PROCEEDINGS OF THE INTERNATIONAL CONFERENCE
NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. 4 No 1, 01NTF16(4pp) (2015)

Effect of Laser Annealing on the Properties of the Surface of Polycrystalline CdZnTe Thick Film

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(Received 10 August 2015; revised manuscript received 14 August 2015; published online 29 August 2015)

In this work effect of laser annealing on properties of surface of $Cd_xZn_{1-x}Te$ (CZT) films was studied. CZT layers were deposited by co-evaporation of CdTe and ZnTe using close-spaced vacuum sublimation (CSVS) method. Structural properties and chemical composition of films were studied by X-ray Diffraction (XRD) and Energy Dispersive Spectroscopy (EDS). The annealing of the sample was carried out with the help of micro-Raman infrared laser of 785 nm wavelength at maximal 100x magnification. It was established that laser annealing of the surface substantially causes redistribution of Zn atoms. More detailed study of the sample by the scanning of surface with the micro-Raman method allows to determine trend in this process and to detect Te-rich zones. Improvement of the crystal quality near annealed area of the thick film was achieved.

Keywords: CdZnTe, CZT, thick films, laser annealing, Raman, semiconductor, X-ray detectors.

PACS numbers: 68.37.Hk, 71.55.Gs, 78.30.Fs

1. INTRODUCTION

Single crystals of CZT ternary semiconductor are widely used for the X and gamma rays radiation detectors [1,2]. It could be explained by the fact that band gap of this material can be adjusted over a wide range from 1.46 to 2.26 eV by the changing of Zn concentration. In turn, increasing in Zn concentration leads to decreasing in conductivity of the material which provides improvement of the detectors performance [3, 4].

Last time, in order to produce low-cost large area imaging X-rays sensors for medical application the thick CZT polycrystalline films are used [3, 5].

Besides, possibility of using of CZT films with graded bang gap as an absorbing layer of thin film solar cells is reported [6]. Graded band gap in CZT films can be achieved with trough-thickness gradient of Zn concentration [7].

The main problems in producing of high performance detectors based on thick CdZnTe polycrystalline films are low crystal quality of the films comparatively with the bulk material and difficulties in controlling of Zn atoms volume distribution. The laser annealing is used for enhancement of crystal quality of material and for redistribution of Zn atoms [8,9]. The effect of laser annealing on main properties of bulk CdZnTe crystal is well known, however the influence of high power laser irradiation on structural properties of the thick polycrystalline CdZnTe films is much less studied. The main task of present research is to obtain high quality CdZnTe thick films suitable for application in hard radiation detectors. Then obtained sample was used to study effect of annealing of the surface by micro-Raman infrared laser in order to achieve improvement of the crystal quality of the thick film. Other important point of this study is to establish possible application of micro-Raman laser for modification with high spatial locality of the CdZnTe thick film surface.

2. EXPERIMENTAL DETAILS

The CZT films were deposited on Mo coated glass substrates by vacuum co-evaporation of the pure CdTe and ZnTe powders from independent sources in closed space chamber [10]. Temperature of CdTe evaporator was $T_{e(CdTe)}$ = 893 K, temperature of ZnTe evaporator was $T_{e(ZnTe)}$ = 993 K, substrate temperature was T_s = 673 K. X-ray diffraction analysis (XRD) was used to study the structural properties of the obtained layers, chemical composition of the films was studied by Energy Dispersive Spectroscopy (EDS). The Renishaw equipment was used to study Raman spectra of films. Spectra were measured with excitation of surface by infrared 785 nm laser. We used low-power excitation, namely, 0.01% from nominal power of laser. Output signal measurement was carried out during 5 accumulations; duration of each measurement was 120 sec.

The annealing of the sample was carried out with using of 50% from nominal power of micro-Raman infrared laser at maximal 100x magnification. It is allowed to provide high spatial locality of the annealed area on the surface of the sample. Namely, the regular shape stripwise annealed area with about 2 μm width was obtained.

3. RESULTS AND DISCUSSION

Investigation of the film by the scanning electron microscopy (SEM) shows that obtained sample is polycrystalline with average grain size of about 5 μm and thickness of about 30 μm (Fig. 1, a).

The analysis of XRD patterns (Fig 1, b) was performed by comparison of the inter-planar distances as well as relative intensities measured from the samples and reference Joint Committee on Powder Diffraction Standards (JCPDS card № 15-0770) data.

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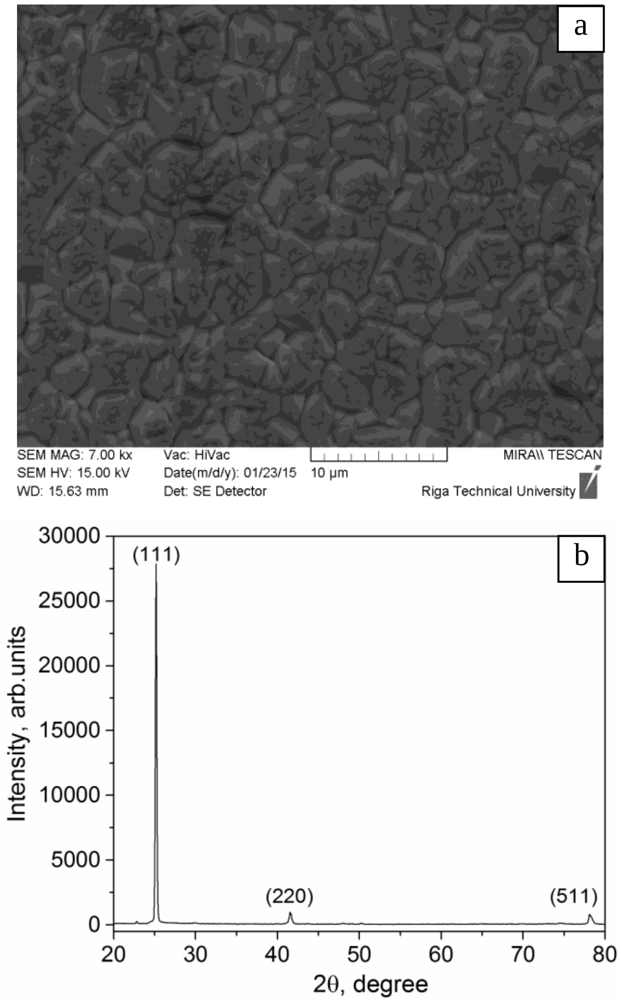

Fig. 1 – Structural properties of CZT film: SEM image of CZT surface (a), XRD pattern (b).

It was determined that the sample has cubic structure with pronounced (111) texture. The high texture and small value of the full width at half maximum of the (111) peak are the evidence of high crystal quality of the film.

It is well-known that variation of Zn concentration in CZT films causes deformations in crystal lattice and changes the lattice parameter, wherein these changes are described by the linear dependence [11]. In this work lattice parameter was calculated from position of (111) peak and had a value a=0.64465 nm. The Zn concentration of 9% was determined according to lattice parameter value using the reference data of lattice parameter-zinc concentration dependencies [11]. This value is in a good agreement with the value of 11 % Zn concentration obtained with the help of EDAX method.

The Raman spectra of the annealed and non-annealed samples are presented on Fig.2. According to the reference data [12,13] with increasing of Zn concentration position of LO_1 mode is shifted from those in pure CdTe (167 cm^{-1}). In particular, the CdTe (LO_1) mode is blue-shifted from the position of CdTe (LO_1) of pure CdTe (167 cm^{-1}), while ZnTe (LO_1) mode is red-shifted. Thus obtained Raman spectra of non-annealed surface (point 1 on Fig. 2) is typical for CZT.

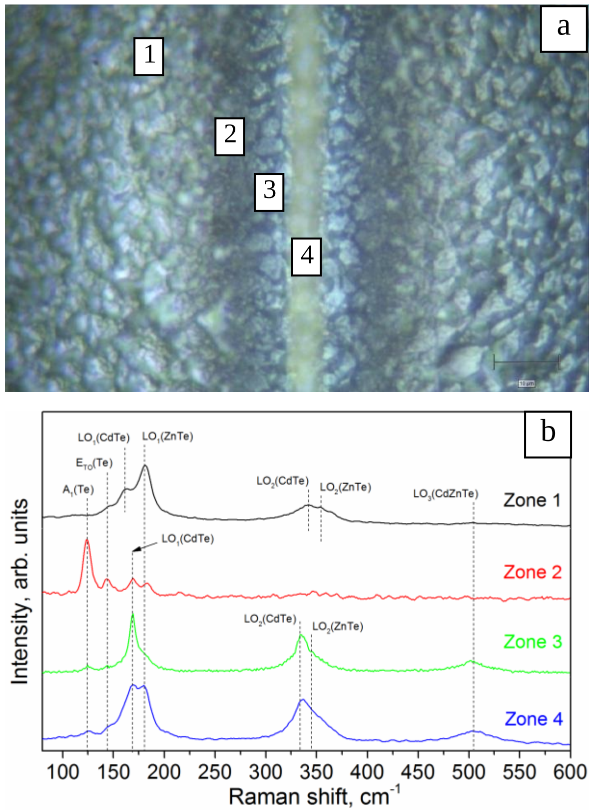

Fig. 2 – Optical image of annealed surface (a) with labels of zones 1, 2, 3, 4. Raman spectra (b) for zones 1, 2, 3, 4.

This Raman spectrum includes CdTe(LO_1) at 161,5 cm^{-1} and ZnTe(LO_1) at 181 cm^{-1} modes, and their phonon repetitions at 342 cm^{-1} and 354 cm^{-1}, which were assigned to CdTe and ZnTe respectively. Presence of LO_2 repetitions is evidence of high crystal quality of the film. Also this spectrum includes the weak peak of Te(E) mode.

Presence of tellurium becomes more appreciable at approach to the annealed zone. Measurements of spectrum in point 2 (Fig. 2) has shown that intensive peak of A_1(Te) mode is appeared on spectrum and intensity of E(Te) mode peak is increased. Generally Te-like modes become dominant, whereas peak intensity of LO_1(CdTe) and LO_1(ZnTe) modes is significantly decreasing. This could be explained by evaporation of Cd atoms from the surface under intensive laser irradiation and formation of Te-rich surface. Moreover shift of LO_1 mode peaks concerning their position on spectrum of non-annealed area was observed, which is the evidence of changing of Zn concentration on the surface of the film. At the same time studying of area, which is placed directly near the annealed area (point 3, Fig. 2), didn't observe Te-rich zones. At that point peak intensity of Te-like modes was significantly smaller than LO_1(CdTe) mode. It is necessary to underline, that comparative peak intensity of LO_1(ZnTe) mode significantly decreased concerning peak intensity of LO_1(CdTe) mode in comparison with spectrum measured on non-annealed surface (point 1, Fig.2). The most probable explanation of such changes in spectrum is decreasing of Zn atoms concentration due to its diffusion from into the volume of the film from the surface.

Analysis of Raman spectrum measured directly on the annealed zone (point 4 on Fig. 2) has shown that positions of LO_1(CdTe) and LO_1(ZnTe) peaks wasn't changed in comparison with spectrum, measured in point 1. At the same time comparative intensity of peaks became approximately equal, which can be caused by decreasing of Zn concentration on annealed surface. It is necessary to underline the fact, the that surface directly on the annealed zone isn't Te-rich, however the effect of evaporation of Cd atoms from the surface is typical for laser annealing of CZT.

The appearance of additional LO_3 repetition on the Raman spectra in the zones 3 and 4 of annealed sample is the evidence of improvement of crystal quality due to re-crystallization of the crystal lattice on the surface.

Also scanning of annealed surface (micro-Raman) was carried out, namely rectangular area about 17×80 µm which covered annealed and non-annealed surface (Fig.3) was studied. Scan step was approximately 1 µm, so measuring was performed on 1300 points of the surface.

Intensity of peak of LO_1 mode may be considered as the criteria of crystalline quality of the material, distribution of intensity allows to study its changing in different zones of the surface. On the Figure 3 (a) changing of intensity of LO_1 mode peaks is presented, namely distribution of intensity of the signal measured in the range of frequencies from 150 to 200 cm^{-1} is shown. As it is seen from Fig. 3 intensity of LO_1 peak is changing in different points of the surface, this changing is similar to measurement of single spectrum (Fig. 2). The surface of the sample can be roughly divided into four zones. The most intensive LO_1 mode is observed on the borders of annealed surface, which correspond to the zone 3. On the annealed stripwise surface (zone 4) intensity of LO_1 mode is reduced and has an intensity approximately equal to intensity of the mode on non-annealed surface (zone 1). The lowest intensity of LO_1 mode peak was observed on the zone between non-annealed area and the border of annealed stripwise area (zone 2).

We fixed similar distribution of intensity over the surface for LO_2 phonon repetition, which is characterized by presence of four zones. Studying of distribution of LO_2 mode intensity confirmed improvement of crystal quality on the borders of annealed surface (zone 3).

In order to determine Te-rich zones on the surface we studied distribution of intensity of A_1(Te) mode peak over the surface. This allowed to establish that the mostly Te-rich zone is zone 2 on the surface of the film.

Thereby the effect of laser annealing on distribution of different phases in CZT thick film was established.

4. CONCLUSION

In this work we determined that it is possible to obtain quality CZT thick films by vacuum co-evaporation of the pure CdTe and ZnTe powders from independent sources in closed space chamber

The annealing of the sample was carried out with the help of micro-Raman infrared laser. It is allowed to provide high spatial locality of the annealed area on the surface of the sample, the regular shape stripwise annealed area with about 2 µm width was obtained.

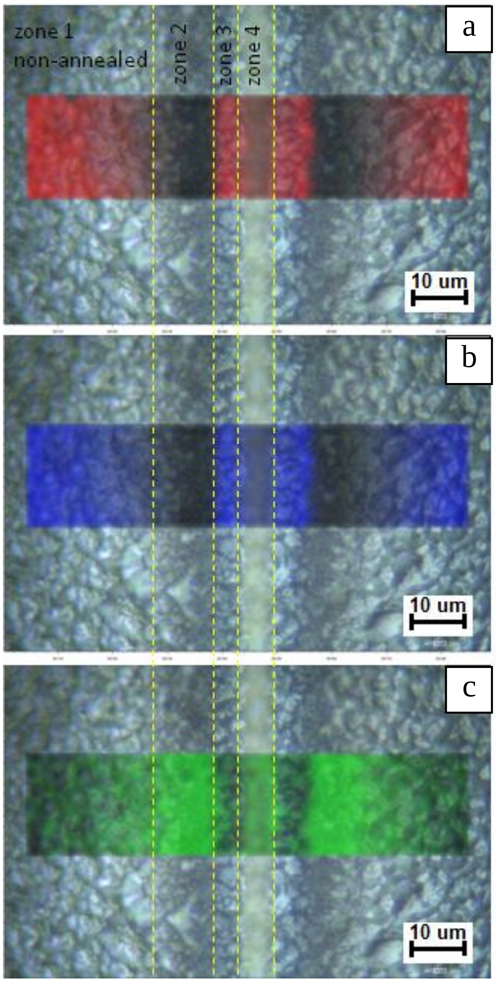

Fig. 3 – Distribution of intensity of Raman spectrum peaks on the surface of sample: LO_1 mode (a), LO_2 mode (b), Te(A1) mode (c).

More detailed study of the sample allowed to determine four zones around annealed area. In particular, the following zones were detected: 1) unchanged zone which is placed on a sufficiently large distance from annealed area; 2) Te-rich zone formed as a result of the evaporation of Cd atoms from the surface; 3) very Zn-poor region near stripwise annealed area, which has enhanced crystal quality; 4) more Zn-rich and Te-rich material on stripwise annealed area, this zone also has enhanced crystal quality.

Our studies have shown that the laser annealing can be applied for enhancement of crystal quality of polycrystalline CZT thick films. Obtained results could be used to improve efficiency of X-ray detectors based on CZT solid solutions.

AKNOWLEDGEMENTS

This research was supported by the Ministry of Education and Science of Ukraine (Grant No. (№ 0113U000131 and 0112U000772)) and Erasmus Ianus Program.

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