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Low-Temperature Deposition of Cd_{1-x}Zn_xTe Layers by Laser Sputtering and their Physical Properties

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CdZnTe films were grown by the method of modulated infrared laser deposition at a substrate temperature $T_{\text{sub}} \leq 120^\circ\text{C}$ from appropriate sources on oriented single-crystal substrates Si, GaAs, InSb in the same technological conditions in one technological cycle. Surface morphology and spectra of low-temperature photoluminescence ($T = 4.2\text{ K}$) in the energy range from 1.30 to 1.70 eV were studied. Luminescence spectra were analyzed and presented from three different energy regions: from 1.70 eV to 1.60 eV with exciton emission, from 1.60 eV to 1.55 eV by donor-acceptor transitions (DAP) and region A-centers from 1.55 to 1.40 eV. The presence in the low-temperature photoluminescence spectra of free exciton bands, excitons on the neutral acceptor and neutral donor, and their phonon replicas on CdZnTe/InSb films testifies to the high structural perfection inherent in materials of detector quality with composition corresponding of the CdZnTe-target.

Keywords: passivating coatings, cadmium telluride, thin films, laser epitaxy, low temperature photoluminescence.

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Introduction

CdTe binary semiconductors and solid solutions based on them are of considerable interest for the creation of infrared radiation detectors, solar energy converters including tandem solar cells, γ - and X-ray detectors [1-5], as well as buffer semi-insulating films in the formation of heterostructures and passive coatings of heterostructures based on narrow-gap semiconductors. Until now, much interest has been focused on single-crystal CdZnTe detectors, but there are some difficulties in manufacturing an ideal CdZnTe bulk single-crystal material to obtain crystals of sufficiently high optical quality with satisfactory electrophysical properties. Therefore, to obtain homogeneous and relatively inexpensive homogeneous materials of large area in recent years, film technological methods for the growth of solid solutions of CdZnTe have been developed. In addition, interest in CdZnTe films is also caused by the possibility of creating quantum dots based on them for spin and quantum information systems with a characteristic spin relaxation time [6]. There are different methods of obtaining Cd₁₋

_xZn_xTe films: molecular beam epitaxy [7-8], electrodeposition [9], close space sublimation [10], laser ablation [11], hot wall epitaxy [12], metalorganic chemical vapor deposition (MOCVD) [13] and magnetron scattering [14, 15].

The main task of this work was to study the possibility of promising use of IR laser methods for deposition of multicomponent semiconductor sources with low dissociation energy (atomization), which for solid solutions of cadmium telluride is less than 1 eV. In traditional technological thin-film methods this problem is a serious obstacle and requires relatively high (more than 120 °C) layer growth temperatures, which leads to deviations from the stoichiometric composition of the material already in the process of growth.

I. Experiment

Cd_{1-x}Zn_xTe films were grown in a vacuum of 10^{-7} - 10^{-6} torr. from single-crystal plates with a given concentration of zinc, cut from Ø40 mm single crystals grown by the vertical Bridgman method. To eliminate the

splashing effect and the implementation of congruent evaporation, the X-Y geometry was used to scan focused infrared laser radiation without overlapping the spray zones.

The spectral region of the laser radiation was significantly below the intrinsic absorption edge of Cd_{1-x}Zn_xTe ($\hbar\omega \ll E_g$). Discreteness and scattering time at each point of the source was set based on the problem. The temperature of the substrates was monitored during growth and did not exceed 120 °C. The layers were deposited on (111)Si, (111)GaAs and (001)InSb single-crystal substrates, which have different constant lattices and coefficients of thermal expansion.

II. AFM study of film morphology

The surface morphology of films of the same thickness ($h = 2.5 \mu\text{m}$) grown in one technological cycle of laser epitaxy on substrates with different constant lattices, but with the same crystallographic orientation, was studied by atomic force microscopy (AFM). Silicon probes had a nominal radius of curvature of the tip up to 10 nm. From a detailed analysis of the topology of the deposited layers, it was found that depending on the constant lattice of the substrates, a different surface relief is formed, and the surface parameters are not so much sensitive to the film thickness as to the substrate material (Fig. 1). The deposited layers on mismatched substrates are characterized, in contrast to CdZnTe/InSb single-crystal films, by a nanocrystalline structure with not only different sizes and roughness, but also different crystal structure, which are formed with the transition from two-dimensional growth to nanocluster structures.

III. Low temperature photoluminescence

Detailed studies of low-temperature photoluminescence (LTP) were carried out in the spectral region 1.3 - 1.7 eV at a temperature of 4.2 K. The excitation was carried out by an argon laser at a wavelength $\lambda = 488.0 \text{ nm}$.

The main attention was paid to the study of the behavior of LTP lines in three characteristic spectral

regions of luminescence - bound exciton (on the neutral acceptor A⁰X and on the neutral donor D⁰X), donor-acceptor emission (DA) and in the low-energy region - (A centers). All films are characterized by the presence of an exciton region of complex structure, but of different intensity depending on the type of substrate (Fig. 2). The exciton region is most intense in films obtained on semiconductor substrates with close lattice constant values.

However, the structuring of the exciton band is observed only on films grown on (001) InSb substrates. The shape of the exciton band in the films on other substrates is expanded, and corresponds to the nanocrystalline structure. According to the position and intensity of the exciton bands on the neutral acceptor A⁰X ($h\nu = 1.6305 \text{ eV}$) and the donor D⁰X ($h\nu = 1.6355 \text{ eV}$) in the original crystal (Fig. 2) and CdZnTe/ InSb films, it can be judged that the concentration of small donors in the crystal is higher than in the obtained films because $(A^0X / D^0X)_{cr} < (A^0X / D^0X)_f$. The determined E_g of the obtained films in comparison with the E_g of source showed a slight difference in the band gap ($E_g \approx D^0X + 0.0128 \approx 1.6483 \text{ eV}$), which is a confirmation of the congruence of evaporation of the target by IR laser radiation. In addition, transverse and longitudinal polariton branches ($X_T = 1.6377 \text{ eV}$, $X_L = 1.6399 \text{ eV}$) of free exciton FE and their phonon replicas $(X_T - 1LO) = 1.6170 \text{ eV}$ and $(X_L - 1LO) = 1.6192 \text{ eV}$ and excited state band of free exciton FE ($n = 2$) = 1.6470 eV with phonon replica $(FE (n = 2) - 1LO) = 1.6263 \text{ eV}$ are observed in the short-wavelength region of the spectrum. The cleavage in CdZnTe between the polariton branches is about 2 meV.

It should also be noted that the presence in the exciton spectral region of the complex structure of the bands and especially FE ($n = 2$) and $(FE (n = 2) - 1LO)$ is evidence of the structural perfection of the grown films in contrast to the films on GaAs and Si satellite substrates, where the exciton region of radiative recombination is extremely weak and is unstructured.

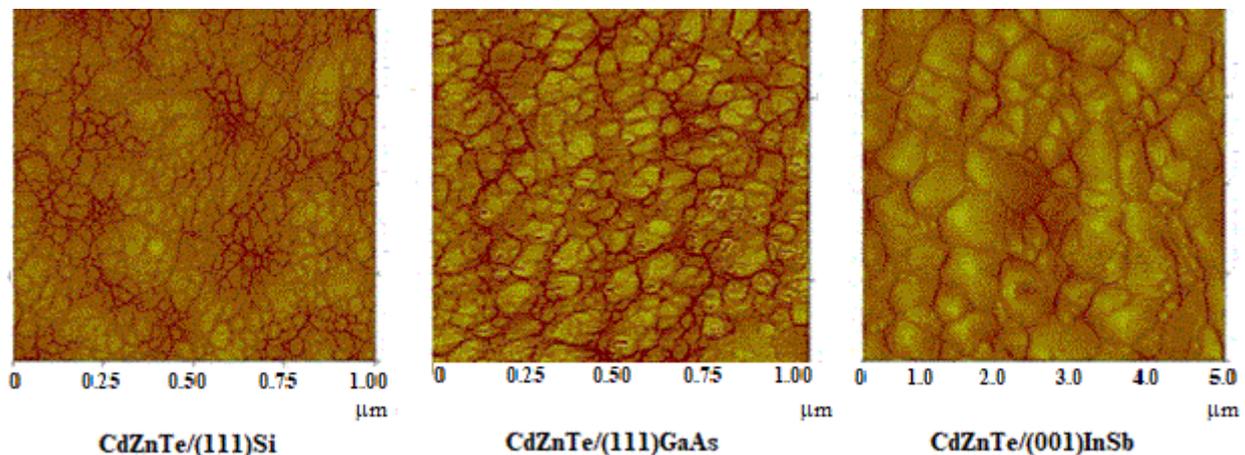


Fig. 1. AFM surface morphology of Cd_{1-x}Zn_xTe films on Si, GaAs and InSb substrates.

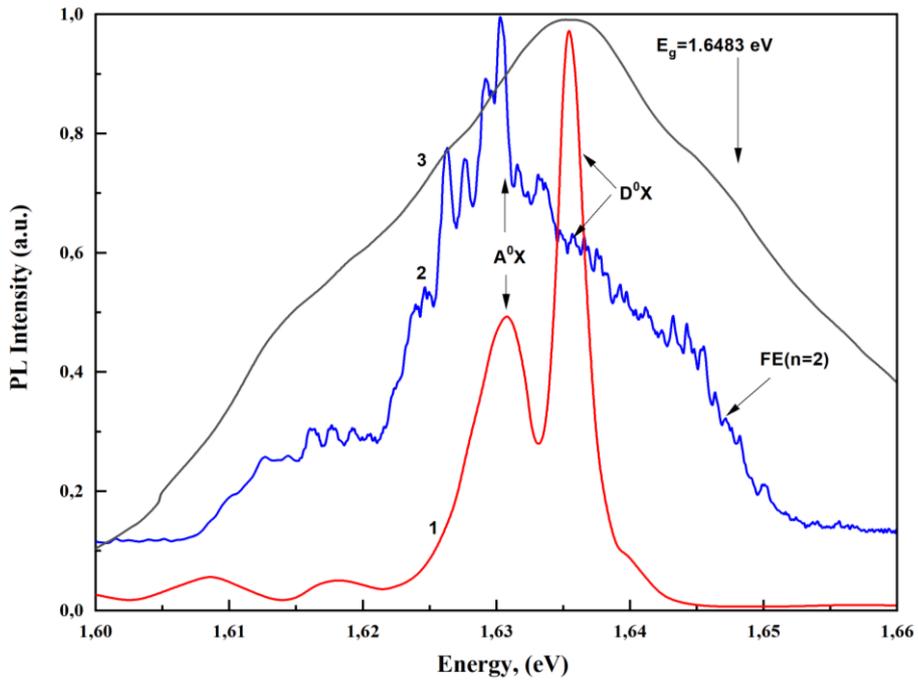


Fig. 2. Exciton region of LTP of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films at a temperature $T = 4.2\text{K}$. 1- $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ target source crystal; 2- $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ film on an InSb substrate; 3- $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ film on a GaAs substrate.

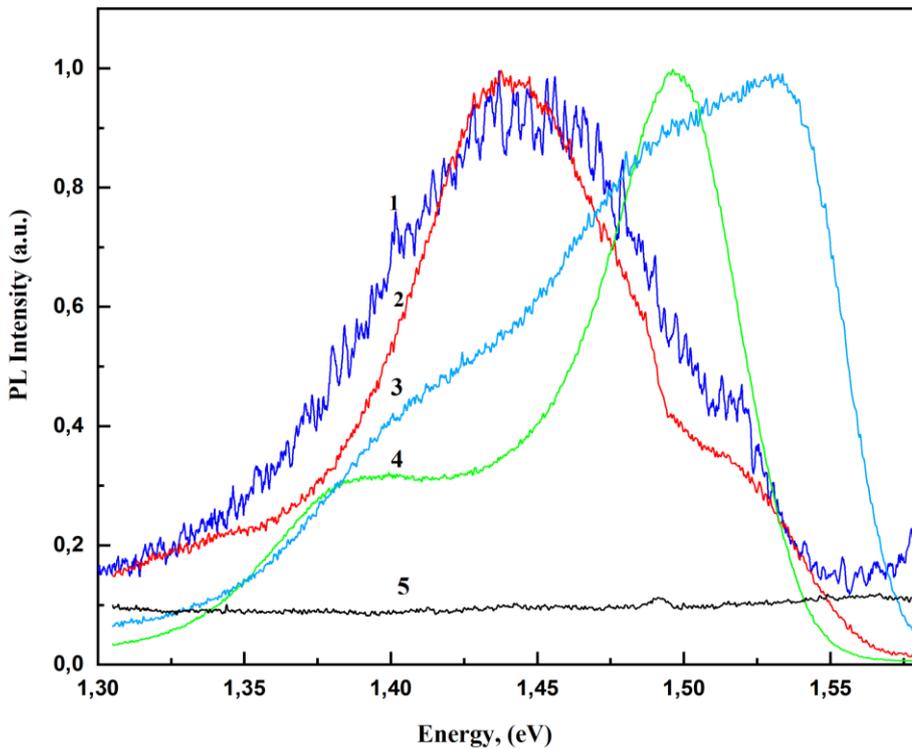


Fig. 3. Spectral dependence of LTP in the area of the zone - acceptor (BA), donor-acceptor pairs (DAP) and A-centers. 1- $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ target source crystal; 2- $\text{Cd}_{1-x}\text{Zn}_x\text{Te} / \text{GaAs}$; 3- $\text{Cd}_{1-x}\text{Zn}_x\text{Te} / (111) \text{Si}$; 4- $\text{Cd}_{1-x}\text{Zn}_x\text{Te} / (001) \text{Si}$., 5- $\text{Cd}_{1-x}\text{Zn}_x\text{Te} / \text{InSb}$.

The low-energy region of the spectrum - DA + BA (1.55 - 1.6 eV) radiation, the region of DAP - 1.5 - 1.55 eV) and A-centers - 1.4 - 1.5 eV are most intensely manifested on single-crystal GaAs and Si substrates. Figure 3 shows that the bands of this spectral region are intense, wide and unstructured, which

complicates their interpretation on the one hand, but on the other hand indicates the presence of defects of the same nature of different concentration.

On InSb semiconductor substrates, there is no radiation in this spectral region, which indicates a much lower concentration of relatively deep donor and acceptor

centers in CdZnTe and radiation centers in the region of the CdZnTe-InSb hetero-paired interface (HP), which can be explained almost by the coincidence of their crystal structures and constant lattices ($a_{\text{InSb}} = 6.479 \text{ \AA}$, $a_{\text{CdTe}} = 6.477 \text{ \AA}$). Calculations show, and the LTP confirms that the expected density of states at the HP InSb–CdTe boundary should not exceed the value of $N_s = 6.2 \times 10^{11} \text{ cm}^{-2}$. In all other cases, the CdZnTe/Si (GaAs) layers change their morphology from amorphous to polycrystalline with different crystallite sizes. An amorphous phase at the intercrystalline boundaries is also not excluded. Therefore, the area - DA + BA, DAP and A-centers of radiation are also due to the presence of recombinant channels of intercrystalline boundaries of different nature.

Conclusion

On the basis of conducted research, it has been shown that when fulfilling the requirements for the use of the IR laser epitaxy method, which are determined by the thermophysical properties of the semiconductor source and laser radiation parameters, the developed

technological method can be used to produce perfect layers based on solid solutions of CdZnTe on different types of substrates at low growth temperatures, which can be used for low-temperature passivation of IR receivers based on HgCdTe, the creation of ionizing radiation detectors and in tandem (multi-stage) solar cell technology. It is established that CdZnTe films obtained by the method of IR laser deposition on substrates with similar lattice parameters and coefficients of thermal expansion are characterized by high structural perfection with the composition corresponding to the material source at much lower deposition temperatures $T_{\text{sub}} \leq 120^\circ\text{C}$, which makes it possible to obtain multilayer structures with specified properties and architecture and thus helps to solve problems in the realization of highly efficient active and passive elements based on them.

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- [1] S. Chander, M.S. Dhaka, Thin Solid Films 625, 131 (2017); <https://doi.org/10.1016/j.tsf.2017.01.052>.
- [2] S. Chander, A. Purohit, S.L. Patel, M.S. Dhaka, Phys. E. 89, 29 (2017); <https://doi.org/10.1016/j.physe.2017.02.002>.
- [3] S. Chander, M.S. Dhaka, Sol. Energy 150, 577 (2017); <https://doi.org/10.1016/j.solener.2017.05.013>.
- [4] G.Q. Zha, Y. Lin, D.M. Zeng, T.T. Tan, W.Q. Jie, Appl. Phys. Lett. 106, 062103 (2015); <http://dx.doi.org/10.1063/1.4907973>.
- [5] H.Q. Le, J.L. Ducote, S. Molloy, Med. Phys. 37, 1225 (2010); <http://dx.doi.org/10.1118/1.3312435>.
- [6] C. Li, N. Murase, Chem. Lett., 34(1), 92 (2005); <https://doi.org/10.1246/cl.2005.92>.
- [7] X. Zhao *et al.*, Appl. Phys. Lett. 105(25), 252101 (2014); <https://doi.org/10.1063/1.4904993>.
- [8] C.L. Littler, B.P. Gorman, D.F. Weirauch, P.K. Liao, H.F. Schaake, J. Electron. Mater. 34, 768 (2005); <https://doi.org/10.1007/s11664-005-0018-4>.
- [9] M. Basol, V.K. Kapur, M.L. Ferris, J. Appl. Phys. 66, 1816 (1989); <https://doi.org/10.1063/1.344353>.
- [10] S.N. Alamri, Phys. Status Solidi (a) 200, 352 (2003); <https://doi.org/10.1002/pssa.200306691>.
- [11] Aydinli, A. Compaan, G. Contreras-Puente, A. Mason, Solid State Commun. 80, 465 (1991); [https://doi.org/10.1016/0038-1098\(91\)90051-V](https://doi.org/10.1016/0038-1098(91)90051-V).
- [12] J. Takahashi, K. Mochizuki, K. Hitomi, T. Shoji, J. Cryst. Growth 269, 419 (2004); <https://doi.org/10.1016/j.jcrysgro.2004.05.054>.
- [13] H. Zhou, D. Zeng, S. Pan, Instrum. Methods Phys. Res. Sect. A: Accel. Spectrom. etect. Assoc. Equip. 698, 81 (2013); <https://doi.org/10.1016/j.nima.2012.09.024>.
- [14] Q. Huda; M.M. Aliyu; M.A. Islam; M.S. Hossain; M.M. Alam; M.R. Karim; M.A.M. Bhuiyan; K. Sopian; N. Amin, (IEEE 39th Photovoltaic Specialists Conference, (PVSC), 2013); <https://doi.org/10.1109/PVSC.2013.6744242>.
- [15] E. Yilmaz; R. Turan; A. Aktağ; Ali Akgöl, 37th IEEE Photovoltaic Specialists Conference (2011); <https://doi.org/10.1109/PVSC.2011.6186216>.

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Низькотемпературне осадження плівок $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ лазерним розпорощенням та їх фізичні властивості

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Плівки CdZnTe , вирощені методом модульованого ІЧ-лазерного осадження при температурі підкладок $T_{\text{sub}} \leq 120^\circ\text{C}$ з відповідних джерел на орієнтованих монокристалічних підкладках Si , GaAs , InSb в однакових технологічних умовах і в одному технологічному циклі. Досліджувалися морфологія поверхні та спектри низькотемпературної фотолюмінесценції ($T = 4.2\text{ K}$) в діапазоні енергій від 1,70 до 1,30 еВ. Спектри люмінесценції проаналізовано і представлено з трьох різних енергетичних областей: від 1,70 еВ до 1,60 еВ з емісією екситонів, від 1,60 еВ до 1,55 еВ переходами донор-акцептор (DAP) та областю А – центрів від 1,55 до 1,40 еВ. Наявність в спектрах низькотемпературної фотолюмінесценції смуг вільного екситону, екситонів на нейтральному акцепторі та нейтральному донорі і їх фононних повторень на плівках CdZnTe/InSb засвідчує високу структурну досконалість, притаманну матеріалам детекторної якості, зі складом, відповідним джерелу CdZnTe .

Ключові слова: пасивуючі покриття, телурид кадмію, тонкі плівки, лазерна епітаксія, низькотемпературна фотолюмінесценція.