Semiconductor Physics, Quantum Electronics & Optoelectronics, 2017. V. 20, N 2. P. 250-253.
doi: https://doi.org/10.15407/spqeo20.02.250

PACS 78.55.Hx, 78.70.Qq

Transformation of impurity-defect centers in single crystals CdTe:Cl under the influence of microwaves

N.D. Vakhnyak[1], O.P. Lotsko[1], S.I. Budzulyak[1], L.A. Demchyna[1], D.V. Korbutyak[1], R.V. Konakova[1], R.A. Red'ko[1], O.B. Okhrimenko[1], N.I. Berezovska[2]
[1]*V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine,*
41, prospect Nauky, 03680 Kyiv, Ukraine
Corresponding author e-mail: div47@isp.kiev.ua
[2]*Taras Shevchenko National University of Kyiv, Physics Department,*
64/13, Volodymyrska str., 01601 Kyiv, Ukraine

Abstract. Performed in this work are the researches of the influence of microwave irradiation (2.45 GHz, 24 GHz) on spectra of low-temperature ($T = 2$ K) photoluminescence (PL) in single crystals CdTe:Cl. Transformation of impurity-defect centers in CdTe:Cl responsible for PL within the spectral range 1.3 to 1.5 eV under microwave irradiation was analyzed. The parameter of electron-phonon interaction (Huang–Rhys factor) for the donor-acceptor PL band, which depends on the time of microwave irradiation, has been calculated.

Keywords: photoluminescence, microwave irradiation, Huang–Rhys factor, donor-acceptor pair, impurity-defect center.

Manuscript received 25.01.17; revised version received 26.04.17; accepted for publication 14.06.17; published online 18.07.17.

1. Introduction

High-resistant single crystal CdTe is a promising material for manufacturing uncooled detectors of X- and γ-radiation [1, 2].

Despite that prospects of CdTe-detectors was repeatedly confirmed, technological difficulties associated with the cultivation of high-quality single crystals of large diameter hinder their widespread implementation. Only the system control and detailed studying the physical, technological and chemical processes that take place from crystal growth to their operation as detectors could provide maximum results to radio-ecological monitoring of individual objects and space exploration as well. Note that the influence of external factors on the impurity-defect structure of high-resistant CdTe single crystals is studied to find cheap and technologically simple external treatments that improve the detector material. Also important there is the study of stability and transformation of impurity-defect complexes in single crystals CdTe:Cl influenced by technological processing.

For single crystals CdTe:Cl, there is some progress in studying the nature of defects and in research the influence of external factors on transformation of impurity-defect state of this material, but the question of optimization of technology, both growing and technological treatments, remains open and requires further research [1, 3]. It contains determining the dominant mechanisms of transformation, thermal and radiation stability of impurity-defect centers, accounting and use of which is very important and often decisive in the development and optimization of manufacturing detectors of X- and γ-radiation based on single crystals

CdTe:Cl. Thus, the study of mechanisms responsible for transformation of complexes of defects in these single crystals under various technological processing and expanded search for optimal regimes capable to improve the structure of this material is very important and topical. If during radiation and thermal processing the mechanism of interaction of external factors of semiconductor material is understandable and predictable, so using the microwave radiation to modify impurity-defect state requires further research and analysis of the data necessary to determine the nature of observed transformations in these cases.

This paper presents the results of researching the influence of microwave irradiation of single crystals CdTe:Cl (frequencies 2.45 and 24 GHz) on the spectra of their photoluminescence at the low temperature (T = 2 K). The features of transformation of impurity-defect complexes within the spectral range 1.3…1.5 eV after microwave treatment have been analyzed.

2. Experimental technique

The investigated single crystals CdTe:Cl were grown using the Bridgman method. Chlorine doping was performed during crystal growth. For this purpose, the ampoule from carbonated silica (diameter 15 mm) filled with synthesized cadmium telluride (pre-cleared by vertical zone melting) and by pre-determined amount of salt $CdCl_2$. Before growing, the ampoule was maintained under melt temperatures reaching the plateau of tubular oven ones (T = 1390 K) for 4 hours. And then, it was put down through the temperature gradient of 10…12 K/cm with the speed 4.8 mm/h. After the growing process, the ampoule was cooled by putting down through the temperature gradient 50 K/cm. The concentration of chlorine injected impurity in the grown crystals was $5\cdot10^{17}$ and $5\cdot10^{19}$ cm^{-3}.

Microwave irradiation of crystals was held in gyrotron complex for microwave processing the materials at the frequencies 2.45 and 24 GHz.

The total time of exposure was a sum of partial irradiation times of 5 s with intervals between irradiation steps in 3 min. Measurements showed that, in every process of radiation, temperature changes did not exceed 2 °C as compared to the initial temperature of the sample. For researching the luminescent properties, we used the crystals CdTe:Cl irradiated at different exposures: 5, 10, 60, 120 and 180 s. After each session of achievement the required dose of microwave irradiation, PL spectra were measured.

The measurements were performed within the range 1.3…1.5 eV at the temperature 2 K, which was provided by helium vapor pumping out from the cryostat by using a computerized system based on monochromator MDR-3 (inverse linear dispersion 2.6 nm/mm). As a source of excitation radiation, the continuous argon Ar^+ laser with the wavelength 514.5 nm was used.

To characterize the degree of electron-phonon interaction, the factor by Huang–Rhys S was used, it was determined using the PL spectra. It reflects the probability of radiative transitions in impurity centers with participation of LO-phonons. Being based on the model [4] S is a function of the distance R between the components of donor-acceptor pair (DAP). Therefore, changes in impurity-defect structure of the samples caused by the microwave treatment are appropriately reflected by changes of the Huang–Rhys factor.

3. Experimental results and discussion

Fig. 1 shows the measured PL spectra of CdTe:Cl within the range 1.3…1.5 eV. For comparison, brought also are PL spectra of undoped CdTe. To investigate the nature of this band, a lot of work was made, but for a long time could not explain all the features of its behavior. Since the beginning of the study of CdTe photoluminescence, it was clear that the band in the vicinity of 1.45 eV is associated with radiative recombination of DAP with longitudinal optical phonons, as evidenced by the regular repetition of the enough intense zero-phonon line (the distance between the maxima that corresponds to the longitudinal optical phonon energy in millielectron-volts). Analyzing the intensity ratio for the phonon replicas can define the constant of electron-phonon interaction for the radiative center. But the nature of the zero-phonon line as well as its exact position in the power scale is still differently interpreted and defined in the works of different authors. This shows that in reality luminescence in this spectral region is likely combined, which is conditioned by superposition of the emission spectra of several centers of different nature, and thus, to properly determine the characteristics of the electron-phonon interaction, it is necessary to account for this effect.

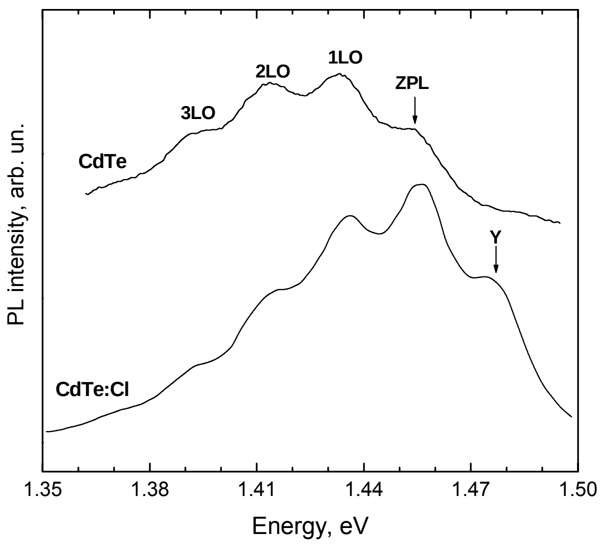

Fig. 1. Spectrum of CdTe undoped and doped with chlorine ($N_{Cl} = 5\cdot10^{19}$ cm^{-3}) within the range 1.3…1.5 eV.

From the short edge, there is the so-called Y-band (E_{max} = 1.478 eV). At first sight, it could be associated with zero-phonon line (ZPL) radiation involving A-centers (DAP consisting of acceptor vacancy of metal and donor impurity), because the energy distance from it to the next peak of the PL side ($E_{max} \approx$ 1.455 eV) approximately coincides with the energy of the longitudinal optical phonons in CdTe. However, this band has very unusual features for the deep recombination centers and has a relatively wide ZPL and weakly expressed long-wave tail of phonon replicas, which is the feature inherent to extended defects in recombination [4] and can be related to recombination of excitons bound to dislocations [5].

Let's analyze the shape of structured PL band observed in single crystals CdTe:Cl within the range 1.3…1.5 eV. As noted above, the indicated PL band is a complex that includes the line of D-A transitions involving A-center with LO-phonon repetitions and Y-phonon line with its repetitions as well. Therefore, for the correct analysis the shape of specified band needs to be decomposed into two components.

Example of description of the experimental PL spectrum by superposition of two lines (Y-line and DAP), which are characterized by different energy positions and different values of *S*, is shown in Fig. 2. Satisfactory adjustment of the experimental PL band shape to the total intensity of two estimated series was achieved by using *S* and the decay parameter Γ as fitting parameters. The energy positions of zero-phonon lines for two series and the value of LO-phonon energy remained unchanged.

The detailed analysis of PL band shape for DAP allowed to ascertain that the Huang–Rhys factor *S* that characterizes the degree of electron-phonon interaction in DAP, depending on the concentration of introduced impurities, changes from $S = 1.68$ (for $N_{Cl} = 5\cdot10^{17}$ cm^{-3}) to $S = 1.5$ (for $N_{Cl} = 5\cdot10^{19}$ cm^{-3}). Thus, the increase in the impurity concentration of chlorine results in reducing the distance between donors and acceptors and causes the corresponding reduction of the Huang–Rhys factor. The physical reason of reduction of this factor when decreasing the distance between donors and acceptors is growing mutual compensation of charge distributions for these centers as well as the corresponding decrease in deformation shift of the centers relatively to their positions in the configurational space in the absence of carriers capture. The second reason of *S* value decrease with increasing the impurity concentration of chlorine in the samples may be higher number of defects in CdTe:Cl single crystals, which shield Coulomb interaction in DAP.

Microwave irradiation at the frequency 24 GHz for 5 s did not lead to significant changes in the observed PL spectrum. However, under further exposure of the samples by microwaves, the spectral dependence was affected. With increasing duration of microwave irradiation, the intensity of Y-PL band decreases. This may indicate a decrease in the concentration of longitudinal defects, on which excitons bind in subsurface crystal region under microwave radiation. These changes are typical for the single crystals CdTe:Cl subjected to ~200 °C thermal annealing [6].

Changes in the ratio of intensities of the observed phonon replica lines of the PL spectrum of single crystals CdTe:Cl are apparently caused by transformation of donor-acceptor centers under microwave treatment with possible changes in their concentration and, consequently, in the distance between donors and acceptors. The latter should lead to a corresponding change in the Huang–Rhys factor value.

For a detailed analysis of the low temperature PL of these crystals within the energy range 1.3 to 1.5 eV after microwave irradiation, we made decomposition of PL spectra (similar to that shown in Fig. 2). It consists of two bands: 1.455 eV – radiative recombination due to DAP (1.470–1.478 eV) and the Y-band with relevant phonon repetitions. Analyzing every curve and calculating Huang–Rhys factor for each one, it was obtained that in the initial state for Y-band ($S_Y = 0.88$), this parameter was significantly less than the same denotation for DAP involving A-center ($S_{DAP} = 1.50$). Thus, S_Y was practically unchanged and S_{DAP} grew in the range of 1.50…1.71 with increasing duration of microwave irradiation of single crystals CdTe:Cl (Table).

The latter may be due to the increasing distance between donors and acceptors and different effects of microwave radiation on the concentration of nonradiative recombination centers and DAP in near-surface field of single crystals. Microwave processing of the samples at the frequency 2.45 GHz, as shown in [7], led to lower values change of the Huang–Rhys factor (from 1.50 to 1.64) than for the 24 GHz frequency. The latter obviously suggests less intense transformation of defect centers at a lower frequency, as the microwave power density in both cases was the same.

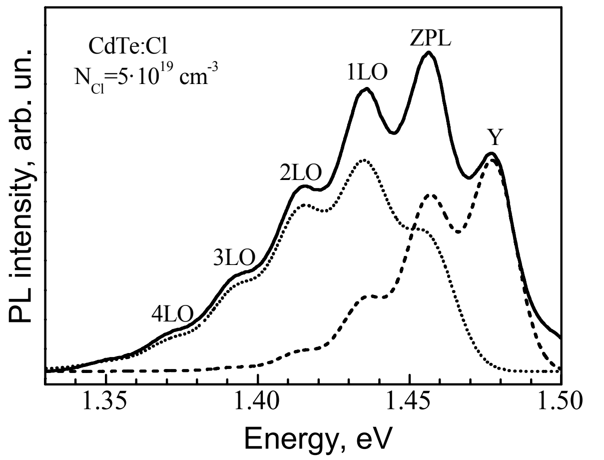

Fig. 2. Decomposition of the experimental PL spectrum (solid line) into two components: DAP (points) and Y-line (dashed line) with their phonon repetitions.

Table. Change in the Huang–Rhys factor value due to microwave treatment.

t_{treat}	Starting position	10 s	60 s	120 s
S_{DAP}	1.50	1.58	1.68	1.71

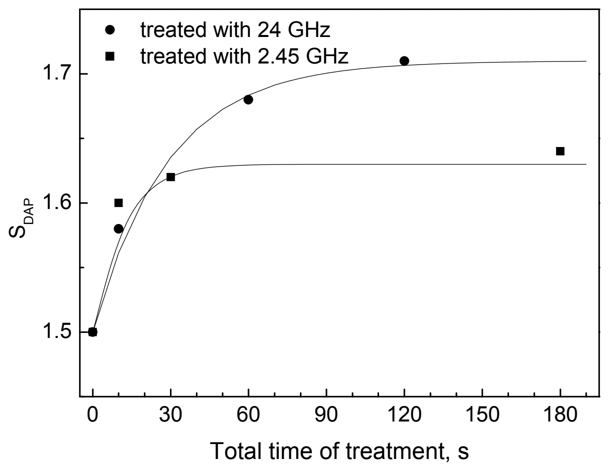

Fig. 3. Dependence of the Huang–Rhys factor on the duration of the microwave treatment of single crystals CdTe:Cl with $N_{Cl} = 5{\cdot}10^{19}$ cm^{-3} at the frequencies 2.45 and 24 GHz. Points – experiment, the line – approximation using Eq. (1).

Using the equation of the following form:

$$S = S_m - A\exp\left(-\frac{t_{treat}}{B}\right), \qquad (1)$$

where S_m is the value of Huang–Rhys factor, t_{treat} – duration of microvawe treatment, A and B are empirical constants. Using the least squares method, we were able to approximate experimental dependence $S(t_{treat})$ with parameters $S_m^{(24\text{ GHz})} = 1.7$, $A^{(24\text{GHz})} = 0.20$, $B^{(24\text{GHz})} = 22.92$; $S_m^{(2.45\text{GHz})} = 1.63$, $A^{(2.45\text{GHz})} = 0.13$, $B^{(2.45\text{GHz})} = 7.36$ for the experimental data, corresponding treatments at the frequencies 24 and 2.45 GHz, respectively (Fig. 3).

4. Conclusions

Performed in this paper researches of the effect of microwave irradiation on the PL spectra of CdTe:Cl within the range 1.3…1.5 eV are indicative of modification of defect structure in the irradiated material. The microwave treatment duration ≥10 s leads to the increase in the distance between components of DAP responsible for the recombination radiation near 1.455 eV. This conclusion has been obtained after analyzing the theoretical calculations concerning the changes of the Huang–Rhys factor for DAP band and has been confirmed experimentally by observation of the long wave shift of the PL peak. It has been obtained that the microwave treatment leads to quenching the band near 1.478 eV associated with extended defects, which indicates effective interaction of microwave fields with dislocations of the corresponding nature. The data obtained in this work together with the results [7] evidence that increase in the dose of microwave irradiation and frequency of the used wavelengths enhance the observed effect.

References

1. Korbutyak D.V., Melnychuk S.V., Korbut E.V., Borysiuk M.M. *Cadmium Telluride: Impurity-Defect States and Detector Properties*. K.: “Ivan Fedorov”, 2000. 198 p. (in Ukrainian).
2. Korbutyak D.V., Venger E.F., Krylyuk S.G. et al. Detectors of X- and γ-radiation on the base of CdTe and CdZnTe single crystals (Review). *Optoelectronics and semiconductor technics*. 2001. **36**. P. 5–34 (in Russian).
3. Komar’ V.K., Puzykov V.M. *Single Crystals of $A^{II}B^{VI}$ Group. Growth, Properties, Application*. Khar’kov, Institute of Single Crystals, 2002. 244 p. (in Russian).
4. Korbutyak D.V., Lotsko A.P., Vakhnyak N.D., Demchyna L.A., Konakova R.V., Milenin V.V., Red’ko R.A. Effect of microwave irradiation on the photoluminescence of bound excitons in CdTe:Cl single crystals. *Semiconductors*. 2011. **45**, No. 9. P. 1175–1181.
5. Dean P.J., Williams G.M., Blackmore G. Novel type of optical transition observed in MBE grown CdTe. *J. Phys. D*. 1984. **17**, No. 8. P. 2291–2300.
6. Korbutyak D.V., Lots’ko O.P., Vakhnyak N.D., Demchyna L.A. Diagnostic of donor-acceptor pairs in CdTe:Cl single crystals. *Naukovyi visnyk KUEITU: Novi tekhnologii*. 2010. № 2(28). P. 8–12 (in Ukrainian).
7. Budzulyak S.I., Korbutyak D.V., Lotsko A.P. et al. Features of transformation of impurity-defect complexes in CdTe:Cl under the influence of microwave irradiation. *Tekhnologiya i konstruirovanie v elektronnoi_apparature*. 2014. №4. P. 45–49 (in Russian).