Proceedings of the 43rd "Jaszowiec", International School and Conference on the Physics of Semiconductors, Wisła 2014

High-Resolution X-Ray Diffraction Studies on MBE-Grown *p*-ZnTe/*n*-CdTe Heterojunctions for Solar Cell Applications

K. Wichrowska*, J.Z. Domagala, T. Wosinski, S. Chusnutdinow and G. Karczewski
Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, 02-668 Warszawa, Poland

High-resolution X-ray diffractometer was used to study structural quality, lattice parameters and misfit strain in p-ZnTe/n-CdTe heterojunctions grown by the molecular-beam epitaxy technique on two different (001)-oriented substrates of GaAs and CdTe. The X-ray diffractometer results indicate that the CdTe layers, grown on lattice mismatched GaAs substrate, are partially relaxed, by the formation of misfit dislocations at the interface, and display residual vertical strain of the order of 10^{-4}. The presence of threading dislocations in the layers effectively limits the efficiency of solar energy conversion in the investigated heterojunctions. Homoepitaxially grown CdTe layers, of much better structural quality, display unexpected compressive strain in the layers and the relaxed lattice parameter larger than that of the substrate. Possible reasons for the formation of that unusual strain are discussed.

DOI: 10.12693/APhysPolA.126.1083
PACS: 61.05.cp, 81.05.Dz, 81.15.Hi, 88.40.jm

1. Introduction

Heterojunctions based on cadmium telluride (CdTe) belong to the most promising devices for fabrication of high-efficient thin film solar cells. CdTe is a II–VI compound semiconductor with a direct band gap of 1.5 eV that is nearly optimally matched to the solar spectrum for photovoltaic energy conversion, and a high absorption coefficient, of about 10^5 cm^{-1}, at the photon energy above the band gap. However, despite these advantages, there are still a lot of difficulties in obtaining high-efficient solar cells based on CdTe. An important issue, in this respect, is the structural quality of CdTe thin films. Recently, we have shown that most likely extended defects act as the main recombination centres responsible for reduction of energy conversion efficiency in CdTe-based solar cells, epitaxially grown on (001)-oriented GaAs substrates [1].

On the other hand, only few papers reporting on investigations of structural quality of CdTe films epitaxially grown on (001)-oriented GaAs substrates have been published so far [2–5]. They present results of X-ray measurements for the symmetrical reflection only, which provide information merely on the lattice parameters of CdTe layers perpendicular to the heterointerface, and possible mosaicity along the basal plane, and do not deliver accurate data on the strain relaxation. To the best of our knowledge, just one publication, by Heinke et al. [6], reported on detailed X-ray diffraction studies in CdTe layers grown by the molecular-beam epitaxy (MBE) technique on (001)-oriented CdTe substrates. Surprisingly, the obtained results revealed an unusual strain existing in the homoepitaxially grown CdTe layers.

In the present paper we report on high-resolution X-ray diffraction (XRD) investigations of p-ZnTe/n-CdTe heterojunctions, dedicated to solar cell applications, grown by MBE on both the highly lattice mismatched GaAs and much more expensive CdTe substrates.

2. Experimental details

The investigated p-ZnTe/n-CdTe heterostructures were grown by the MBE technique, under various conditions of stoichiometry, on two different substrates: (i) lattice mismatched by 14.6%, (001)-oriented GaAs and lattice matched, (001)-oriented CdTe. Initially, a highly iodine doped n-type CdTe buffer layer of above 10μm thickness was grown. Then it was covered by a 2μm thick undoped CdTe absorber and, in turn, by a 1μm thick nitrogen doped p-type ZnTe layer. The p-type ZnTe layer with the free carrier concentration of above 10^{18} cm^{-3} facilitates for preparing low-resistivity contacts to the p-type side of the junction and increases the utilized spectral range of the solar spectrum.

The XRD measurements were performed using a high resolution Philips X'Pert MRD diffractometer, equipped with X-ray mirror, four bounce Ge 220 asymmetric monochromator and Ge 220 three bounce analyzer, in triple axis configuration [7]. The structural quality, lattice parameters and misfit strain were evaluated from the measured $2\theta/\omega$ scans and reciprocal lattice maps for the symmetrical 004 and asymmetrical $\bar{3}\bar{3}5$ Bragg reflections of Cu K_{α_1} radiation. X-ray reciprocal lattice maps were recorded by performing a series of $2\theta/\omega$ scans.

3. Experimental results and discussion

During the CdTe layer growth process, and the post-growth temperature lowering to the room temperature, the cubic crystal structure can be deformed to thetetragonal one. The values of the lattice parameters

*corresponding author; e-mail: olender@ifpan.edu.pl

perpendicular, c, and parallel, a, to the interface between the CdTe layers and GaAs or CdTe substrates were determined from the measured $2\theta/\omega$ scans for the symmetrical 004 and asymmetrical $\bar{3}\bar{3}5$ reflections, respectively. Typical $2\theta/\omega$ scans for the CdTe layers grown on two different substrates, as well as for the CdTe substrate, are presented in Fig. 1. The results for the 004 reflection, presented in Fig. 1a, show that the diffraction peaks corresponding to both the CdTe layers, grown on the GaAs and CdTe substrates, shift to smaller Bragg angles, with respect to that of the CdTe substrate, pointing to a larger vertical lattice parameter c than that of the CdTe substrate. On the other hand, the in-plane lattice parameters a, determined from the results obtained for both the 004 and $\bar{3}\bar{3}5$ reflections, are smaller than the lattice parameter of CdTe substrate. The obtained values of c and a are listed in Table I.

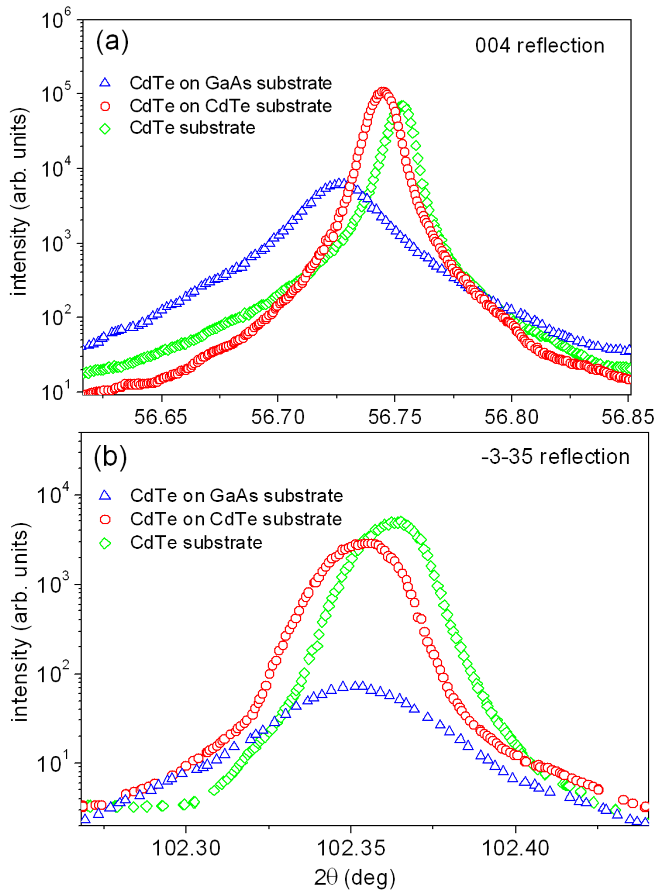

Fig. 1. XRD $2\theta/\omega$ scans for CdTe layers grown on GaAs and CdTe substrates, as well as for the CdTe substrate for the symmetrical 004 reflection (a) and the asymmetrical $\bar{3}\bar{3}5$ reflection (b). The presented scans have been smoothed for better clarity.

The relaxed lattice parameters were calculated from Eq. (1):

$$a_{\mathrm{relax}} = (c + 2ba)/(1 + 2b), \tag{1}$$

TABLE I

Lattice parameters perpendicular and parallel to the interface plane for the CdTe layers grown on GaAs and CdTe substrates and for the CdTe substrate. The calculated relaxed lattice parameters and residual vertical strains are also shown.

Sample (substrate)	c [Å] ($\pm$0.0001)	a [Å] ($\pm$0.0003)	a_{relax} [Å]	Vert. strain [$\times 10^{-4}$]
CdTe (GaAs)	6.4851	6.4811	6.4833	2.78
CdTe (CdTe)	6.4834	6.4817	6.4826	1.23
CdTe substrate	6.4822	6.4823	–	–

where $b = (1-\nu)/(1+\nu)$, and ν is the Poisson ratio given by $\nu = C_{12}/(C_{11}+C_{12})$, where $C_{11} = 5.351\times10^{10}$ N/m^2, $C_{12} = 3.681\times10^{10}$ N/m^2 [8] are the elastic stiffness constants of CdTe. The calculated a_{relax} parameters are listed in Table I. Surprisingly, in the both measured layers this parameter was larger than that of the CdTe substrate, in contradiction to the expectation of the same lattice parameters of the layer and substrate in the case of homoepitaxial growth.

CdTe layers grown epitaxially on GaAs substrates suffer from biaxial compressive strain due to the lattice parameter mismatch and the difference in thermal expansion coefficient between CdTe (4.8×10^{-6} K^{-1}) and GaAs (5.7×10^{-6} K^{-1}) [2]. Usually, at the growth temperature, the strain caused by lattice mismatch between CdTe and GaAs is rapidly relaxed within about 3 μm by formation of misfit dislocations at the interface. The residual strain observed in thicker layers results from the difference between the thermal expansion coefficients of the layer and substrate. At room temperature this strain is of the order of 10^{-4} [3]. For homoepitaxial layers these effects should not occur due to the same lattice constant and expansion coefficient of the substrate and layer material. Vertical strain ε in the measured layers was calculated from Eq. (2) and is presented in Table I:

$$\varepsilon = (c - a_{\mathrm{relax}})/a_{\mathrm{relax}}. \tag{2}$$

The XRD results indicate that the CdTe layers, grown under compressive strain on GaAs substrate, are almost fully relaxed and display only residual vertical strain of the order of 10^{-4} caused by different expansion coefficients between CdTe and GaAs. Unexpectedly, compressive vertical strain of the same order of magnitude was also revealed in the homoepitaxially grown CdTe layers. Qualitatively similar results, of even larger vertical strain of about 5×10^{-4}, were reported by Heinke et al. [6] for CdTe layers MBE-grown on CdTe substrates.

In order to elucidate this phenomenon we performed reciprocal lattice mapping of the investigated structures. The exemplary maps presented in Fig. 2 clearly evidence that the structural quality of the CdTe layers grown on CdTe substrate was significantly better than that of the layers grown on GaAs substrate and similar to that of the CdTe substrate. Table II contains values of full width at half maximum (FWHM) of 004 and $\bar{3}\bar{3}5$ reflections of the measured intensity integrated along the horizontal angle axis $2\theta/\omega$ and the vertical angle axis ω. It is seen that for the layers grown on GaAs substrate the values of FWHM are an order of magnitude larger than those obtained for the layers grown on CdTe substrate. High density of threading dislocations, generated at the mismatched interface with the substrate and propagated through the layers grown on GaAs, are expected to be responsible for the considerable increase in the FWHM values. In fact, our recent transmission electron microscope (TEM) measurements [9] confirm the presence of threading dislocations in the layers grown on GaAs, which may limit the efficiency of solar energy conversion in the investigated heterojunctions.

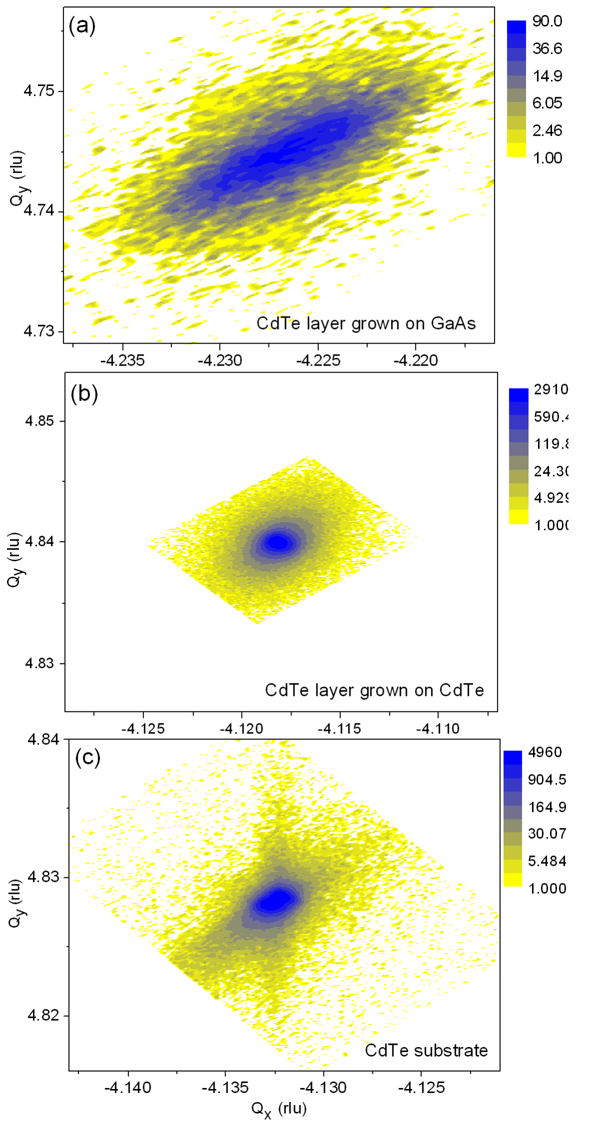

Fig. 2. Reciprocal lattice maps of the CdTe layers grown on GaAs (a) and CdTe (b) substrates and of the CdTe substrate (c) for the $\bar{3}\bar{3}5$ XRD reflection, where the horizontal and vertical axes correspond to the $2\theta/\omega$ and ω angles, respectively, in the reciprocal lattice units.

TABLE II

Values of FWHM [arcsec] for the 004 and $\bar{3}\bar{3}5$ reflections of the measured intensity integrated along the horizontal angle axis $2\theta/\omega$ and the vertical angle axis ω.

Sample (substrate)	$FWHM_\omega$ 004	$FWHM_{2\theta/\omega}$ 004	$FWHM_\omega$ $\bar{3}\bar{3}5$	$FWHM_{2\theta/\omega}$ $\bar{3}\bar{3}5$
CdTe (GaAs)	288	288	388.8	144
CdTe (CdTe)	28.8	39.6	28.8	72
CdTe substrate	32.4	36	39.6	72

On the other hand, the FWHM values obtained for the homoepitaxially grown CdTe layer are even lower than those for the CdTe substrate, indicating for better structural quality of the layer than that of the substrate. Moreover, the relaxed lattice parameter of this layer is the same as the recent theoretical value $a_0 = 6.4827$ Å [10], which is distinctly larger than the lattice parameter of the CdTe substrate; cf. Table I.

Heinke et al. [6] suggested a twin formation as the most likely mechanism responsible for producing the unexpected compressive strrain in the homoepitaxially grown CdTe layers. However, our thorough TEM investigations [9] did not reveal a presence of any twins in the homoepitaxially grown CdTe layer. To verify possible influence of free charge carriers to the layer lattice parameters [11] we calculated lattice changes due to the presence of free electrons in the CdTe layers. The calculated effects were much smaller than the experimentally observed ones. Taking into account our present results, we suggest that not enough good structural quality of CdTe substrates could be responsible for the unusual strain observed in homoepitaxially grown CdTe layers. Bulk CdTe crystals grown by the Bridgman technique contain usually a high concentration of CdTe vacancies [12], which may result in slightly decreased lattice parameter of the substrates employed for homoepitaxial CdTe growth.

4. Summary

We have studied the structural quality and the influence of substrate on epitaxially grown p-ZnTe/n-CdTe heterojunctions for solar cell applications. The CdTe layers, grown under compressive strain on GaAs substrate, are almost fully relaxed and display residual strain of the order of 10^{-4}. This strain is caused by different expansion coefficients between CdTe and GaAs. The strain associated with lattice mismatch completely relaxed at the growth temperature by the formation of misfit dislocations. The CdTe layers grown on CdTe substrate display much better structural quality. However, they exhibit unexpected compressive strain and the relaxed lattice parameter larger than that of the substrate. On the ground of our results, we exclude a twinning, which was previously proposed for explanation of that unusual strain, and point to a rather inadequately good structural quality of CdTe substrates as responsible for that unusual strain.

Acknowledgments

This work was supported by the European Union within European Social Fund through Human Capital Programme and within the European Regional Development Fund through the Innovative Economy grant MIME (POIG.01.01.02-00-108/09).

References

[1] G. Karczewski, S. Chusnutdinow, K. Olender, T. Wosiński, T. Wojtowicz, *Phys. Status Solidi C* **11**, 1296 (2014).

[2] H. Tatsuoka, H. Kuwabara, H. Fujiyasu, Y. Nakanishi, *J. Appl. Phys.* **65**, 2073 (1989).

[3] H. Tatsuoka, H. Kuwabara, Y. Nakanishi, H. Fujiyasu, *J. Appl. Phys.* **67**, 6860 (1990).

[4] J.F. Wang, K. Kikuchi, B.H. Koo, Y. Ishikawa, W. Uchida, M. Isshiki, *J. Cryst. Growth* **187**, 373 (1998).

[5] J. Domagała, J. Bąk-Misiuk, J. Adamczewska, Z.R. Zytkiewicz, E. Dynowska, J. Trela, D. Dobosz, E. Janik, M. Leszczyński, *Phys. Status Solidi A* **171**, 289 (1999).

[6] H. Heinke, A. Waag, M.O. Möller, M.M. Regnet, G. Landwehr, *J. Cryst. Growth* **135**, 53 (1994).

[7] O. Yastrubchak, T. Wosiński, J.Z. Domagała, E. Łusakowska, T. Figielski, B. Pécz, A.L. Tóth, *J. Phys. Condens. Matter* **16**, S1 (2004).

[8] D.G. Thomas, *J. Appl. Phys.* **32**, 2298 (1961).

[9] K. Wichrowska, T. Wosinski, S. Kret, M. Rawski, O. Yastrubchak, S. Chusnutdinow, G. Karczewski, to be published.

[10] Inorganic Crystal Structure Database (ICSD) 01-070-8041.

[11] M. Leszczynski, J. Bak-Misiuk, J. Domagala, J. Muszalski, M. Kaniewska, J. Marczewski, *Appl. Phys. Lett.* **67**, 539 (1995).

[12] A. Carvalho, A.K. Tagantsev, S. Öberg, P.R. Briddon, N. Setter, *Phys. Rev. B* **81**, 075215 (2010).