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Correlated transport and optical phenomena in Ga-doped CdO films

A.A. Dakhel *

Department of Physics, College of Science, University of Bahrain, P.O. Box 32038, Bahrain

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Abstract

Series of samples of lightly Ga-doped CdO thin films (3%, 6%, and 9%) have been prepared by evaporation method on glass substrate. The prepared films were characterised by X-ray diffraction (XRD), UV–VIS–NIR absorption spectroscopy, and dc-electrical measurements. The investigation shows that Ga doping widens the energygap of CdO. The optical properties were easily explained by using Tauc et al. band-to-band transitions and classical Drude theory. The electrical behaviour of the samples shows that they are degenerate semiconductors. The 6% Ga-doped CdO sample shows increase its mobility by 3.2 times, increase its conductivity by 1.5 times, increase its intrinsic bandgap, and a slight increase its transmittance relative to undoped CdO film. Explanation was given concerning these variations. From transparent conducting oxide (TCO) point of view, Ga is not sufficiently effective for CdO doping comparing to other dopants like In, Sn, Sc, and Y.

Keywords: Optical properties; Gallium–cadmium oxide; Ga-doped CdO; Mobility; Oxides; Degenerate semiconductors

1. Introduction

CdO has n-type degenerate semiconducting properties with a bandgap of 2.2–2.6 eV and a resistivity of 10^{-2}–10^{-4} Ω cm (Chopra and Ranjan Das, 1993; Choi et al., 1996; Carballeda-Galicia et al., 2000; Zhao et al., 2002). It is used as a transparent conducting oxide (TCO) (Zhao et al., 2002; Su et al., 1984; Gomez-Daza et al., 2001) for solar cells and other optoelectronic applications (Zhao et al., 2002; Su et al., 1984; Santos-Cruz et al., 2006; Yan et al., 2001). Theoretically, it was established that CdO has a direct bandgap of 2.18 eV (Kondo et al., 1971) or 2.38 eV (Finnkenrath et al., 1966) and two indirect bandgaps of 0.8 eV and 1.2 eV (Maschke and Rossler, 1968) or 0.95 eV and 1.11 eV (Tewari, 1973), or 1.12 eV and 1.18 eV (Breeze and Perkins, 1973). The n-type conduction of undoped CdO was attributed to its native oxygen vacancies and cadmium interstitials. Therefore, the conductivity of CdO films can be controlled by those native defects (Zhao et al., 2002) or by doping with metallic ions like: In (Freeman et al., 2000), Sn (Zhao et al., 2002; Yan et al., 2001), Al (Maity and Chattopadhyay, 2006), Sc (Shu et al., 2004), and Y (Yang et al., 2005). Generally, it was observed that doping with ions of radius less (to a limited extend) than that of Cd^{2+} slightly shrinks the CdO lattice parameters, increases the apparent energygap, increases the carrier mobility and concentration, and hence increases the conductivity. These variations were explained by the application of Moss–Burstein (BM) model (Burstein, 1954; Moss, 1954). Increasing of carrier concentration leads to enhance the optical absorption, which is not welcomed in TCO applications. For solar cell and other optoelectronic applications, it is welcomed to dope CdO with some ions in order to increase both the conductivity as well as the transmittance.

Gallium Ga^{3+} ion has a standard ionic radius (0.062 nm) smaller than that of Cd^{2+} (0.097 nm). Thus the doping of CdO by Ga ions might increase its conductivity especially

* Fax: +973 17449148.
E-mail address: adakhil@sci.uob.bh

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that Ga ions doping was tested to increase the conductivity of ZnO oxide in many previous works (Robbins et al., 2005; Ma et al., 2007). Furthermore, to our knowledge, no report on Gallium-doped CdO thin films exists. Therefore, It is interesting from physical and technical point of view to investigate the effect of a light Ga dopant in CdO (CdO:Ga) films on their structural, optical and electrical properties.

2. Experimental

High purity CdO and Ga_2O_3powders (Fluka A.G/Germany) were grinded separately. An appropriate amount of fine powder of Ga_2O_3 was completely mixed with CdO powder and grinded together before cold pressing (at about 750 MPa) to make a tablet. Then, the tablets were heated in an oven at 500 °C for 2 h keeping them in the closed oven during heating and cooling cycle. Finally, the prepared tablets were evaporated from Mo boat in a vacuum system of about 10^{-3} Pa onto ultrasonically cleaned glass slides maintained at room temperature. The prepared films with atomic ratio concentration Ga to Cd of 0%, 3%, 6%, and 9% were annealed in a closed furnace at 400 °C for 1 h. Keeping them during heating and cooling cycle. Film thickness was monitored during deposition with thickness monitor and measured after annealing by a Gaertner L117 ellipsometer to be around 300 nm. The structure of the prepared films were studied by X-ray diffraction (XRD) method using a Philips PW 1710 θ–2θ system with Cu K_α radiation (0.15406 nm) and a step size of 0.01°. The spectral optical transmittance $T(\lambda)$ and reflectance $R(\lambda)$ were measured at normal incidence in 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 using silver paste dot contacts in a magnetic field of about 1 T and using a Keithley 195A digital multimeter and a Keithley 225 current source.

3. Results and discussion

3.1. Characterisation by X-rays

Fig. 1 shows the X-ray diffraction (XRD) patterns of the prepared undoped CdO and CdO:Ga films. All the patterns show polycrystalline of cubic CdO structure (NaCl structure of a space group *Fm3m*). The lattice constant calculated for a undoped CdO sample was 0.469 nm, which is almost identical with those values given in Subramanyam et al. (1998), Reddy et al. (1998). No other crystalline structure was detected in the patterns focusing on a cubic CdO_2 structure (NaCl structure of a space group Pa3 with a lattice constant of 0.5313 nm (Hoffman et al., 1959), which naturally transforms into CdO when annealed at 400 °C (Han et al., 2005; de Leon-Gutierrez et al., 2006), and $Cd(OH)_2$, which decomposes at 280 °C (Lide, 2003–2004).

The intense peak (1 1 1) of CdO:Ga samples is slightly shifted by about +0.03° due to a strain $\varepsilon_s = -\Delta\theta_{(hkl)}\cot\theta_{(hkl)}$ of about -8.83×10^{-4}. This strain is caused by a compressive stress estimated to be 0.42 GPa (the estimation was done with a help of data on CdO given in Liu et al. (2004). This stress is far to be capable creating a crystal-structural transformation; it can only produce a very slight decrease in the lattice constant by about -4.2×10^{-4} nm. The tiny change in lattice parameter is attributed to the smaller ionic radius of adsorbed Ga^{3+} ions into the crystalline structure of CdO. This also refers to the absence of the formation of one dilute Cd–Ga–O solid solution since as Ga^{3+} ionic radius is about 64% of that of Cd^{2+}ion, then

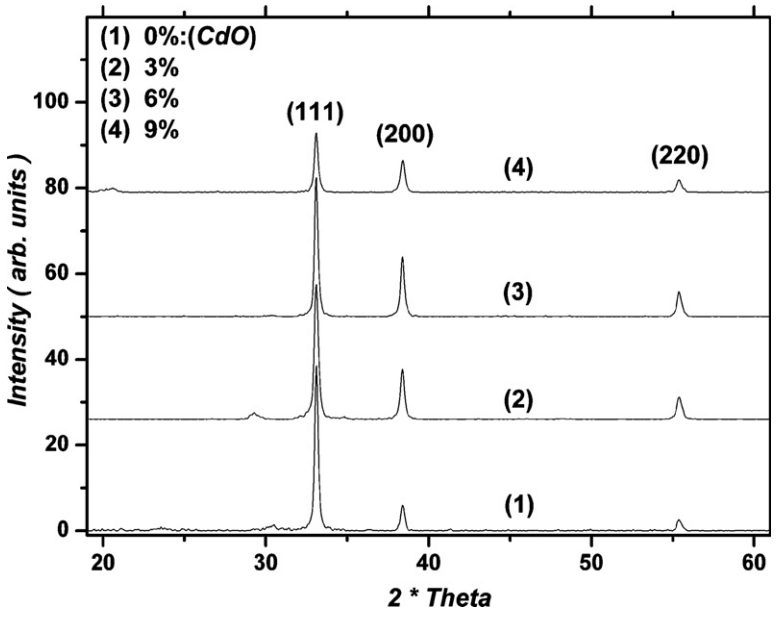

Fig. 1. X-ray diffraction patterns from undoped CdO and CdO:Ga films prepared at different Ga dopant concentration levels. The exciting radiation was Cu K_α-line.