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Optical properties of large band gap β-$In_2S_{3-3x}O_{3x}$ compounds obtained by physical vapour deposition

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Abstract

Thin films of large band gap β-$In_2S_{3-3x}O_{3x}$ compounds have been synthesised by annealing a multilayer structure of indium and sulphur sequentially deposited. X-ray diffraction measurements, electronic microprobe analysis and quantitative X-ray photoelectron analysis have been performed to characterise the samples. The absorption coefficient, determined from transmission and reflexion measurements, shows that the absorption threshold is blue shifted when oxygen is present in In_2S_3 and the gap increases about 30%. A theoretical modelisation of these compounds, using the known spinel structure Al_2MgO_4, is reported. The electronic structure has been calculated with the ab initio Tight Binding Linear Muffin Tin Orbitals method. We obtain an enhancement of the gap under lattice compression. Although this trend also appears in the absence of oxygen, the lattice compression is more favourable when oxygen is present.

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1. Introduction

I–III–VI_2 chalcopyrites are attractive candidates for developing active layers in polycrystalline thin film solar cells [1]. The production of efficient devices, based on Cu(In,Ga)Se_2 films as absorber, has been related with the use of CdS window layer [2]. However, the CdS is deposited by chemical bath deposition, being not easily suitable for industrial processes, and besides cadmium raises apprehension of consumers due to ecological reasons. Therefore, the substitution of CdS by another material with similar or more adapted properties is an important research objective nowadays. In_2S_3 is a chalcogenide semiconductor, which can be deposited by physical vapour deposition [3]. It has generally a n-type accessibility but its optical band gap (around 2.1 eV) is quite small to achieve high performing solar cells. One possibility to raise its optical band gap is to partially substitute indium by another element like aluminium to finally obtain $In_{2-2x}Al_{2x}S_3$ compounds [4]. Another possibility is to substitute some sulfur by oxygen in order to synthesise an homogeneous $In_2S_{3-3x}O_{3x}$ phase. The performance obtained with $In_x(OH,S)_y$ deposited by chemical bath deposition as a buffer layer makes this material very promising for solar cells application [5,6].

In the present work, we show that thin films of $In_2S_{3-3x}O_{3x}$ can be grown by physical vapour deposition (PVD) of indium and sulfur layers sequentially deposited, followed by an annealing at 673 K during half an hour under argon flow. We examine the band gap evolution when the relative oxygen concentration x increases from 0 to 0.14. In order to get improved insight in this behaviour of the band gap, the electronic

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structure of these compounds has been self-consistently calculated through the ab initio TB-LMTO method. The next two sections are devoted to the samples obtention and characterisation. The band gap evolution is discussed in Section 4 and the main conclusions are given at the end.

2. Thin film synthesis

The films have been obtained by two different techniques. The obtention process is divided in two steps, the deposition of the constituents on substrates and the post-deposition annealing under flowing argon of the evaporated samples [7,8].

The deposition of the constituents is carried out by vacuum thermal evaporation at gas pressure of 5×10^{-4} Pa using a tungsten crucible for indium and a ''Laboratory made'' Pyrex crucible for the sulfur. The purity of indium and sulfur is 99.999%. The films were deposited on Na free lime glasses (alumine silicate) chemically cleaned before evaporation. In order to obtain the films, thin indium and sulfur layers were sequentially deposited, their thickness and evaporation rate being controlled in situ by an h.f. quartz monitor. The thickness ratio has been experimentally determined to finally have homogeneous and stoichiometric films. The structures carried out by this process were then annealed in a tubular oven for 30 min under constant argon flow of 0.6 $dm^3 min^{-1}$. It has been shown earlier [8] that the optimum annealing temperature is 673 K; therefore this temperature has been systematically used in the present work. The thickness of the samples studied in this work varied from 50 nm to 300 nm. As it will be shown below, the oxygen content of the films varies with the film thickness.

In order to demonstrate that the optical properties are not related to the film thickness but to their oxygen content, a second technique is used to obtain films with same thickness but with different oxygen concentration. The process to synthesise such films consists in the co-evaporation of indium and sulfur on substrates which temperature is between 300 K and 473 K [9]. Those films are then in situ annealed during half an hour at 473 K. The oxygen content of the films (value of x) is controlled in that case by the temperature of the substrates during their deposition process.

3. Thin film characterisation

The obtained films were analysed by X-ray diffraction (XRD) to investigate composition and structure; a Siemens X-ray goniometer with CuKα line was used. The surface and depth profiling quantitative and qualitative composition of the films were obtained from X-ray photoelectrons spectroscopy (XPS) measurements. Electron microprobe analysis (PGT-IMIX PTS model) was used to determine the chemical composition. The optical measurements were performed at room temperature using a spectrophotometer CARY and the transmittance and reflectivity measured in a wavelength interval of 300–800 nm (Fig. 1).

We have observed that the first process described in Section 2 allows the synthesis of β-In_2S_3 thin films which crystallites are randomly oriented [8] (Fig. 2). An XPS study has first been performed on each film. A qualitative analysis has shown that the 300 nm thick films only contain indium and sulfur as expected, while thinner samples contain also oxygen. Fig. 3 shows the O1s peaks obtained before and after 3 min of etching from a 100 nm thick film. One can observe that before etching the main contribution of the O1s is situated at 532–533 eV corresponding to oxygen issued from superficial contamination [10] (this contamination is systematical when a sample has been in contact with air). One can also observe on the O1s peak, before etching, a shoulder at about (530 eV) corresponding to indium–oxygen bonds like in indium oxide [11]. After only 3 min of etching the contribution of the oxygen from contamination has totally disappeared, only remaining the In–O bonds contribution. In Fig. 4, we have plotted the O1s peak obtained after 3 min of etching from films of different

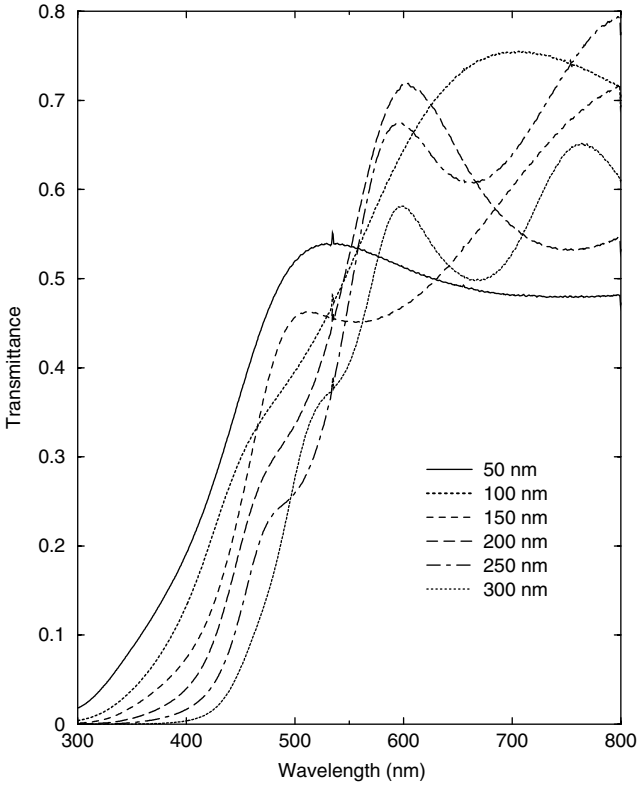

Fig. 1. Transmission curves of the thin films, the thickness of the films is given in the figure.