Synthesis and characterization of cobalt-doped cadmium oxide thin films prepared by sol–gel spin coating method

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Abstract—In this work, cobalt-doped Cadmium oxide thin films are prepared by sol-gel spin coating technique on the glass substrate. The effects of annealing temperature and Co concentration on Structural, optical properties of the thin films are studied. XRD pattern indicates that a CdO single phase with a cubic polycrystalline structure is formed in all the samples. Prepared thin film samples were revealed by EDX analysis. Optical measurements show that the optical transmission of the layer is reduced and the optical-band gap decreases due to the increase in molar concentrations. The optical-band gap is decreasing while increasing of Co concentration and annealing temperature.

Keyword: Thin films, Cadmium oxide, Sol-gel, Spin coating, annealing

1. Introduction

In recent years, Oxide based materials such as ZnO, CdO, SnO₂, TiO₂, and In₂O₃ have attracted increasing interest [1]. Due to the optical, physics and electron properties including excellent transmission of visible light and electrical conductivity CdO thin films have gives more attracted amid the numerous metal oxides [2]. In solid-state devices, Cadmium Oxide (CdO) makes an important semiconductor material for developing of various technologies. In visible and NIR spectral regions CdO thin films are transparent [3]. At 540 nm it is transparent in the solar spectrum. In the field of optoelectronic devices like solar cells, transparent electrodes, and photodiodes CdO have wide applications among others. To fabricate CdO/CdTe heterostructure solar cells with 9.1% efficiencies, CdO transparent conducting oxide with optical-band gap of 2.3 eV and an electron affinity of 4.5eV were used in DC magnetron sputtering [4].

The properties like structural, morphological and optical were affected by changing annealing temperature in successive ionic layer adsorption and reaction (SILAR) method. The optical-band gap was changed due to change in annealing temperature of 300 °C and 400 °C [5]. In thermal annealing method hydroxide phase with the structural transformation can be achieved.

CdO thin films were prepared in different methods like sol-gel [6], pulsed laser deposition [7], spray pyrolysis [8], sputtering [9], chemical bath deposition (CBD) [10], e-beam evaporation technique [11], pulsed filtered cathodic arc deposition (PFCAD) [12], successive ionic layer adsorption and reaction (SILAR) method [13,14]. Sol-gel spin coating method add more advantage to process high smoothness of the films, simplicity, low sintering temperature, the possibility for coating over the large-area substrate, high smoothness of the films, reliability, controllability, reproducibility, etc [15–20]. Moreover, some parameters are optional for coating like spin, speed, ambient, solution morality, drying, and annealing process [21].
Various dopant elements have been students such as B [22], In [23], Sn [24], Cu [25,26], Al [27,28], F [29,30] and additives like organic (coumarin [31]) and inorganic (InO3/2 [32, 33]) to control the properties of thin films. The drying agent like metal cobalt is used in paint, varnish, and ink industry for the preparation of pigments like cobalt blue and cobalt green, in ground coats for porcelain enamels, in lithium-ion battery electrode, as a catalyst in petroleum and chemical industries, in electroplating industry [34, 35]. In TiO2 [36] and ZnO [37] thin films cobalt also used as a dopant.

In this study focusing on the effect of annealing temperature and the molar concentration of starting Cd2+ solution and influence of Co dopant ratio on the structural, optical properties of the sol-gel spin coated cobalt-doped CdO thin films.

2. Experimental

Pure and cobalt-doped cadmium oxide thin films prepared using sol–gel technique by spin coating method using speed controlled VTC - 200 (MTI CORP.) spin coater. The contamination on glass substrate was cleaned and boiled in H2O, NH3 and H2O2 (5:1:1) for 10 min at 100°C and then in H2O, H2O2 and HCl (5:1:1) for 10 min at 100°C. The solute was prepared from Cadmium acetate dehydrate Cd(CH3CO2)2 (2g) , solvent and stabilizer were prepared from 2 - methoxy ethanol (C3H8O2) and monoethanol amine (C2H7NO, MEA) respectively. High purity chemical materials (99%) were purchased from Sigma Aldrich Company. The dissolving of cobalt (II) chloride (CoCl2.6H2O) in 2 - methoxy ethanol to prepare cobalt and doping with the original solution in different volume proportions. The obtained mixtures were stirred at 60°C for 2 hours. The temperature of obtained homogeneous, colorless and transparent coating solution is reduced to room temperature (RT) and aging for a day. The prepared solution was dropped on the glass substrate and rotated at 1250 rpm for 50 seconds. After the coating, the samples were dried at 100°C for 20 minutes on a hot plate to remove the solvent and organic residuals. This coating and drying procedure was repeated for three times, the obtained solid films were annealed in oven at 200°C, 400°C and 600°C for 2 hours.

A. Measurements

XRD diffraction spectra of prepared thin films was observed by using Bruker D8 advance, X-ray diffractometer with Cu Kα (λ Cu Kα = 1.5418 Å) radiation, for 2θ values in the range of 20°–80°. Compositional analysis of the prepared thin film are carried out by KEVEX 7000-77 EDX spectrometer. The optical absorbance spectra of prepared thin films are recorded using double beam UV-VIS spectrophotometer (mega-2100, scinco co ltd) in the wavelength range of 300 to 700 nm at room temperature.

3. Results and discussions

A. Structural properties

XRD spectra of pure, 4.0 %, 8.0% and 12.0% Co - doped CdO films on the glass substrate by Sol-gel spin coating method are shown in figure 1a and for different annealing temperature are shown in figure 1 (b & c). The diffraction peaks are 2θ = 33.08°, 38.40°, 55.39°, 66.0° and the weak intense peak are 69.39° are characteristics of cubic phase of CdO and the peaks are matching with (111), (200), (220), (311) and (222) plans, respectively (JCPDS File No.: 75-0592). No peaks were found related to Co, CoO or Co3O4. Also, the shark peaks indicates the good crystalline nature and almost no impurity exists in the sample and complete transformation take place into CdO phase.
The results indicate that instead of new phase the Co ions replace the Cd$^{2+}$ ions in lattice without changing the crystal structure. The position of peaks for the as-deposited film and the annealed films are slightly shifted to higher 2θ due affect the lattice parameters and the volume of the unit cell of CdO films. The same results were reported for Mg, Cl (CBD method) and Ni – doped Cds quantum dots prepared by co-precipitation method [38, 39].

**B. Compositional Studies**

Figure 2 shows the representative EDX spectra of prepared thin film. The EDX spectra confirm the presence of Cd and O in the pure and Co doped film.
Fig. 2: EDX analysis of pure and Co-doped CdO film.

From EDX spectra the thin films are Cd rich and no peaks were found related to Co, CoO or Co$_2$O$_4$. Due to increasing concentration of Co, the interaction of ions with substrate can affect the film deposition process; Cd-rich nature of samples can also be dictated by difference in ionic bond on substrate surface.

C. Optical properties

Figure 3 shows the optical transmittance spectra for annealed pure and Co doped CdO thin films samples measured at 27°C in air atmosphere. From results of transmission spectra the average optical transmission values in the visible region for all the samples are low. The average optical transmittance in the wavelength between 550 nm to 1100 nm for pure and Co doped CdO thin films is about 81%. Due to heat treatment there is a slight change in the transmittance spectra of the films. But the results are similar to that of as-deposited sample. The absorption coefficient ($\alpha$) was analyzed using the following expression $\alpha = \frac{\ln(\frac{I}{I_0})}{t}$.
Fig. 3: Optical transmittance spectra of pure and Co doped CdO thin films for different annealing temperature.

From figure 4 it is evident that absorbance are very low and also decreases in the visible region for all films. But in ultraviolet region absorption are high and also increases for all films. Due to annealing process slight changes occur in the absorbance spectra of all samples. But the overall results are similar to that of as-deposited sample. The optical absorption in the UV-vis. Region is dominated by the optical-band gap ($E_g$) of a semiconductor that is related to the optical absorption coefficient ($\alpha$) and the incident photon energy ($h\gamma$) by the relation $(\alpha h\gamma) = C(h\gamma-E_g)^m$, Where C is an energy independent constant and m is an index which depends on the kind of optical transition that prevails [40]. From the results (Figure 5) CdO film is known to be a direct-allowed semiconductor [41, 42].
Fig. 4: Variation of absorbance (A.U) with wavelength $\lambda$ (nm) for pure and Co doped CdO thin films for different annealing temperature.
Fig. 5: Variation of $(\alpha h\nu)^2$ vs $h\nu$ for pure and Co doped CdO thin films for different annealing temperature.

Fig. 6: Variation of direct band gap with annealing temperature for Co doped CdO thin film
**Table 1: Band gap energy of the films as a function of Co concentration and annealing temperatures.**

| Cobalt Concentration | Optical-band gap (eV) | As deposited | T = 200°C | T = 400°C | T = 600°C |
|----------------------|-----------------------|--------------|-----------|-----------|-----------|
| Pure CdO             | 3.303                 | 3.275        | 3.195     | 3.151     |           |
| CdO & 4% Co          | 3.290                 | 3.262        | 3.125     | 3.115     |           |
| CdO & 8% Co          | 3.750                 | 3.225        | 3.118     | 3.036     |           |
| CdO & 12% Co         | 3.275                 | 3.200        | 3.106     | 3.022     |           |

The $E_g$ values are listed in Table 1 and it is decreases with increasing Co concentration and annealing temperature. It is seen that optical-band gap energy decreases [43,44] with increasing annealing temperature which may due to improvement in crystalinity and structural modification of CdO [45].

4. Conclusions

As a conclusion, the effect of Co concentration in a sol gel spin coating process of CdO films was investigated with different annealing temperatures. The processed samples were annealed at 200, 400 and 600°C. XRD pattern shows that polycrystalline single phase cubic structure is obtained in the samples and due to doping of Co with CdO leads changes in the peak intensity. Structural and optical properties were changed due to incorporating of Co into CdO. The average optical transmittance in the wavelength between 550 nm to 1100 nm for pure and Co doped CdO thin films is about 81%. The optical-band gap energy values changes with Co concentration and annealing temperature. Based on these results, the Cobalt-doped CdO thin film by sol-gel spin coating method is opt for various optoelectronic applications.

5. References

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