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Electrical and optical properties of iron-doped CdO

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ABSTRACT

Thin films of Fe-doped CdO with 1.3, 2.0, 2.3, 3.0, and 5.7 wt.% were prepared by a vacuum evaporation method on glass and Si wafer substrates. The prepared films were characterised by X-ray fluorescence and diffraction. Results show that doping of CdO with Fe enhances the film's [111] preferred orientation and causes slight shifts in the (111) Bragg angle towards higher values. The samples were investigated with a UV–VIS–NIR absorption spectroscopy and dc-electrical measurements. It was observed that there is a complicated dependence of bandgap on the Fe wt.% content in the film. In addition, light doping with Fe improves the dc-conduction parameters of CdO, so that with 1.3 wt.% Fe doping, the mobility increases by about 6 times, conductivity by 24 times, and carrier concentration by about 4 times, relative to undoped CdO film. The observations were analysed by using the available models (with a slight modification) for the coexistence of bandgap widening and bandgap narrowing.

1. Introduction

Metal-doped degenerate semiconductor cadmium oxide (CdO) has been used extensively in transparent conducting oxide, solar cells, smart windows, and in many other optoelectronic applications [1–5]. These applications are based on its suitable optical and electrical properties [1,6,7]. It was observed that with doping by different types of metallic ions, the physical properties of CdO could be controlled for optoelectronic applications. So that doping with ions like In, Sn, Al, Sc, and Y, improves its n-type conductivity and increases optical bandgap. Doping of CdO with transition metals or magnetic ions introduces magnetic properties resulting dilute magnetic semiconductors. In the present study, we investigate the influence of Fe doping on the electrical and optical properties of CdO films.

2. Experimental procedure

The starting materials were complex iron acetylacetonate [8] and pure CdO (from Fluka A.G., Germany). The alternating deposition (layer-by-layer, etc.) method was used to deposit the starting materials on ultrasonically clean glass substrates and chemically cleaned (by using HF) silicon-wafers in a vacuum chamber of residual oxygen atmosphere of a pressure about 1.3×10^{-2} Pa. The CdO was evaporated by using an alumina basket (Midwest tungsten service, USA) and the acetylacetonate was sublimated by using a heated Pyrex crucible. The as-grown films were annealed in a pure oxygen atmosphere at 400 °C for 2 h. This annealing temperature is sufficient to oxidise the deposit and decompose the complex [9,10]. All samples were prepared in almost the same conditions including the reference pure CdO film. The evaporated mass and thickness were controlled during preparation by a Philips FTM 5 thickness monitor and measured after annealing with an MP100-M spectrometer (Mission Peak Optics Inc., USA) to be in the range of 0.2–0.3 μm. The structure of the prepared films was studied by using the X-ray diffraction (XRD) method with a Philips PW1710θ –2θ system of Cu K_α radiation (0.15406 nm), in a 2θ range of 10°–70° and a step size of 0.02°. Our setup used for the energy-dispersion X-ray fluorescence method consists of an X-ray beam obtained from a Cu-anode Philips tube (Philips PW-1710) operated at 15 kV and 5 mA and an Amptek XR-100CR detector. The measured relative contents of Fe to Cd in the studied samples are about 1.3, 2.0, 2.3, 3.0, and 5.7 wt.%. The spectral optical transmittance, $T(\lambda)$, and reflectance, $R(\lambda)$, were measured at normal incidence in the UV–VIS–NIR spectral region (300–3000 nm) with a Shimadzu UV-3600 double beam spectrophotometer. The electrical measurements were carried out with a standard Van-der-Pauw method with aluminum dot contacts in a magnetic field of about

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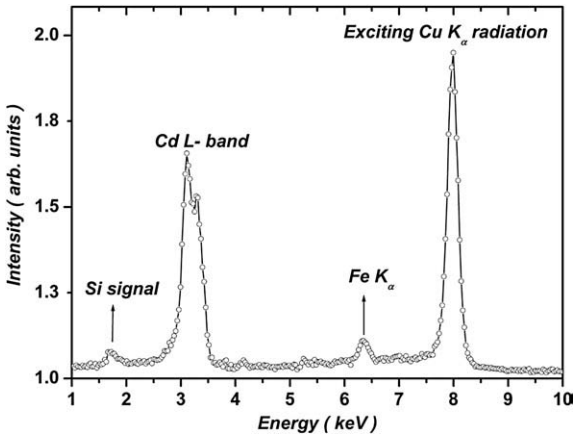

Fig. 1. X-ray fluorescence of Fe-doped CdO film grown on Si substrate. The exciting radiation was Cu K_α with a wavelength of 0.1543 nm.

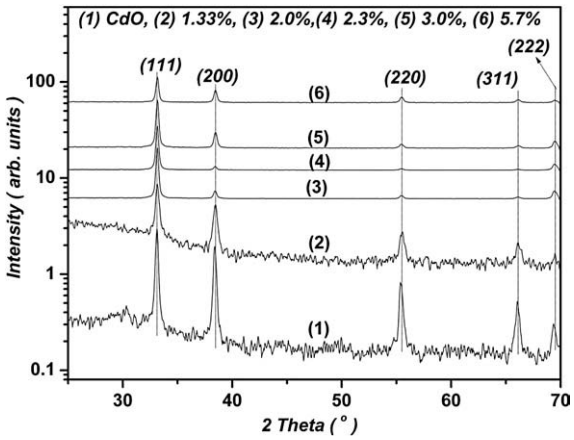

Fig. 2. X-ray diffraction patterns from pure and Fe-doped CdO films prepared at different Fe dopant concentration levels. The used radiation was the Cu K_α-line.

1 T and using a Keithley 195A digital multimeter and a Keithley 225 current source.

3. Characterisation by X-rays

Fig. 1 shows the energy-dispersion X-ray fluorescence spectrum for one of the prepared thin Fe-doped CdO film on Si substrate. The spectrum shows Cd L-band (3.133–3.528 keV) and Fe K_α (6.403 keV) line in addition to some signals from the source and Si substrate. The relative fraction ratio of Fe to Cd in film samples was determined by measuring the ratio of integral intensity of Fe K_α-signal to that of Cd L-signal and using the known method of micro radiographic analysis [11]. The reference samples were pure CdO thin film and sublimated Fe-acetylacetonate thin film. The results are given in Table 1.

Fig. 2 shows the XRD patterns of the prepared pure and Fe-doped CdO films. The patterns reveal that all films are polycrystalline of cubic (Fm3m) CdO structure. The lattice constant of pure CdO is 0.468 nm that is very close to JCPDS data [12]. The usually energetically favourable (111) preferred orientation growth of CdO films [13–15] was investigated here through texture coefficient (TC) that is defined in Ref. [16] as: $TC = [nI_m(hkl)/I_0(hkl)]/[\sum I_m(hkl)/I_0(hkl)]$, where I_m (hkl) is the measured relative intensity of reflection from a given (hkl) plane, I_0(hkl) is the relative intensity of the reflection from the same plane as indicated in a standard randomly oriented polycrystalline CdO powder quoted from Ref. [12], and n is the total number of reflections used, which are in the present investigation four: (111), (200), (220), and (311) reflections. Therefore, the highest value of TC is 4 for a perfectly oriented film and is 1 for a randomly oriented one. The calculated values of TC in the present work are given in Table 1, which show that, in general, doping with Fe increases the CdO film's [111] preferred orientation and with 2.3–3.0 wt.% doping level, the films become almost totally oriented. The mean X-ray grain size (D) was estimated by using Scherrer's relation [17] and the results are given in Table 1. In general, the average CdO grain size, and hence the dislocation surface density was not greatly influenced by Fe doping, and it is in the range of 35–42 nm. It was also observed that there is a slight shift $\Delta(2\theta_{111})$ in the Bragg angle of the intense CdO (111) peak towards higher values, from 33.13° for pure CdO to 33.175 for 1.3 wt.% Fe-doped (Table 1) associated with a slight reduction in the lattice parameter. This slight peak shift resulted from the created structural strain (of order -10^{-3}) accompanied with Fe doping, which has a slightly lower ionic radius (0.0645 nm [18]) than that of Cd ion (0.097 nm).

4. dc-electrical properties

The room temperature electrical parameters: resistivity (ρ), mobility (μ_{el}), and carrier concentration (N_{el}) were measured by a standard Van-der-Pauw method and the results are presented in Table 2 and Fig. 3. The main experimental error in Van-der-Pauw method is being due to the aluminum-contact spots size relative to sample's size, which is estimated to be about 5%. The measured electrical parameters of pure CdO film agree with those published earlier [1]. The present results show that doping of CdO with Fe ions changes its electrical parameters. The concentration of conduction electrons for all Fe-doped films is more than that of pure CdO. The mean-free-path (mfp) of conduction electrons can be estimated by [19], $l = (h/2e)(3N_{el}/\pi)^{1/3}\mu_{el}$, which gives 15–40 nm. This mfp is comparable to the X-ray grain size D that means the grain boundary scattering mechanism has its contribution in reducing the mobility of free carriers in the films together with other scattering mechanisms like impurity and lattice scattering. In summary, the present work shows that light doping with Fe improves the dc-conduction parameters of CdO films so that with 1.3 wt.% Fe doping level, the mobility increases by about 6 times, conductivity by 24 times, and carrier concentration by about 4 times, relative to the parameters of undoped CdO film.

Table 1
The Bragg angle ($2\theta^\circ_{111}$), the lattice parameter, the average X-ray grain size perpendicular to [111] direction (D_{111}), and the texture coefficient (TC) for the prepared pure and Fe-doped CdO films on glass substrates.

Sample	$2\theta^\circ_{111}$	a (nm)	D_{111} (nm)	TC
CdO	33.130	0.4677	32.6	1.54
1.3 wt.%	33.175	0.4671	34.7	2.79
2.0 wt.%	33.170	0.4672	34.7	1.91
2.3 wt.%	33.165	0.4673	41.7	3.55
3.0 wt.%	33.165	0.4673	41.7	3.26
5.7 wt.%	33.145	0.4675	41.7	1.43

Table 2
Summary of the measured electrical parameters and bandgap for pure and Fe-doped CdO films on glass substrates.

Sample	ρ ($\times 10^{-3}\Omega$ cm)	μ_{el} (cm^2/V s)	N_{el} (10^{19} cm^{-3})	E_g (eV)
CdO	20.1	7.1	4.42	2.25
1.3 wt.%	0.8	43.3	17.5	2.34
2.0 wt.%	1.2	39.6	13.0	2.23
2.3 wt.%	1.5	35.1	12.0	2.27
3.0 wt.%	2.2	23.8	12.2	2.18
5.7 wt.%	3.8	14.5	11.0	2.51