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Structural and optical characterizations of spin coated cobalt-doped cadmium oxide nanostructured thin films

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ABSTRACT

$Cd_{1-x}Co_xO$ thin films (with molar ratios $x=0.0$–8.0%) were grown onto glass substrates via the sol–gel spin coating technique. XRD results indicate that a CdO single phase with a cubic polycrystalline structure is formed. The crystallinity of CdO thin films is gradually deteriorated with increasing the Co ratio. AFM images of the films confirm the decrease of the grain size of the CdO films with increasing Co content. The direct optical band gap is red shifted from 2.580 eV to 2.378 eV with the increase of Co content. The refractive index, the dispersion parameters, and the optical conductivity of CdO thin films showed an enhancement with increasing cobalt dopant ratio. The correlation between the structural modifications and the resultant optical properties are reported.

1. Introduction

The strong interest in the nanostructured materials arises from the viability on designing and building structures that exhibit outstanding electrical, mechanical, chemical, optical and magnetic properties compared to the bulk materials. These materials have a large fraction of surface atoms, high surface energy, spatial confinement, and reduced imperfections [1]. Thin films of polycrystalline semiconductors now occupy a prominent place in basic research and solid state technology [2]. Cadmium oxide (CdO) is a promising II–VI compound and one of the transparent conducting oxides (TCOs). It can have high electrical conductivity ($10^3\ \Omega^{-1}\ cm^{-1}$) [3] combined with high optical transmittance in the visible region of the solar spectrum and high reflectance in the infrared region [4]. CdO powders and films have *n*-type semiconducting properties [3,5,6] and mobility as high as $\mu=146\ cm^2\ V^{-1}\ s^{-1}$ with carrier concentration $N=1.5\times10^{20}\ cm^{-3}$ [7–10]. Depending on the deviation from ideal CdO stoichiometry (e.g., due to cadmium interstitial $Cd_{(1+x)}O$ or oxygen vacancies $CdO_{(1-x)}$), its direct band gap varied from 2.2 to 2.6 eV and its indirect band gap varied from 1.36 to 1.98 eV [3,4,7,10–14]. These unique properties have prompted its applications in heat mirrors, paint pigments, solar cells, CdO/Cu_2O solar cells, photoelectrochemical (PEC) devices, phototransistors, photodiodes, liquid crystal displays, IR detectors, antireflection coatings, gas sensors, etc. [5,6,15–19].

Un-doped and doped CdO thin films have been prepared by various physical and chemical deposition techniques such as vapor phase epitaxy (MOVPE) [7,10], DC reactive magnetron sputtering [20], spray pyrolysis [15,21–23], e-beam evaporation [24], electrodeposition [25], pulsed filtered cathodic arc deposition (PFCAD) [26], chemical bath deposition (CBD) [27,28], successive ionic layer adsorption and reaction (SILAR) method [5,6], and sol–gel coating [9,14,18,29,30]. Among these techniques, the sol–gel method, which is a process concerning transition of a system from liquid 'sol' into solid 'gel', attracts

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much attention due to some unique advantage, including low cost, simple deposition equipment, easy adjusting composition and dopants, the possibility of having a homogeneous mixture of two cations in the liquid state, fabricating large area films, and no volatile compounds are used, which is of great importance for safe handling reasons [11,30–33].

On the other hand, various dopant elements have been used to control the surface morphology, crystalline structure, optical, electrical, mechanical as well as the gas sensing properties of CdO films such as B [9], In [26], Sn [27], Cu [18,29], Al [30,34], F [22,35]. In addition, other organic (coumarin [6]) and inorganic ($InO_{3/2}$ [11,24]) additives have also been used as dopants for CdO thin films. The transition metal cobalt (Co; [Ar] $3d^7 4s^2$) is widely used in paint, varnish, and ink industry as a drying agent, in 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 [36,37]. Also, Co extensively used as a dopant for TiO_2 [31] and ZnO [38] thin films. However, the literature survey reveals that there are no reports on the effect of Co incorporation on the physical properties of CdO films or nanoparticles. This work was devoted to study the influence of Co dopant ratio on the structural, morphological, and the optical properties and optical constants of the sol–gel spin coated CdO thin films.

2. Experimental

2.1. Materials preparation

$Cd_{1-x}Co_xO$ films with Co content in the range $x=0.0$–8.0% were grown onto glass substrates via the sol–gel spin coating technique using TC100 spin coater. The used precursors were cadmium acetate dihydrate [$Cd(CH_3COO)_2\cdot 2H_2O$, $M_W=266.52$ g/mole, Merck, purity > 99%], 2-methoxethanol ($C_3H_8O_2$) as a solvent and monoethanol amine (C_2H_7NO, MEA) as a stabilizer. The dopant source of the Co was cobalt (II) chloride [$CoCl_2\cdot 6H_2O$, $M_W=237.93$ g/mole, WINLAB Lab. Chem., UK, purity > 99%]. All of these chemicals were used without any further purification. The molar ratio of MEA to cadmium acetate dihydrate was maintained at 1:1. Cobalt (II) chloride and cadmium acetate dihydrate of 0.5 M solutions were mixed together in different volume proportions. The obtained mixtures were stirred at 60 °C for 2 h to yield a homogeneous and clear solution, which was then served as the coating source after cooling down to room temperature (RT) and aging for 24 h.

The glass substrates were firstly cleaned in methanol and acetone baths for 10 min using an ultrasonic cleaner and then, the substrates were rinsed with deionized water and dried before using. The coating solution was dropped onto the glass substrate, which was rotated at 1100 rpm for 60 s. After the spin coating, the film was dried at 150 °C for 10 min on a hot plate to evaporate the solvent and to remove organic residuals. This coating/drying procedure was repeated for six times and after this process, the obtained solid films were annealed in an air furnace at 450 °C for 1 h.

2.2. Measurements

The crystal structure and lattice parameters of the films were analyzed by X-ray diffraction (XRD, Philips X'Pert Pro MRD) using Cu K_α radiation ($\lambda=1.5418$ Å), with a step 0.02°. The surface morphology, roughness, and particle size of Co-doped CdO thin films were investigated using an atomic force microscope (AFM, PARK SYSTEM, XE-100E). Also, the film thickness was evaluated, using the AFM, as a height of the step which was obtained after the scratching of the films using a sharp scissor. The absorbance spectra (A) and the transmittance spectra (T) of the films were recorded at 200–1000 nm wavelength using SHIMADZU UV-3600 UV–vis–NIR spectrophotometer at RT.

3. Results and discussions

3.1. Structural and morphological properties of Co-doped CdO thin films

XRD patterns of the sol–gel spin coated Co-doped CdO thin films are shown in Fig. 1. The films are of polycrystalline nature. All of the diffraction peaks can be indexed to the cubic phase of CdO with a lattice parameter $a=4.69483$ Å and $Fm3m$ space group. Similar results were also reported [39,40]. The peaks at 2θ values of 33.08°, 38.40°, 55.39°, 66.0°, and the weak intense peak at 69.39° are matching with the (111), (200), (220), (311), and (222) plans, respectively (Joint Committee for Powder Diffraction Studies (JCPDS) File no. 75-0592). This indicates the formation of CdO with excellent crystallinity [12]. No diffraction peaks arising from Co, CoO or Co_3O_4 are observed in the XRD pattern even for the highest [Co]/[Cd] content used (8.0%), indicating that almost no impurity exists in the sample and the precursor had completely transformed into CdO phase. Also, this indicates that Co ions substitute the Cd^{2+} in the lattice without changing

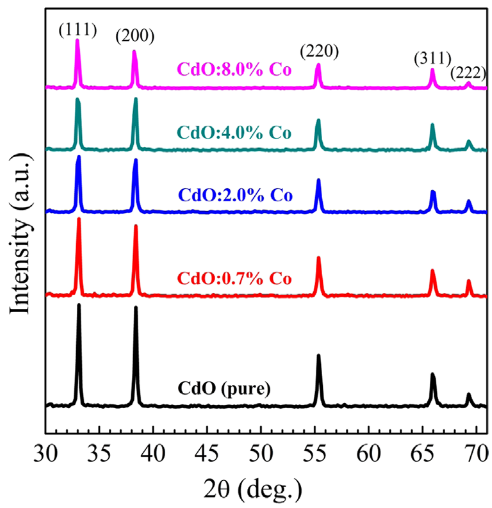

Fig. 1. XRD spectra of spin coated $Cd_{1-x}Co_xO$ ($x=0.00$:0.08) thin films.