

## GRADED BAND-GAP FORMATION IN SEMICONDUCTOR SINGLE CRYSTAL BY LASER RADIATION

## GRADIENTA VEIDOŠANAS PUSVADĪTĀJĀ MONOKRISTĀLĀ LĀZERA STAROJUMA IEDARBĪBĀ

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*Keywords: Cd<sub>1-x</sub>Zn<sub>x</sub>Te; laser; Thermogradient effect; Graded band-gap*

### Introduction

One of the most perspective methods of processing of semiconductors providing high localness, "technological" cleanliness, speed of processing by their operated updating of electric and recombination properties is laser operating methods. Change of structure of a material [1], occurrence of barrier structures [2] at laser processing the semiconductor is the most important problem of electronics.

CdTe and solid solutions on its basis are the basic materials of modern optoelectronics applied for manufacturing solar batteries, semiconductor detectors of X- and  $\gamma$  - radiations. Laser processing CdTe causes generation various point defects of their redistribution under action of a temperature gradient [1]. For example, generation A-centers and interstitial Cd in CdTe (CI) by laser irradiation [2]. Works [3-13] are devoted to research of influence of laser radiation on structure of a material and property of semiconductors. So, in work [3], theoretical calculations were made, and they assume enrichment of Cd<sub>x</sub>Hg<sub>1-x</sub>Te near to a surface layer by Hg what is caused by "phonon wind" arising during a laser irradiation. However, submitted calculations do not allow making an unequivocal conclusion by mechanisms of mass transfer. For example, the increase of pulse duration of an irradiation in a microsecond range leads to increase in efficiency of "phonon wind" influence. But the reduction of a temperature gradient causes the reduction of efficiency of "phonon wind" influence that contradicts early made to conclusions. Tauc [14] was the first who pointed out a possibility of TGE for electron-hole pairs and created his theory. In [15] authors have showed theoretically the essential difference of laser induced impurity diffusion on an example GaAs on a comparison with isothermal process. Authors of [16] have developed the theory of this phenomenon for common case.

According to the TGE theory [15] the interstitial atoms Cd ( $Cd_i$ ) move in the temperature gradient field against  $\text{grad } T$ . Accordingly, the vacancies Cd ( $V_{Cd}$ ) move in opposite direction i.e. -towards the minimum temperature. The purpose of the given work is the further studying processes occurring near to surface areas  $Cd_{1-x}Zn_xTe$  under action of laser radiation.

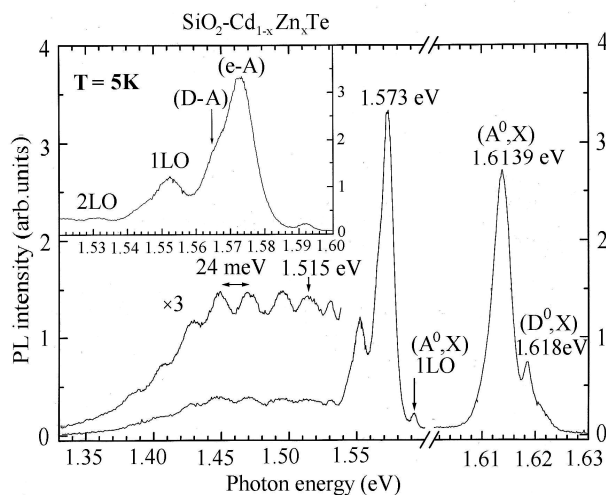
$Cd_{1-x}Zn_xTe$  was chosen as an investigation object, because this material is widely used in radiation techniques for the production of detectors of X- and  $\gamma$ -radiation, and other hard radiation

## Experimental details

The following method has been used in the work: photoluminescence (PL). The PL method allows one to investigate the energy spectrum and concentration of luminescence centers. Single crystals of  $Cd_{1-x}Zn_xTe$  ( $x=0,06$ ), growing from the melt by the modified Bridgman method under an overpressure of Cd, were used in our experiments. Irradiation was carried out at room temperature and atmospheric pressure. The samples have been irradiated by the second harmonic ( $\lambda = 532 \text{ nm}$ ,  $\tau=15\text{ns}$ ) of the YAG:Nd laser in Q-modulation with the intensity from  $0,2\text{MW}/\text{cm}^2$  to  $2\text{MW}/\text{cm}^2$ . It is necessary to use the second harmonic of YAG:Nd laser with higher absorption coefficient for creation high  $\text{grad } T$ . The irradiated surface of crystal was covered with a thin layer of  $\text{SiO}_2$  in order to avoid material evaporation by laser heating. The thickness of  $\text{SiO}_2$  layer was  $0,3\mu\text{m}$  and it was transparent for laser radiation. PL spectra were measured at 5 K using 514 nm line of an Ar+ laser with excitation powers of less than 200mW. The samples were sides to  $10\times 10\times 2 \text{ mm}^3$ .

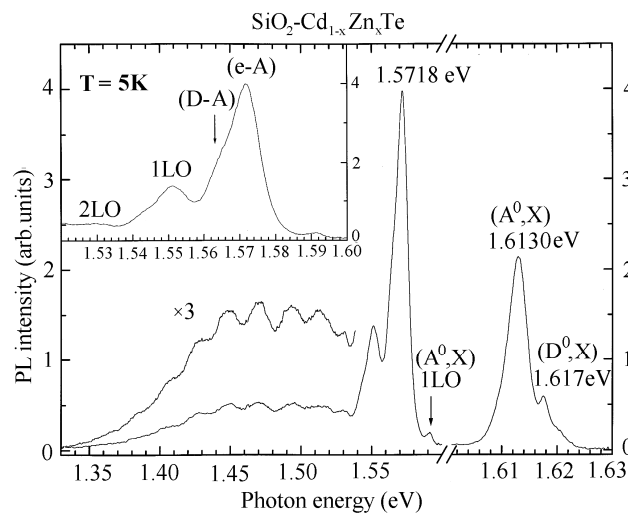
## Results and discussion

Low-temperature PL is a nondestructive method, by which optical emission processes occurring in the semiconductor can be individually observed. For the best resolution the PL spectra were measured at 5K in range of 1.35 to 1.63 eV. The PL spectra before laser radiation is presented in Fig.1 The initial PL spectrum contains an intensive line ( $A_0, X$ ) at 1.6139 eV ascribed to excitons bound to shallow acceptors (Cd vacancies -  $V_{Cd}$ ) and a weaker line ( $D^0, X$ ) of excitons bound to shallow donors at 1.6186 eV

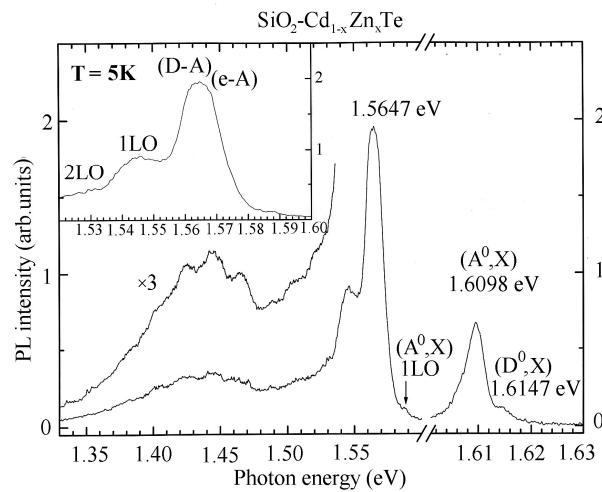


**Fig.1.** PL spectra measured from  $Cd_{1-x}Zn_xTe$  sample before laser radiation.

The PL band around 1.55 eV is caused by recombination of donor-acceptor pairs (DAP) and consists of the zero-phonon line (ZPL) at 1.592 eV and its LO-phonon replicas. After laser irradiation of  $Cd_{1-x}Zn_xTe$  crystal with intensity  $0.2 \text{ MW/cm}^2$  all the lines of PL spectra start to shift to lower energy of spectra (red shift). The shift of  $A^0X$  line at this intensity was 7 meV (Fig.2). In turn, spectral shift of the  $A^0X$  line at maximal laser intensity  $I=2\text{MW/cm}^2$  was 41meV (Fig. 3). Such laser treatment of the semiconductor leads to the generation of additional point defects at the interface, first of all  $V_{Cd}$  and  $Cd_i$ . In a recent study [17] have shown that the incorporation of Zn into the CdTe lattice results in a significant reduction of cadmium vacancies in the structure of the mixed crystal.

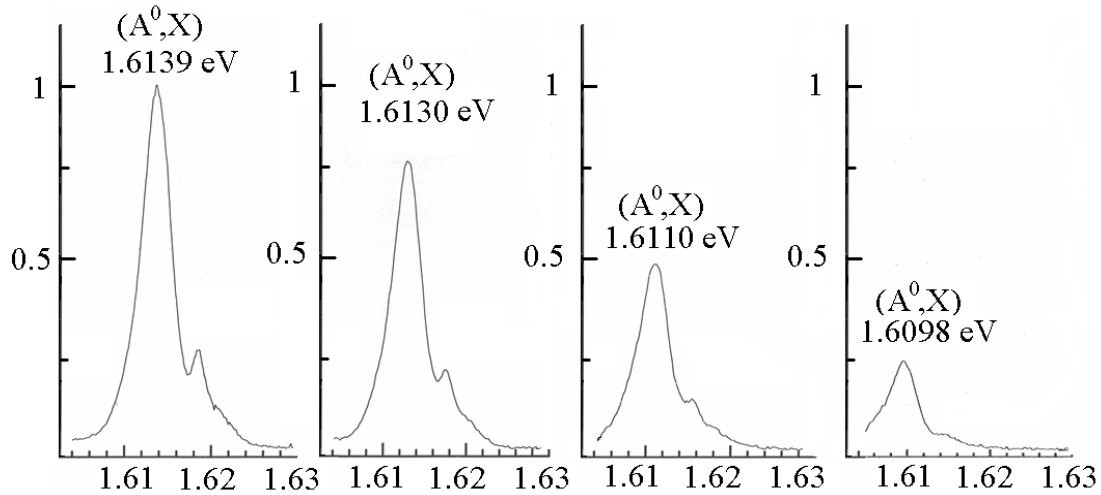


**Fig.2.** PL spectra measured from  $Cd_{1-x}Zn_xTe$  sample after laser radiation with intensity  $0.2 \text{ MW/cm}^2$ .



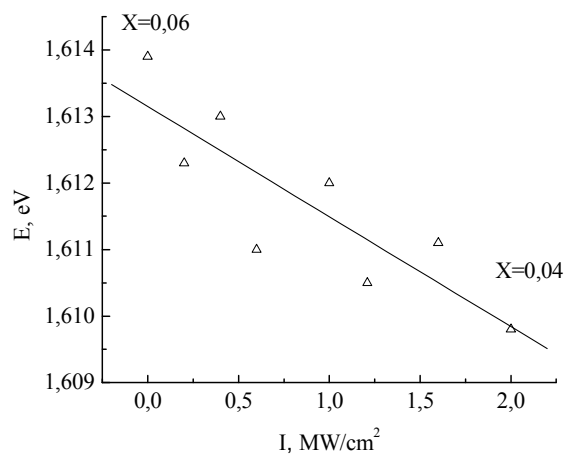
**Fig.3.** PL spectra measured from  $Cd_{1-x}Zn_xTe$  sample after laser radiation with intensity  $2\text{MW/cm}^2$ .

The movement of  $A_0X$  can be explained by redistribution of Zn atoms and  $V_{Cd}$ . Calculation of the distribution of the Zn atoms and the  $Cd_I$  in the presence of temperature gradient (grad T) in direction of laser beam propagation has shown that concentration of Zn atoms increased in the bulk of the semiconductor [12].



**Fig.4.** Photoluminescence spectra of  $Cd_{1-x}Zn_xTe$  crystals after laser radiation with causes change of composition  $X$

It follows that the concentration of the  $V_{Cd}$  is increased in the same place as concentration of the Zn atoms. As a result the situation in the bulk of semiconductor becomes favorable for recombination  $V_{Cd}$  by Zn atoms. In the ternary the decrease of Zn concentration leads to decreasing of the  $Cd_{1-x}Zn_xTe$  [18] band gap near the irradiated surface, correspondingly. As it follows from fig.4 the Zn concentration near irradiated surface decreases by 2 %.



**Fig.5.** Evolution of the 1.6139eV exciton bound energetic position depending on laser intensity.

The change of Zn concentration from  $X=0,06$  to  $X=0,04$  (Fig. 4) in direction of the bulk of the sample assume to change of band-gap into the  $Cd_{1-x}Zn_xTe$ . The monotone change of band-gap by coordinate in the bulk of the sample lead to creation of graded band-gap into bulk of the sample. The intensities of the exciton luminescence peaks decrease appreciably due to increasing of absorption of PL and its excitation light as deepening of the exciting layer. The peaks shift to the lower energy due to decrease of the energy band gap that is well visible from fig 5. The change of energetic position of  $A^0X$  exciton recombination (experimental) can be explained by decrease of width of semiconductor band-gap.

## Conclusions

The TGE has the main role in the redistribution of Zn at the irradiated surface of  $Cd_{1-x}Zn_xTe$ . A mechanism of formation of graded band-gap based on Thermogradient Effect (TGE) is proposed in  $Cd_{1-x}Zn_xTe$  at irradiation by second harmonic of a Q-switched YAG:Nd laser. According to the effect, the interstitial atoms of Cd ( $Cd_i$ ) in  $Cd_{1-x}Zn_xTe$  move along the temperature gradient while the Cd vacancies ( $V_{Cd}$ ) and Zn atoms – in the opposite direction, into the bulk of the semiconductor where temperature is lower. The possibility to form the graded band - gap in  $Cd_{1-x}Zn_xTe$  crystal by the second harmonica of YAG:Nd laser radiation have shown .

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**Mičko A., Medvis A., Barloti J. Gradiēta veidošanas pusvadītājā monokristālā lāzera starojuma iedarbībā.** Balstoties uz termogradiēta efektu (TGE), tika izskatīts aizliegtās zonas gradiēta veidošanās mehānisms  $Cd_{1-x}Zn_xTe$  kristālā, iedarbojoties uz to ar YAG:Nd lāzera starojuma otro harmoniku Q-switched režīmā. Saskaņā ar TGE starpmēžģu atomi Cd ( $Cd_i$ )  $Cd_{1-x}Zn_xTe$  kristāla iekšpusē pārvietojās temperatūras gradiēta virzienā, bet vakances Cd ( $V_{Cd}$ ) atomi pārvietojās pretējā virzienā, pusvadītāja tilpumā, kur temperatūra ir zemāka. Fotoluminiscences spektra pētīšana pie temperatūras 5K parādīja to, ka Zn atomu koncentrācija pusvadītāja tilpumā palielinās lāzera starojuma ietekmē. Tika parādīta aizliegtās zonas gradiēta veidošanas iespēja  $Cd_{1-x}Zn_xTe$  kristālā, apstarojot to ar YAG:Nd lāzera starojuma otro harmoniku.

**Mychko A., Medvid' A., Barloti J. Graded band-gap formation in semiconductor single grystal by laser radiation.** A mechanism of formation of graded band-gap based on Thermogradient Effect (TGE) is proposed in  $Cd_{1-x}Zn_xTe$  at irradiation by second harmonic of a Q-switched YAG:Nd laser. According to the effect, the interstitial atoms of Cd ( $Cd_i$ ) in  $Cd_{1-x}Zn_xTe$  move along the temperature gradient while the Cd vacancies ( $V_{Cd}$ ) and Zn atoms – in the opposite direction, into the bulk of the semiconductor where temperature is lower. Photoluminescence (PL) spectra studied at 5 K show that concentration of Zn atoms in the bulk of the sample increases after laser irradiation. Formation of a graded band-gap in  $Cd_{1-x}Zn_xTe$  crystal at irradiation by second harmonica of YAG:Nd laser by is shown to be possible

**Мычко А., Медвидь А., Барлотти Я. Формирование градиентной запрещенной зоны в полупроводниковом монокристалле лазерным излучением.**

Рассмотрен механизм формирования градиентной запрещенной зоны основанный на действии термоградиентного эффекта (ТГЭ) в  $Cd_{1-x}Zn_xTe$  под действием второй гармоники YAG:Nd лазера работающего в режиме модулированной добротности. В соответствии с ТГЭ междоузельные атомы Cd ( $Cd_i$ ) в  $Cd_{1-x}Zn_xTe$  перемещаются в направлении градиента температуры, а вакансии Cd ( $V_{Cd}$ ) в противоположном направлении, в объем полупроводника, где температура меньше. Изучение спектра фотолюминесценции температуре 5K показало, что концентрация атомов Zn в объеме полупроводника увеличивается под воздействием лазерного излучения. Показана возможность формирования градиентной запрещенной зоны в кристалле  $Cd_{1-x}Zn_xTe$  под действием излучения второй гармоники YAG:Nd лазера.