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Influence of hydrogenation on the electrical and optical properties of CdO:Tl thin films

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ABSTRACT

Electrical and optical properties of Tl-doped CdO films (CdO:Tl) post-annealed in hydrogen atmosphere for different durations (15 min, 30 min, 45 min, and 60 min) were studied. The prepared films were characterised by the X-ray diffraction method and UV–VIS–NIR absorption–reflection spectroscopy. Experimental data indicate that annealing in H_2-atmosphere removes gradually with time the internal structural micro-stress that created as a consequence of Tl doping into CdO structure. The band gap of the hydrogenated Tl-doped CdO samples changes with H_2-annealing time following the changing in the free-electron concentration. These results were found to be in agreement with the available bandgap widening and narrowing models. The optical properties were easily explained within the framework of Hamberg band-to-band transitions and classical Drude theory. It was found that the greatest enhancement of the electrical conduction parameters occurs by annealing of CdO:Tl films in H_2-atmosphere for 30–45 min when the conductivity increased by about 37% and the free-electron concentration increased by about 6%. The results of the present investigation are important for the transparent conducting oxide preparation technique.

1. Introduction

Due to the n-type degenerate-semiconducting properties and transparency in the visible and NIR spectral regions, CdO films is extensively used in optoelectronic applications such as transparent conducting oxides (TCO), solar cells, smart windows, optical communications, flat panel displays, photo-transistors, as well as other types of applications like IR heat mirror, gas sensors, low-emissive windows, and thin-film resistors, etc [1–5]. CdO films prepared by different methods have been widely studied and found that their electrical resistivity in the range (10^{-2}–10^{-4} Ω cm) [1,6] and optical direct energy band in the range (2.2–2.7 eV) [7–9]. The conduction of pure CdO is attributed to native defects of oxygen vacancies and cadmium interstitials. Therefore, it is possible to control the conductivity of CdO films by controlling those native defects. It was found that the doping of CdO with some metallic ions like In, Sn, Al, Sc, and Y [1,5,10–13] increases its electrical conductivity (σ) and concentration of the free electrons (N_{el}), which blue-shifts the optical energy band according to Moss–Burstein effect [14,15]. Thallium ion Tl^{3+} has a standard ionic radius of 0.095 nm, which is slightly less than that of Cd^{2+}, 0.097 nm [16] and an electronegativity of 1.8 Pauling slightly lower than that of Cd (1.7 Pauling). This information permits predicting that Tl^{3+} ions can substitute Cd^{2+} ions in its crystalline structure leading to an increase in the concentration of conduction electrons and improve the electrical conductivity. Moreover, the electrical-property parameters (σ and N_{el}) can be more improved (from TCO point of view) by reducing the effect of depletion regions or potential barriers formed on grain boundaries that can be done by employing various treatments with hydrogen including low-temperature post-annealing [17,18]. Furthermore, during post-annealing in H_2-atmosphere, hydrogen in form of ions enter into the structure of the annealed semiconductor acting either as a donor or an acceptor [19]. It was observed experimentally that the adsorbed hydrogen has a tendency to contradict the prevailing conductivity for most semiconductors and wide bandgap materials [20,21]. But, it was established that hydrogen adsorbed into InN and ZnO oxides, although of their n-type conduction, behaves as a donor (H^+), which increases the concentration of free electrons in those oxides [19,22–24].

The present study focuses on the variation of the electrical and optical properties of Tl-doped CdO (CdO:Tl) films because of low-temperature post-annealing process in hydrogen atmosphere for different durations.

2. Experimental details

High purity CdO and Tl_2O_3 powders (from Fluka A.G/Germany) were grinded separately. An appropriate amount of a fine powder of Tl_2O_3 was completely mixed with CdO powder so that the molar ratio Tl to Cd was 3%. The mixture was grinded before cold pressing (at

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about 750 MPa) to make a tablet. Then, the tablet was heated in a closed oven at 500 °C for 2 h. Finally, the prepared tablet was evaporated from alumina coated tungsten basket filament (Midwest tungsten service/USA) in a vacuum system of about 10^{-3} Pa onto cleaned (HF cleaning) Si wafers and ultrasonically cleaned Corning 2947 glass slides maintained at about 150 °C during film deposition. The prepared films were annealed at 400 °C for 1 h in a closed oven. All samples were prepared in the same conditions including the reference pure CdO film. Film thicknesses were monitored during deposition with a thickness monitor and measured after annealing by a Gaertner L117 ellipsometer to be in the range 0.27–0.30 μm. One CdO film and one CdO:Tl film were investigated as reference samples while other CdO:Tl films were post-annealed at 300 °C in pure hydrogen atmosphere for 15 min, 30 min, 45 min, and 60 min. The structure of the films were investigated by the 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 XRD patterns of the reference pure and Tl-doped CdO, and the post-annealed CdO:Tl films in H_2-atmosphere for different durations 15 min, 30 min, 45 min, and 60 min. The patterns reveal that all films are polycrystalline and exhibit only the cubic CdO structure (NaCl structure of space group Fm3m). The lattice constant calculated for a pure CdO film was 0.469 nm, which is almost identical with the standard value [25]. The variation of the structural parameters of CdO due to Tl doping and hydrogenation are given in Table 1. The usually favourable [111] orientation growth in CdO films prepared by different techniques [1,26,27] is preserved for all the investigated films. The 45 min hydrogenated CdO:Tl film is almost totally textured in [111] direction. But, with the 60-min hydrogenated film, the structure begins to deteriorate. The mean X-ray grain size perpendicular to [111] direction (gs_{111}) was estimated by using Scherrer's relation [28] and the results are given in Table 1. The 15-min hydrogenation strongly increased the gs of the CdO:Tl film, then the gs was reduced with increasing of hydrogenation time and becoming the lowest (34.7 nm) in the 60-min hydrogenated film. Thus, a noticeable microstructural changes in the crystallinity of the

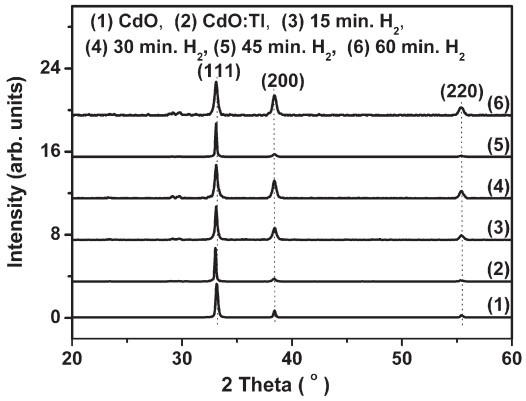

Fig. 1. X-ray diffraction patterns from pure and Tl-doped CdO film, and hydrogenated (H_2) CdO:Tl films for 15 min, 30 min, 45 min, and 60 min. The exciting radiation was Cu K_α-line.

Table 1
The Bragg angle ($2\theta_{111}$), the average X-ray grain size perpendicular to [111] direction (gs_{111}), the internal strain (ε_s), and the bulk stress (σ_{st} for the pure and Tl-doped CdO, and hydrogenated CdO:Tl films for 15 min, 30 min, 45 min, and 60 min

Sample	$2\theta_{111}$	gs_{111} (nm)	ε_s ($\times 10^{-3}$)	σ_{st} (GPa)
CdO	33.15	139.0	–	–
CdO:Tl	33.05	166.8	3.89	1.84
15 min	33.06	278.1	2.55	1.21
30 min	33.05	92.4	2.76	1.31
45 min	33.07	92.7	2.09	0.99
60 min	33.08	34.7	1.88	0.89

films were observed due to the hydrogenation. The exact angular positions of (111) reflection from all samples were observed to be slightly shifted (relative to pure CdO) toward lower Bragg angles, as given in Table 1. This means that the ionic radius of Tl^{3+}, which is slightly lower than that of Cd^{2+}, is not the sole factor that affects the lattice parameter of Tl-doped CdO but also the distribution of thallium ions in the crystalline structure of CdO and on the grain boundaries have also their contribution. In the result, as observed experimentally, the lattice constant of Tl-doped CdO shows a slight increase. It was also observed that there is a slight shift $\Delta(2\theta_{111})$ in the position of the intense (111) reflection towards higher Bragg angle from 33.15° for pure CdO to 33.05° for Tl-doped CdO sample. This slight peak shift is resulted from the created structural strain ($\varepsilon_s = -\Delta\theta_{(111)} \cot \theta_{(111)}$), which is of order 10^{-3} relative to the pure CdO. This strain that increases the cubic lattice parameter should be caused by a tensile stress (σ_{st}) that can be estimated in Table 1 by the relation: $\sigma_{st} \approx (3\varepsilon_s)B$, where B is the average bulk modulus of CdO, which is about 158 GPa [29]. The tensile stress σ_{st} created with Tl doping was gradually removed from the film by H_2-doping, which means that the adsorbed hydrogen ions stabilize the microstructure including the grain boundaries. However, this stress is far to be capable creating a crystal-structural transformation, it can only produce a very slight increase in the lattice constant of order 0.2–0.4% relative to the pure CdO.

3.2. Electrical properties

The result of the measurements of the room temperature direct-current (dc) electrical parameters (electrical resistivity (ρ), mobility (μ_{el}), and carrier concentration (N_{el})) for the reference pure and Tl-doped CdO, and the hydrogenated CdO:Tl samples are given in Table 2 and shown in Fig. 2. The main source of experimental error is being due to the Van-der-Pauw technique itself, i.e. due to the sample size and the contact spot size, which estimated to be about 5%. The measured electrical parameters of pure reference CdO film in the present work are in agreement with those data published for CdO films prepared by different techniques [1,26,27,30–32]. However, the measured resistivity of CdO, in the present work, is larger than those values mentioned in some other references ~10^{-3}–10^{-4} Ω cm due to the different method and procedure of preparation. For example, the density and the structure of the grain boundaries in CdO film have a significant effect on its electrical conduction since the grain boundaries can be considered as carrier-trapping centres and potential barriers, which reduce the effective

Table 2
Summary of the results of the electrical measurements on the resistivity, mobility, carrier concentration, and ratio $(N/\mu)_{el}$ for the pure and Tl-doped CdO, and hydrogenated CdO:Tl films for 15 min, 30 min, 45 min, and 60 min

Sample	ρ ($\times 10^{-3}$ Ω. cm)	μ_{el} (cm^2/V s)	N_{el} (10^{20} cm^{-3})	$(N/\mu)_{el}$ ($\times 10^{29}$ V s/m^5)
CdO	20.1	7.03	0.443	0.630
CdO:Tl	3.67	7.77	2.19	2.82
15 min	2.72	5.99	3.83	6.39
30 min	2.69	5.85	3.96	6.76
45 min	2.68	5.72	4.06	7.10
60 min	2.83	5.67	3.87	6.83