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Structural characterization of thin films based on II–VI ternary compounds deposited by evaporation

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Abstract

Thin films of Zn(S, Se), (Zn, In)Se and Cd(S, Te) compounds, deposited by evaporation were characterized through X-ray diffraction (XRD) measurements and analyzed with the help of a simulation program. The interest in studying these materials is due to their potential for photovoltaic applications, especially as buffer materials in $Cu(In,Ga)Se_2$ (CIGS) and CdTe based solar cells. The XRD measurements allowed us to determine the effect of the chemical composition on the structure and lattice parameter, which must be known to predict an optimum mechanical match between the buffer and absorber layers; a good mechanical match improves the hetero-interface of the solar cell.

The studies revealed that In-rich $Zn_xIn_{1-x}Se$ films and Te-rich CdS_xTe_{1-x} films grow with hexagonal structure; however, their structure is changed to cubic when they become Zn-rich and Te-rich, respectively. On the contrary, the $Zn_xIn_{1-x}Se$ films grow with cubic structure, independently of its chemical composition. It was also found that the variation of the chemical composition leads to a significant variation of the optical gap Eg, which was determined by extrapolation of the curve $(\alpha h\nu)^2$ vs. $h\nu$, assuming that, for this type of compounds, the relation $\alpha h\nu = A(h\nu - \mathrm{Eg})^{1/2}$ is valid. It was observed, in the three type of compounds studied, that their Eg values increase with the decreasing of the lattice constant, which in turn varies according to Vegard's Law. Comparing the lattice parameters of the ZnS_xSe_{1-x} and $Zn_xIn_{1-x}Se$ compounds, with those reported in the literature for $Cu(In_{1-x},Ga_x)Se_2$ thin films, helpful information was found to achieve a good lattice match between the studied II–VI compounds and the CIGS film.

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1. Introduction

Various kinds of binary, ternary and quaternary semiconductors are currently being investigated for potential photovoltaic applications. Among them, CdTe, $CuInSe_2$ and $Cu(In,Ga)Se_2$ (CIGS) thin films have demonstrated to be promising candidates for high efficiency, low cost solar cells [1,2]. The highest efficiency has been achieved, up to now, using a CdS buffer layer processed in a wet chemical bath [3]. However, the chemical deposition of the CdS complicates the establishment of the in-line process to fabricate this kind of devices. Therefore, for industrial production and for environmental protection, it would be desirable to replace CdS for a less toxic buffer material deposited by a dry process. Materials such as InSe, ZnSe and $Zn_xIn_{1-x}Se$ have demonstrated to be promising candidates for buffer layer, in substitution of the CdS. Efficiencies greater than 11% have been achieved with CdTe and CIGS based solar cells fabricated using these new materials as buffer layer [4–6].

It is known there is a 10% lattice mismatch between CdS and CdTe, which should generate a large density of defects at the interface of CdS/CdTe solar cells. Intermixing at the CdS/CdTe interface is considered crucial for the device performance, as it is expected to reduce the effect of lattice mismatch by forming a graded layer at the interface [7].

In this work, we present results on the structural characterization of $Zn_xIn_{1-x}Se$, ZnS_xSe_{1-x} and CdS_xTe_{1-x} thin films, deposited by evaporation, carried out through XRD measurements. Special emphasis was put on studying

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the influence of the chemical composition on the crystalline structure and lattice constants. The analysis of the XRD spectra was made with the help of a theoretical simulation program.

2. Experimental details

Polycrystalline thin films based on ternary compounds of the II–VI groups were deposited on soda-lime glass substrates by co-evaporation of binary precursor materials. The source used for the preparation of the films consists of a cylindrical graphite crucible, which includes two coaxial chambers, from where the precursor compounds are simultaneously evaporated.

The evaporation source is heated by radiation coming from a cylindrical graphite heater. Any desired chemical composition of the ternary compounds can be achieved by varying the ratio of the flux of the respective precursor species. This is done varying the cross section of the coaxial chamber's exit nozzles. The evaporation temperature also affects the chemical composition of the films, because each of the precursors sublimates at different temperature. Details of the evaporation source are given elsewhere [8,9] and Table 1 shows the main deposition parameters used to prepare the studied samples.

The XRD measurements were done with a Phillips diffractometer, using the Cu–K_α line; the interpretation of the diffractograms was performed with the help of the PDF tables and the Powder Cell simulation program. The chemical composition of the ternary compounds was determined by X-Ray Fluorescence measurements.

The optical gap Eg was determined through the relation: $(\alpha h\nu)=A(h\nu-\mathrm{Eg})^{1/2}$, which is valid for direct band gap semiconductors, like those studied in this work. The absorption coefficient α was obtained using the transmittance spectrum and calculations based on a procedure described in detail in Ref. [10] and in a paper published previously by the authors [8].

3. Results and discussion

3.1. Influence of the chemical composition on the optical gap

First we investigate the conditions to deposit thin films of the mentioned three types of ternary compounds with chemical compositions varying in a wide range. Subsequently, the effect of the chemical composition on the optical gap was studied. For that, the chemical composition and optical energy gap Eg of the samples were determined by X-ray fluorescence and transmittance measurements, respectively. Fig. 1 shows curves of Eg vs. x, corresponding to thin films of ZnS_xSe_{1-x}, $Zn_xIn_{1-x}Se$ and CdS_xTe_{1-x} with chemical compositions varying between $x=0$ and $x=1$. The increase of Eg, observed in the compounds studied, when the parameter x (determining the chemical composition) increases, seems to be related with a broadening of the energy band gap caused by a decrease of the lattice constants (see Fig. 6). The decrease of the lattice constant gives rise to an increase of the interaction between the wave functions associated to the valence electrons which in turn lead to the broadening of the energy band gap. The values of Eg and its relationship with the lattice constant, found in this work for the ZnS_xSe_{1-x}, $Zn_xIn_{1-x}Se$ and CdS_xTe_{1-x} compounds, are in agreement with those reported by other authors [5,14,15].

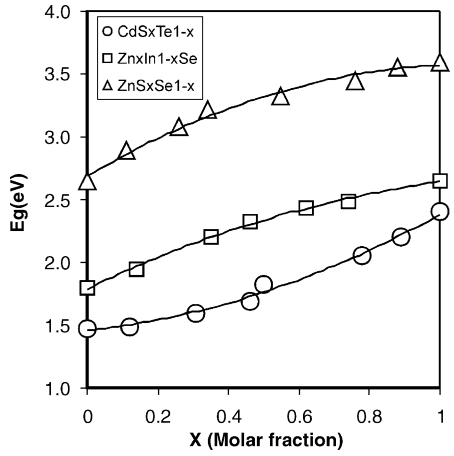

Fig. 1. Variation of the optical gap of thin films of CdS_xTe_{1-x}, $Zn_xIn_{1-x}Se$ and ZnS_xSe_{1-x} as a function of their chemical composition x.

3.2. Influence of the chemical composition on the structural properties

The influence of the chemical composition on the structural properties of thin films of CdS_xTe_{1-x}, $Zn_xIn_{1-x}Se$ Se and ZnS_xSe_{1-x} was studied trough XRD measurements. Fig. 2 shows typical XRD spectra of thin films of the mentioned three types of compounds, where the influence of the chemical composition can be observed. It is observed that the XRD spectra of samples with different chemical

Table 1
List and variation range of the parameters used to deposit thin films of II–VI ternary compound with chemical compositions varying in a wide range

Preparation parameters	ZnS_xSe_{1-x}	$Zn_xIn_{1-x}Se$	CdS_xTe_{1-x}
Precursors	ZnS and ZnSe	In_2Se_3 and ZnSe	CdS and CdTe
Substrate Temperat. (°C)	200–300	250–350	200–250
Evaporat. Temperat. (°C)	850–1030	850–950	850–1000
Exit nozzle ϕ (mm)	$\phi_{ZnS}=6$; $\phi_{InSe}=0.8$–2.5	$\phi_{ZnSe}=4$; $\phi_{ZnSe}=0.8$–2.5	$\phi_{CdS}=3$; $\phi_{CdTe}=0.7$–1.6