat-panel displays. Due to its large band gap and binding energy in the cubic crystal structure at room temperature, CdO is a promising material for many applications. So far, 3d transition metal elements, such as Mn, Fe and Co, have been alloyed with CdO and their properties have been investigated. It has been found that the magnetic semiconductors formed by replacing the cations of III–V or II–VI nonmagnetic semiconductors by ferromagnetic Mn, and Fe exhibit a number of unique optical and electrical properties, applicable for TCO applications. To the best of our knowledge, the Fe doped CdO films prepared by a spray pyrolysis method have not been used so far in gas sensor applications. It is well known that the gas sensing properties of oxide materials are related to the surface morphology, resistivity and are grain size dependent. Therefore, one can improve the gas response by controlling the grain size and surface morphology. In this work, Fe is taken as a dopant for CdO thin films and try to enhance the sensing property with respect to doping concentrations. In this work, we have studied the effect of Fe concentration on the structural, optical, electrical and sensing properties of Fe doped CdO thin films.

5.2 Experimental

Pure and Fe doped CdO thin films were deposited using spray pyrolysis technique. CdO films were prepared using 0.1 M cadmium acetate [Cd(CH$_3$(COO)$_2$)] dissolved in double distilled water. Doping of Fe concentration was achieved by adding aqueous solution of ferric chloride (0.5 - 2 wt %) with the precursor solution. All films
transparent and ethanol sensing applications

were deposited at the constant substrate temperature of 573 K. The distance between the tip of the nozzle and the surface of the glass substrate was kept constant (25 cm). The compressed air was used as a carrier gas (4 Mpa), spray angle (about 45°) and the flow rate of the solution (~ 3ml/min) were kept constant. The resultant precursor solution was sprayed on preheated substrates. After deposition, the coated substrates were allowed to cool down to room temperature.

5.3 Results and Discussion

5.3.1 X-ray diffraction studies

Fig. 5.1 (a) show the XRD patterns of the pure and Fe doped CdO films. The preferential orientations of all the films have been found to be along (1 1 1), (2 0 0) directions and less intense peaks are seen along (2 2 0), (2 2 2). XRD analysis revealed that all the films are of polycrystalline in nature having a face – centred cubic crystal structure (NaCl structure of a space group \( Fm-3m \)) according to the JCPDS file No. 05-0640 and no peaks regarding the formation of secondary phases are their complex oxides are observed. This suggests that the films do not have any phase segregation.
The calculated lattice constant value of $a = 4.672$ Å (standard value of $a = 4.69$ Å) agrees with standard JCPDS value. From Fig 5.1, it is observed that the pure CdO thin film has a growth orientation along (200) direction, whereas Fe doped CdO thin films the intensity of (200) plane decreases and the intensity of (111) peak increases. Thus the preferential growth orientation is shifted from (200) to (111) direction for 1.5 wt% Fe-doping. The reason for the change in growth orientation is incorporation of Fe ions into the Cd lattice sites. Fig. 5.1 (b) shows the diffraction angle of (111) and (200) planes slightly shifted to higher (2θ) angle for Fe doped CdO as compared to that of pure CdO. This may be attributed to the shrinkage of the lattice plane and Fe doping as the radius of Fe$^{2+}$ is smaller than that of Cd$^{2+}$. The refined unit cell parameter ‘$a$’ of pure and Fe doped CdO films (pure, 0.5, 1, 1.5 and 2 wt%) was found to be 4.672(2) Å,
4.670(6) Å, 4.668(4) Å, 4.666(5) Å and 4.661(2) Å, respectively. The slight decrement in lattice parameter values is due to the substitution of smaller Fe$^{2+}$ ions (0.078 nm) in larger Cd$^{2+}$ ions (0.095 nm). The decrease of lattice parameter and shifting of XRD reflections to higher angle with increasing concentration of Fe clearly suggests the incorporation of Fe$^{2+}$ into the Cd lattice sites. The crystalline size of the Fe doped CdO thin films was estimated using Scherrer’s relation and the results are given in Table 5.1 [105].

![Graph](image)

**Fig. 5.2. Variation of crystalline size and strain values of pure and Fe doped CdO thin films**

The variation of crystalline size and average strain as a function of Fe concentrations is given in table 5.2. It can be observed from Fig. 5.2, the crystalline size of the Fe doped CdO films increases with increasing Fe concentrations whereas the strain value decreases, which indicates that the large amount of Fe doping may create lattice distortion and this may be due to the smaller radius of Fe$^{2+}$ ions than that
of Cd$^{2+}$ ions and which leads to a decrease in the lattice constants, which in turn is responsible for the change in the crystalline size.

Table 5.1 Comparison of crystalline size, strain, resistivity, mobility, and carrier concentration of Fe doped CdO thin films

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Sample</th>
<th>Crystalline size (nm)</th>
<th>Strain × 10^{-3} (lin$^{-2}$ m$^{-1}$)</th>
<th>Resistivity (ρ) (Ω cm)</th>
<th>Mobility (μ) (cm$^{2}$V$^{-1}$s$^{-1}$)</th>
<th>Carrier concentration (N) (cm$^{-3}$) ×10^{20}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CdO</td>
<td>18</td>
<td>1.550</td>
<td>2.03×10^{-3}</td>
<td>12</td>
<td>1.968×10^{20}</td>
</tr>
<tr>
<td>2</td>
<td>Fe:CdO (0.5%)</td>
<td>19</td>
<td>1.548</td>
<td>2.14×10^{-3}</td>
<td>13</td>
<td>2.149×10^{20}</td>
</tr>
<tr>
<td>3</td>
<td>Fe:CdO (1%)</td>
<td>21</td>
<td>1.306</td>
<td>7.67×10^{-4}</td>
<td>39</td>
<td>2.092×10^{20}</td>
</tr>
<tr>
<td>4</td>
<td>Fe:CdO (1.5%)</td>
<td>24</td>
<td>1.146</td>
<td>2.09×10^{-4}</td>
<td>46</td>
<td>6.341×10^{20}</td>
</tr>
<tr>
<td>5</td>
<td>Fe:CdO (2%)</td>
<td>25</td>
<td>1.141</td>
<td>1.57×10^{-3}</td>
<td>21</td>
<td>1.834×10^{20}</td>
</tr>
</tbody>
</table>

5.3.2 Surface morphology studies

Fig. 5.3. shows the AFM images of the pure CdO and Fe doped CdO thin films with different Fe doping concentration. From figure it can be clearly seen that the change in the surface morphology depending on Fe concentration. The pure CdO thin film shows a relatively spherical shaped grains and surface roughness as indicated in Fig. 5.3 (a), Fig. 5.3 (b) and Fig. 5.3 (c) show the granules possess different irregular shapes, sizes and separation for the doping concentration of 0.5 and 1 wt%. For higher (1.5 and 2 wt %) doping concentration CdO thin films shows (Fig. 5.3 (d) and 5.3 (e)) the homogeneous and densely packed grains. The roughness of the pure CdO thin film is 12 nm. Further, roughness of the CdO thin film decreases with increase in Fe doping concentration. The surface morphology of the CdO was effectively modified by Fe doping. The reason for this morphological change is the change in the preferred growth orientation of the doped films.
Fig. 5.3. 2D and 3D AFM images of CdO thin films as a function of Fe doping level
5.3.3 Chemical composition studies

Fig. 5.4 (a) shows the wide scan XPS spectrum of the spray deposited Fe doped CdO thin film. XPS measurements were performed to confirm the chemical binding states of the Fe doped CdO thin film. Fig. 5.4 (b-d) shows the measured XPS spectra of Cd 3d \(^{3/2}\), \(^{5/2}\), Fe 2p and O1s core level. The sharp peaks observed at 407 and 413.5 eV are attributed to the existence of Cd\(^{2+}\) and this exactly matched with the binding energy of Cd–O. Figure 5.4 (c) shows the measured XPS spectra of O 1s level in which the peaks centered at 535.5 eV is indicates the chemisorbed oxygen in the samples and it is attributed to the existence of O\(^{2-}\). Fig. 5.4 (d) confirms the existence of Fe\(^{2+}\) ions in the Fe doped CdO thin film. A peak centered at 711.5 eV clearly agrees the Fe 2p\(_{1/2}\) in CdO structure. Thus, the XPS data gives an obvious evidence for the existence of the Fe\(^{2+}\) ion in Fe doped CdO thin film.

Fig.5.4. XPS spectra of Fe doped CdO thin film
5.3.4 Optical properties

The influence of Fe ion on the optical properties of Fe doped CdO thin films are depicted in Fig. 5.5. It is observed that all the films are highly transparent in the visible range. It is seen that the transparency of the films completely depends on Fe dopant. The transmittance of the films decreases with increasing of Fe doping concentration. The decrease in transmittance of Fe doped CdO thin films can be owing to the incorporation of more Fe ion in the lattice and interstitial positions.

![UV-Vis optical transmittance spectra of CdO thin films](image)

**Fig.5.5. UV-Vis optical transmittance spectra of CdO thin films as a function of Fe doping level**

(Fig. 5.6). The pure CdO film shows a band gap of 2.51 eV. The optical band gap is found varying between 2.51 and 2.17 eV for various doping concentration. This decrease in optical band gap of CdO thin film due to Fe doping can be related to the Burstein–Moss effect [108].
Fig. 5.6. Plots of $(\alpha h \gamma)^2$ against $h \gamma$ of CdO films as a function of Fe doping level

5.3.5 Electrical studies

The room temperature electrical resistivity ($\rho$), mobility ($\mu$), and carrier concentration ($N$) of pure and Fe doped CdO were measured using Vander-Pauw method in a constant magnetic field of 5 kilogauss and the results are presented in Table 5.1. The negative sign of hall coefficient confirms n-type conductivity. The present results show that the Fe ions change the electrical properties of CdO films. Pure CdO thin film shows a resistivity of $2.03 \times 10^{-3}$ cm and it decreases to $7.67 \times 10^{-4}$ cm for 1 wt% Fe doping. The resistivity value decreases for initial Fe doping concentration upto 1% and then increases for higher concentrations of Fe (1.5 and 2 wt%). This may be due to the Fe ions are placed into the CdO lattice effectively and act as donors by supplying a free electron when they occupy the sites of
Cd$^{2+}$ ions at the lower level for the resistivity values increases 1.5 and 2 wt% Fe doping, owing to increase phonon scattering and ionised impurity scattering. The pure CdO film exhibits a carrier concentration of $1.968 \times 10^{20}$ cm$^{-3}$. This value increases with increasing Fe doping level and reaches to a maximum value of $6.341 \times 10^{20}$ cm$^{-3}$ for 1.5 wt% of Fe and then decreases at higher doping concentration (2 wt%). The increase in carrier concentration may be the most of Fe ions homogeneously placed in Cd lattice to provide more carriers. For higher Fe doping concentration (2 wt%) the carrier concentration value has been decreased. This is may be owing to the excess amount of Fe ions cannot be accommodated into the Cd lattice due to its limited solid solubility. The Hall mobility value increases from 12 to 46 cm$^2$ V$^{-1}$s$^{-1}$ with increasing the Fe doping concentration of Fe upto 1.5 wt%. For further increasing of Fe doping concentrations the mobility value found to be decreases (2 wt%). Thus the reduction of mobility as a function of Fe doping levels may be attributed to ionised impurity scattering centres in CdO films. At higher doping concentration of Fe ion increases the electrical resistivity and lead to build up of carrier traps in the lattice, which in turns reduce the mobility. Further, as the ionic radius of Fe smaller than that of Cd, therefore the excess Fe atoms may occupy the interstitial positions and hence they deform the crystal structure.

5.3.6 Ethanol sensing characteristics

The gas sensing mechanism of semiconducting metal oxide thin films is based on a change in electrical conductance or resistance due to the gas adsorption and desorption on surface of the film. On the surface of the Fe doped CdO thin film, the interaction occurs between the chemisorbed ethanol and absorbed oxygen. At low operating temperature, O$^2_-$ is chemisorbed, while at higher temperatures O$^{2-}$ and O$^-$ are chemosorbed and O$^2_-$ disappear rapidly. The oxygen adsorption can be described by following equations [140].
On exposure to ethanol gas at different operating temperatures, the reaction between the ethanol vapour and oxygen that is adsorbed onto the surface of the film can be expressed by following equation [141],

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH (adsorbed)} + 6\text{O (adsorbed)}^- & \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} + 6e^- \quad \cdots \quad (5.2)
\end{align*}
\]

Due to the reaction, a number of free electrons are re-injected into the film, so that the resistance of the films decreases as the ethanol gas flows into the chamber and is subsequently adsorbed onto the surface of the Fe doped CdO thin film. The gas sensing
experiments were carried out in the operating temperature ranging from 423 to 648 K in the exposure of 1000 ppm ethanol gas. Fig. 5.7 shows the sensing response curve of Fe doped CdO thin film in the doping concentration from 0.5 to 2 wt%. It is clearly seen that the Fe doped CdO thin film shows different gas sense response at the same ethanol gas concentration. From the figure the maximum gas sensitivity 56.12 % is observed for 1 wt% Fe doped CdO thin film, which is decreased to 52 % for 0.5 wt% of Fe doping and 43 %, 38% of sensitivity is observed for 1.5 and 2 wt% of Fe doping, respectively. The change in gas sensitivity is attributed to the variation in effective surface area and grain size. It is well-known that the sensitivity of the metal-oxide semiconductor sensors is mainly determined by the interactions between the target gas and the surface of the sensors. Hence, it is observable that for the greater surface area of the materials, the interaction between the adsorbed gases and the sensor surface are stronger and gas sensitivity is higher [142].

5.4 Conclusions

Pure and Fe doped CdO thin films were prepared using facile spray pyrolysis technique. The effect of Fe doping concentration on structural, optical, electrical and ethanol sensing properties of CdO thin films were investigated. XRD patterns reveal that all the films exhibit cubic crystal structure with no evidence of Fe$_2$O$_3$ or mixed phases and slight variation of lattice parameter due to the replacement of Cd by Fe ions. AFM images show that the roughness of the film decreases with increasing of Fe doping concentration. XPS measurements were confirmed the chemical binding states of the Fe doped CdO thin film. Optical transmittance and band gap values are decreased with increasing Fe doping concentrations. 1 wt% of Fe doped CdO thin film shows a very low electrical resistivity of $7.67 \times 10^4$ Ω cm, which is attributed to the increase of carrier concentration due to the substitution of Cd$^{2+}$ ions by Fe$^{2+}$ ions in CdO film. The maximum gas sensitivity of 56.12% is observed for 1 wt% of Fe doped CdO thin film.