



Graded composition $\text{Cd}_x\text{Zn}_{1-x}\text{Te}$ films grown by Isothermal Close Space Sublimation technique

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ABSTRACT

Graded composition $\text{Cd}_x\text{Zn}_{1-x}\text{Te}$ films were prepared by growing several alternate layers of CdTe and ZnTe by the Isothermal Close Space Sublimation technique. The thickness of both kinds of layers was modified along the structure to produce an increase of the average concentration of CdTe towards the surface of the films. Due to Zn/Cd inter-diffusion during the growth process the sequence of layers was converted into a relatively smooth graded composition film. According to X-ray diffraction characterization the layers grew coherently with the (100) oriented GaAs substrates although they showed a relatively high mosaicity. $\theta-2\theta$ plots show very wide diffraction peaks as expected from variable composition samples. The band gap grading effect in light absorption was also verified through transmission measurements, using transparent substrates. Graded composition profiles of the thin films were confirmed by x-ray photoelectron and secondary ion mass spectroscopies. Moreover, quantitative Cd, Zn and Te profiles were obtained by the analysis of Rutherford backscattering spectra of the samples. This analysis showed a CdTe molar fraction profile ranging from approximately $x=0.8$ at the surface of the sample and $x=0.35$ at the interface with the substrate. The possibility of growing graded composition layers using a simple and cost-effective procedure was demonstrated. This could be interesting in technological applications like $\text{Cd}_x\text{Zn}_{1-x}\text{Te}$ layers of variable composition in CdS/CdTe solar cells.

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1. Introduction

Thin film semiconductor alloys with graded composition (GC) result in spatial variation of several properties such as the refractive index, band gap, effective mass, and light absorption coefficient among others. This fact has encouraged several applications in practical devices and in particular in solar cells technology. In fact, $\text{Cd}_x\text{Zn}_{1-x}\text{Te}$ and $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$ with different composition profiles have been proposed as absorbers in order to increase the efficiency of CdTe and $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$ based thin film solar cells [1,2]. In these cases, the band gap variation leads to a quasi-electric field that enhances the drift-diffusion length and reduce the back surface recombination velocity. Also, $\text{Cd}_x\text{Zn}_{1-x}\text{Te}$ with constant Cd

composition and band gap ranging between 1.6 and 1.7 eV (x ranging around 0.2–0.45) has been proposed for top absorber in tandem solar cells [3,4].

Other applications of GC films include variable refractive index profiles used in optical filters or antireflection coatings [5,6] and strain relief by accommodation of lattice misfit in heterostructures [7]. In particular, CdTe epitaxial growth on GaAs substrates has been proved to be a difficult task due to the large mismatch between both materials. Because of that ZnTe buffer layers are used to favor the epitaxial growth and to enhance the crystal quality of CdTe layers [8,9].

Separate confinement heterostructure lasers use refractive index grading (induced by GC) in order to enhance carrier trapping efficiency, trapping time and carrier confinement [10]. GC structures have been also used in thermoelectric materials to enhance the figure of merit of the devices locating the most suitable material composition in the temperature profile along the structure [11]. Finally, ohmic contacts preparation [12], increased

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resistance of surfaces to damage or contact deformation [13] are also process beneficiaries of GC materials.

Several techniques have been employed to prepare GC layers. In relation with solar cells applications, CdZnTe/CdTe heterostructures have been made using co-deposition of CdTe and ZnTe compounds or sputtering using $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{Te}$ targets. On the other hand, CdTe/ZnTe bilayers have been used to obtain both uniform or graded profiles in $\text{Cd}_x\text{Zn}_{1-x}\text{Te}$ films using 300 nm thick CdTe layers and 300 or 500 nm thick ZnTe layers grown by RF sputtering [14].

Electron Cyclotron Resonance-Plasma Enhanced Chemical Vapor Deposition (ECR-PECVD) [15] was used to grow SiO_xN_y alloys with different composition profiles while Molecular Beam Epitaxy (MBE) has been frequently used for growing high quality GC layers among them $\text{ZnTe}_x\text{Se}_{1-x}$ [8] and $\text{Pb}_x\text{Eu}_{1-x}\text{Se}$ [16].

In this paper we demonstrate the use of the Isothermal Close Space Sublimation (ICSS), a cost-effective technique, to prepare $\text{Cd}_x\text{Zn}_{1-x}\text{Te}$ alloys with GC. This physical vapor deposition technique, in which the substrate is exposed sequentially to the elemental sources, has been previously employed for growing epitaxial as well as polycrystalline ZnTe, CdTe and $\text{Cd}_x\text{Zn}_{1-x}\text{Te}$ with constant composition [17,18]. This technique revealed a regulated growth rate determined by the multilayer adsorption of the vapor elements in every exposure, the growth rate being controlled by both the exposure and the purge time.

Samples grown on GaAs (100) as well as transparent substrates (glass/ITO) were characterized by x-ray diffraction (XRD), x-ray photoelectron (XPS) and optical transmission and secondary ion mass (SIMS) spectroscopies, and Rutherford Backscattering (RBS) Spectrometry.

2. Experimental

2.1. Sample preparation

ICSS procedure has been described elsewhere [17]. In this technique the growth of the films proceeds by cyclic exposure of the substrate to the elemental sources (Cd and Te for CdTe layers, Zn and Te for ZnTe layers). These sources are heated in a graphite crucible inside a quartz reactor with flowing gas or vacuum atmosphere.

To produce the GC samples, thin layers of CdTe and ZnTe were grown alternately in such a way that the thickness of both layers (controlled by the number of cycles) was modified along the structure to produce an increase of the average concentration of CdTe towards the surface of the sample. Different GC samples were studied in the present work. Sample A was grown with the cycle sequence (the numbers represent number of cycles): 4 ZnTe–1 CdTe–3 ZnTe–2 CdTe–2 ZnTe–3 CdTe–1 ZnTe–4 CdTe, for a total of 20 cycles. A thicker sample B was grown starting with 7 cycles of ZnTe and following a sequence 7 (ZnTe)–1 (CdTe)–6 (ZnTe)–2(CdTe) ..., for a total of 56 cycles. These two samples were grown onto GaAs substrates. For transmittance measurements a sample C was grown with the same conditions of sample B but using a glass/ITO substrate. Moreover, samples of pure ZnTe and CdTe with 20 cycles and the same growth temperature were also grown for comparison, both in GaAs and in transparent glass/ITO substrates. Prior to the growth, the substrates were degreased in acetone and alcohol; GaAs (100) substrates were subjected to a further chemical etch in $5\text{H}_2\text{SO}_4:1\text{H}_2\text{O}_2:1\text{H}_2\text{O}$ solution for 3 min, followed by HF (48%) for 20 s. In all cases the exposure times to the sources were 20 s and the purge times 10 s for a total cycle duration of 60 s.

The idea of these experiments is that Zn/Cd inter-diffusion (ID) must play a role in transforming the successive ZnTe and CdTe stacked layers on a relatively smooth ternary alloy with graded composition. If there would be excessive ID, composition gradients

would cancel out and consequently a ternary alloy with a constant composition will be obtained after the growth process. On the other hand, if ID were insignificant, instead a GC layer, alternated CdTe and ZnTe films with different thickness will be obtained. Then, for a GC film to be formed, a moderate Zn/Cd inter-diffusion should be present. The criterion we followed as a guide to estimate the proper growth conditions was consider that the interface spreading due to ID, $2\sqrt{Dt}$ (with D the Zn/Cd ID coefficient and t the growth duration) must be of the same order of magnitude of the thickness grown per cycle. With this consideration we expect that local diffusion will be enough for smoothing the ZnTe/CdTe interfaces without forming a constant composition across the whole sample. The growth rate of pure CdTe and ZnTe were calibrated in previous experiments to be 8 and 4 nm/cycle, the growth process duration for the samples grown with 20 cycles (at a rate of 1 min per cycle) was 20 min. With this time and the condition for the interface spreading to be 6 nm (the average of the growth rates of CdTe and ZnTe) we estimate the ID coefficient (D) as $1 \times 10^{-16} \text{ cm}^2/\text{s}$. According the temperature dependence data of D for Cd/Zn ID in CdTe/ZnTe heterostructures [19] this coefficient corresponds to a temperature of 400 °C, which was used in the growth experiments.

2.2. Structural characterization and composition profiles

To determine the structure of the samples XRD $\theta-2\theta$ scans were performed using a Siemens D-5000 powder diffractometer with the wavelength (λ) of $\text{Cu K}\alpha_1$ radiation. Reciprocal space maps were obtained for the samples grown onto GaAs substrates by means of a high resolution PANalytical XPert PRO MRD diffractometer, using a Pixel solid state detector at 0.05° omega increments.

SIMS and XPS were used to obtain a qualitative or semi-quantitative evaluation of the composition profiles. SIMS measurements were made using a Cameca 6F IMS spectrometer. In order to reduce the matrix effect a CsM^+ mode was used. XPS depth profile analysis of the samples was performed on a VG-ESCALAB 220i-XL system (base pressure of 2×10^{-10} mbar) equipped with photoelectron spectroscopy (XPS) and ion sputter gun for sample etching. The Al $\text{K}\alpha$ line (1486.6 eV) was used as x-ray source. As XPS is a surface sensitive technique, giving chemical information of the last atomic layers of the film, a depth profile of the sample in terms of photoemission line intensities was obtained by combining a sequence of etching cycles interleaved with photoemission measurements. Argon ion sputtering cycles were performed with ion beam energy of 2 keV. The As2p, Ga2p, Cd3d, Te3d, Zn2p lines were monitored as function of etching cycles.

Optical transmission measurements were performed using a double beam Hitachi UV–vis 150-20 photo-spectrometer equipped with an integrating sphere. Normal incidence was used in the range 200–900 nm.

RBS measurements were done in order to obtain the composition profile and to determine the stoichiometry and the thickness of the samples. A 7 MeV alpha beam provided by a 3 MV Tandem accelerator was employed. In this way we were able to obtain a good mass resolution in order to be able to identify the Te and Cd signals. The resolution of the detector and associated electronics was better than 13 keV.

3. Results and discussion

Fig. 1 shows the diffractograms for samples A and B. Also, diffractograms for CdTe and ZnTe samples grown at the same temperature and with the same number of cycles that sample A are

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