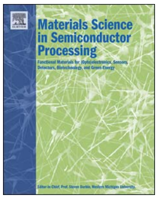
Materials Science in Semiconductor Processing 63 (2017) 64–71

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp



The surface morphology, structural properties and chemical composition of $Cd_{1-x}Zn_xTe$ polycrystalline thick films deposited by close spaced vacuum sublimation

Y.V. Znamenshchykov[a,*], V.V. Kosyak[a], A.S. Opanasyuk[a], E. Dauksta[c], A.A. Ponomarov[b], A.V. Romanenko[b], A.S. Stanislavov[b], A. Medvids[c], I.O. Shpetnyi[a,d], Yu.I. Gorobets[d]

[a] *Sumy State University, 2, Rymsky Korsakov Str., 40007 Sumy, Ukraine*
[b] *Institute of Applied Physics of the National Academy of Sciences of Ukraine, 58, Petropavlivska str., 40030 Sumy, Ukraine*
[c] *Riga Technical University, 3 Paula Valdena Str., LV-1048 Riga, Latvia*
[d] *Institute of Magnetism of the National Academy of Sciences of Ukraine and the Ministry of Education and Science of Ukraine, 36-b Vernadsky Ave., 03142 Kyiv, Ukraine*

ARTICLE INFO

Keywords:
Semiconducting ternary compounds
X-ray diffraction
Crystal structure
Polycrystalline deposition
Solid solutions

ABSTRACT

Thick polycrystalline $Cd_{1-x}Zn_xTe$ films with x ranged from 0.37 to 0.80 were obtained by the close spaced vacuum sublimation method. In order to investigate properties of the films structural, PIXE and Raman studies were carried out. Determination of chemical composition of the films by EDS, PIXE and XRD has shown good correlation of results. Raman spectroscopy reveals the relation between zinc concentration and vibrational properties of the films. Studies of the spatial distribution of the chemical elements on the film surface by micro-PIXE and micro-Raman spectroscopy have shown that films are uniform and free of secondary phases such as CdTe, ZnTe and Te inclusions.

1. Introduction

The $Cd_{1-x}Zn_xTe$ (CZT) single crystals are widely used for room temperature detectors of the hard radiation [1–3]. It is possible due to such characteristics of CZT as high resistivity, high atomic number, high binding energy and tunable band gap in the range 1.50–2.26 eV depending on Zn concentration. However, it is difficult to obtain high-quality single crystals with $x > 0.10$ and uniform distribution of the chemical elements. Thus, the CZT crystals contain defects such as Te-precipitates, twins and dislocations [4,5], which lead to deterioration of detector properties.

Despite the fact that polycrystalline materials contain more structural defects than single crystals, the polycrystalline thick CZT films are also used as a detector material [6–9]. It is due to ability to produce low-cost, large-area flat panel detectors [8,10] based on thick films free of Te-inclusions with zinc concentration $x > 0.10$ and uniform zinc distribution [11]. At the same time application in electronic devices, especially fabrication of radiation detectors, requires high-quality CZT films with big grain size, high texture, low concentration of defects, and uniform distribution of chemical elements.

Distribution of secondary phases in CZT single crystals was studied by IR transmission microscopy [12,13], micro-photoluminescence [14] and micro-Raman spectroscopy [15,16].

The Raman spectroscopy is very sensitive to phase composition of materials. In particular, this method allows detecting Te-inclusions in CZT films and single crystals [12,15,16]. Also, the Raman spectroscopy was used for study of the distribution of chemical elements in epitaxial CdTe thin films [17]. However, the spatial distribution of secondary phases and chemical elements in thick polycrystalline CZT films has not been studied yet.

As a rule Raman spectra of cubic phase CZT include CdTe and ZnTe-related modes of longitudinal (LO) and transverse (TO) optical phonons. However, the presence of Te inclusions leads to the appearance of Te-related modes on Raman spectra of CZT films [18].

Particle-induced X-ray emission (PIXE) technique allows simultaneous determining the elemental concentrations of the major and trace elements of the samples without standards usage by detecting and processing the characteristic X-rays of elements induced by accelerated ion beam [19]. Usually in μ-PIXE the H+ beam with energy of about 2 MeV from electrostatic accelerator is focused into several μm probe, which scans over the sample surface. Such probe penetrates few tens of μm into the sample without its spreading and sample destruction.

---

[*] Corresponding author.
E-mail address: yaroslav.znamenshchykov@gmail.com (Y.V. Znamenshchykov).

http://dx.doi.org/10.1016/j.mssp.2017.02.004
Received 3 August 2016; Received in revised form 30 January 2017; Accepted 3 February 2017

Table 1
Studying of chemical composition of CZT films by EDS, XRD and PIXE methods.

Sample	EDS				XRD				PIXE			
	Concentration (at%)			x	Concentration (at%)			x	Concentration (at%)			x
	Cd	Zn	Te		Cd	Zn	Te		Cd	Zn	Te	
CZT1	33.8	21.3	44.9	0.39	34.5	15.5	50	0.31	31.3	18	50.7	0.37
CZT2	28.3	26.2	45.5	0.48	27	23	50	0.46	26.9	22.7	50.4	0.46
CZT3	19.3	34.4	46.3	0.64	17.5	32.5	50	0.65	15.9	33.8	50.3	0.68
CZT4	12.0	42.7	45.3	0.78	11.5	38.5	50	0.77	9.9	39.8	50.3	0.80

Therefore, μ-PIXE provides high-resolution elemental mapping of near-surface region with the detection limits of about 1–20 ppm.

The PIXE method was used for analysis of chemical composition and distribution of elements in compound and multicompound thin films [20–23]. But this method has not been used for analysis of CZT films.

The goal of this work is to study the effect of zinc concentration on structural properties of thick CZT films, obtained by close spaced vacuum sublimation (CSVS) method. Also, in order to determine the presence of secondary phases in thick CZT films with different Zn concentration the surface distribution of the chemical elements is established.

2. Experimental details

The CZT films were deposited on ITO-coated glass substrates by close-spaced vacuum sublimation method, which was described in our previous works [24–26]. The mixture of CdTe and ZnTe powders was used for evaporation; the total mass of evaporated powder was 100 mg. In order to obtain CZT films with different Zn concentration, the mass ratio (M_R) between cadmium telluride and zinc telluride powder has been varied as follows: 9, 2.3, 1 and 0.4 for CZT1, CZT2, CZT3 and CZT4 samples, respectively. The growth conditions for films were the same, namely, the substrate temperature was 400 °C and the evaporator temperature was 700 °C.

The surface morphology of the films has been investigated by REM-100 scanning electron microscope (SEM). The average grain size (D) of the layers was estimated by Jeffries method [27].

The chemical composition of the films was studied by energy dispersive spectroscopy (EDS) on the surface area of 200×200 μm. The measurement parameters were as follows: beam exposure of 100 s, beam energy of 20 keV. In order to achieve the highest signal-to-noise ratio, the average value of output signal intensity was adjusted to be of about 1000 counts/sec. It should be noted that surface of the samples was not etched or polished for more precise EDS measurements, and the surface of the film was assumed to be flat. However, the roughness of the film could lead to increasing in error of quantitative EDS analysis up to 5% [28].

The chemical composition of the samples was also studied by particle-induced X-ray emission μ-PIXE technique using the scanning nuclear microprobe. After collimation the proton beam of energy of 1 MeV was focused on 5×5 μm area of the sample. The beam was scanned across the geometrical raster of 250 μm×250 μm. The X-ray emission signal generated from each pixel was collected by Amptek XR-100CR Si (Li) X-ray detector with Be window of 25.4 μm thickness positioned at 135° to the incident beam direction. That allows to obtain two-dimensional maps of spatial distribution of concentration of compound elements. General PIXE spectra from each scanned area were processed by using the GUPIX software [29] to quantify the elemental composition of the samples.

The X-ray diffraction (XRD) analysis was used to study the structural properties of the layers. The measurements of XRD spectra were carried out by DRON 4–07 diffractometer in a conventional Bragg-Brentano $\theta-2\theta$ geometry (2θ is the Bragg's angle) using Ni-filtered CuK_α radiation (λ=0.15406 nm). The samples were measured in the 2θ angle range from 20° to 80°. The peak intensities were normalized to the intensity of (111) peak of the cubic phase. Phase analysis was performed by comparison of the inter-planar distances as well as relative intensities measured from the samples with reference Joint Committee on Powder Diffraction Standards (JCPDS card No. 15–0770) data [30]. Precise values of the lattice parameter were determined by the extrapolated Nelson–Riley method [31].

Room temperature Raman spectra were studied using semiconductor IR (λ=785 nm) and an Ar (λ=514 nm) lasers as an excitation source. Measurement parameters were the same as in previous work [32].

3. Results and discussion

The study of chemical composition by EDS method shows that CZT films have following Zn concentrations: 21.3 at%, 26.2 at%, 34.4 at% and 42.7 at% for the CZT1, CZT2, CZT3 and CZT4 samples, respectively. Thus, Zn concentration is expectedly increasing with decreasing of M_R. The results of the films chemical composition study are presented in Table 1.

The SEM images of the surface of CZT films are shown in Fig. 1. The CZT1 sample consists of well-faceted grains with smooth flat surfaces (Fig. 1(a)) and the size of grains (D) is ranged from 10 to 22 μm (Fig. 1(a)). The investigation the surface of CZT2 sample shows irregular grains with D of about 8 μm (Fig. 1(b)). The surface of CZT3 sample includes non-uniform grains with D of 3 μm, most grains contain sub-grains with the size of about 1 μm (Fig. 1(c)). The shape of grains of CZT4 sample is very similar to those in CZT2 sample, whereas D value of 3.5 μm was almost twice smaller (Fig. 1(d)). Thus, the concentration dependence of surface quality in CZT films has a non-linear character. With increasing of x from 0.37 to 0.68 deterioration of surface was observed, with further increasing of x from 0.68 to 0.80 the surface morphology of the films shows improvement.

The changes of the film surface morphology could be caused by two factors:

1) Deformation of the crystal lattice due to increasing amount of Zn atoms similarly to CZT single crystals [33,34], where relationship of crystalline quality of CZT from x was described by parabola with the minimum at x=0.5.
2) The effect of the growth conditions on properties of CZT films. In particular, chosen growth conditions (T_s=400 °C, T_e=700 °C) are more equilibrium for deposition of Zn-poor films (CZT1 and CZT2) than for Zn-rich films (CZT3 and CZT4). This could be explained by the fact that sublimation temperature of ZnTe is higher than of CdTe. It leads to the decreasing of vapour pressure above the evaporator and substrate (the vapour above the substrate consists of gas flux from the evaporator and re-evaporated gas from the substrate [35]). Thus the level of saturation of vapour in a close-spaced sublimation chamber is decreased with the amount of Zn in initial powder.