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Influence of deposition temperature on the properties of sputtered films grown from a $Cu_2O-CdO-TeO_2$ composite target: Electronic properties of $CdTe_2O_5$

A. Beristain Bautista[a], Emilia Olivos[b], R. Arroyave[b], F. Rodríguez Melgarejo[a], S. Jiménez Sandoval[a,*]

[a] Centro de Investigación y de Estudios Avanzados del I. P. N., Libramiento Norponiente No. 2000, Fracc. Real de Juriquilla, C. P. 76230, Querétaro, Qro, Mexico

[b] Texas A&M University, Department of Materials Science & Engineering, College Station, Tx, 77840, USA

ABSTRACT

Thin films were grown by sputtering targets made by compressing a mixture of the binary oxides Cu_2O, CdO and TeO_2. Their properties were studied as a function of the substrate temperature, which was varied from room temperature up to 450 °C. All the analyses were carried out on as-grown films. The elemental composition was analyzed by energy dispersive spectroscopy. A structural analysis was carried from grazing-angle X-ray diffraction patterns, which showed the formation of Cu_2O (at 350 °C and above) and $CdTe_2O_5$ (at 400 °C and above) clusters immersed in an amorphous background. Raman scattering (room temperature) and photoluminescence (room temperature and 80 K) spectra were dominated by the signals originating from the Cu_2O clusters. The optical transmittance spectra presented characteristics in agreement with the phases present in the films, as determined by X-ray diffraction. Due to the lack of information on $CdTe_2O_5$ in the literature, density functional theory calculations were carried out to analyze the optical properties of the films containing this compound in terms of the calculated electronic band structure. It was determined that $CdTe_2O_5$ is an indirect gap material. The theoretical band gap was 3.06 eV, which compares well with the experimental one ~3.16 eV.

1. Introduction

Prevailing technological developments have produced the need for novel materials that could meet the increasingly demanding functionality in new technologies, and for the development of fast and robust sensors, electronic and opto-electronic devices. Along this line, binary and a large number of ternary compounds have been extensively studied to date. Quaternary compounds and composite systems are materials that have not been fully exploited due to their complexity and to the lack of control over deposition methods. These materials, however, possess an enormous potential that has led to a wide variety of research topics, aimed not only to take advantage of the unique properties that these materials can present, but also to get a better understanding of their physical properties. Among these efforts, it may be mentioned the studies on films of solid solutions and composites based on cadmium telluride with copper and oxygen. The growth of such films has been carried out following two approaches: *i*) by reactive co-sputtering using two targets, one of Cu and the other of CdTe, with a flow of O_2 and Ar in the chamber [1–3]; and *ii*) by means of sputtering a single target prepared by pressing mixtures of CdTe and CuO powders [4,5]. As a result, in both cases it was possible to improve and control the electronic properties of the films.

In recent years, the synthesis of transparent conductive oxides has been directed, among other routes, towards the investigation of quaternary materials by means of the combination of binary oxides. Examples of this approach are the systems $Ga_2O_3 - ZnO - In_2O_3$

* Corresponding author.
E-mail address: sergio.jimenez@cinvestav.mx (S. Jiménez Sandoval).

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[6], $SnO_2 - ZnO - In_2O_3$ [7], $SnO_2 - CdO - In_2O_3$ [8] and $TeO_2 - CdO - In_2O_3$ [9]. Following this approach and our previous work, we have investigated the Cd—Te—Cu—O system by sputtering targets made of a mixture of the binary oxides Cu_2O, CdO and TeO_2, in the 1:1:1 M ratio. We report here the results of the characterization carried out on the chemical composition, structure, microstructure and photoluminescence of the as-grown films, as a function of substrate temperature during growth. This experimental characterization is followed by density functional theory calculations of the structural and electronic properties of $CdTe_2O_5$, one of the resulting materials when high substrate temperatures were employed.

2. Experimental details

Films were grown by rf sputtering on glass and silicon substrates using a single cold-pressed composite target prepared from a mixture of the binary compounds: copper(I) oxide, cadmium(II) oxide and tellurium dioxide. For that end, a target was made in our laboratory by cold-pressing Cu_2O (99.99%), CdO (99.5%) and TeO_2 (99.995%) powders from Sigma-Aldrich in a 1:1:1 mol ratio. For different runs, the substrate temperature was fixed to values starting from room temperature (*i.e.* unheated on purpose: at the end of the deposit the temperature was ~70 °C), 100 °C, and up to 450 °C in 50°C-steps. The substrates were cleansed prior to deposition following standard procedures. For a single run, glass and silicon substrates were placed simultaneously in the substrate holder to assure the same chemical composition. During film growth, the Ar flow in the chamber was 11 sccm, resulting in a working pressure of $\sim 1 \times 10^{-3}$ Torr. The substrate-to-target distance was 8 cm. A radio frequency power of 40 W was applied to the target, which was previously pre-sputtered for 5 min. The deposition times were 150 min for all growths. The growth rate was of ~10.7 nm/min for substrate temperatures (T_s) not higher than 250 °C; when T_s was in the range from 300 to 450 °C, the growth rate decreased to ~7 nm/min as a consequence of atomic re-evaporation at the film surface during growth on a hotter surface.

The chemical composition of the samples was determined from the films deposited on Si substrates through wavelength dispersive spectroscopy (WDS) in an electron probe micro analyzer (EPMA) JXA – 8530F. The photoluminescence (PL) studies were performed at 80 K and room temperature, in a micro-Raman system (Labram from Dilor) using the 488 nm excitation line of an Ar^+-laser. For low-temperature PL measurements, a liquid-nitrogen Oxford cryostat was employed. The X-ray diffraction experiments were obtained in a Rigaku, D/Max-2100, using the Cu K_α radiation (1.5406 Å), with 30 kV and 20 mA as working parameters.

3. Results and discussion

3.1. Elemental analysis

The chemical composition in the films presented some deviations from the nominal concentrations used in the targets. Fig. 1 presents the results of the chemical composition obtained by WDS as a function of substrate temperature (T_s). According to the 1:1:1 ratio of Cu_2O, CdO and TeO_2, the target was composed of 50 at. % of oxygen, 25% at. of copper, 12.5% at. of cadmium and 12.5% at. of tellurium. These nominal concentrations in the target were the same for all growths. As a precaution, the target in use was ground and re-manufactured after each growth to avoid variations in the chemical composition on its surface, as a consequence of preferential sputtering during the previous deposition. In Fig. 1 the nominal concentrations are indicated by the dotted lines. For the growth at room temperature (RT), the amount of oxygen in the films was around 10 at. % below the nominal concentration, while the amount of tellurium is *ca.* 8 at. % above the nominal concentration. However, the concentrations of cadmium and copper in this film were close to their corresponding nominal concentrations. In general, we can see that as T_s increases in the substrate, the amount of oxygen increases until reaching values close to its nominal value. The tellurium concentration remained higher, around 20 at.%, than

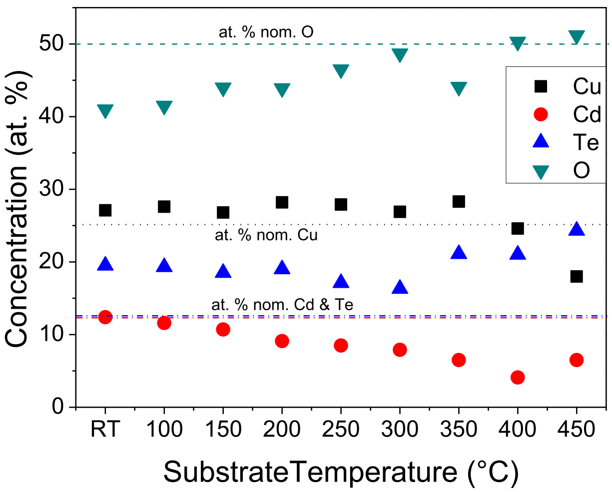

Fig. 1. Chemical composition of the films obtained from wavelength dispersive spectroscopy as a function of the substrate temperature.