PHYSICS AND CHEMISTRY OF SOLID STATE
V. 21, N 1 (2020) p. 52-56

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 21, № 1 (2020) С. 52-56

DOI: 10.15330/pcss.21.1.52-56

PACS numbers: 61.43.Gt, 68.37.Ps, 78.30.Fs, 78.55. – m

ISSN 1729-4428

T.M. Mazur[1,2], V.V. Prokopiv[1], M.M. Slyotov[3], M.P. Mazur[2], O.V. Kinzerska[3], O.M. Slyotov[3]

Optical properties of CdTe doped Ca

[1]*Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine, volodymyr.prokopiv@pnu.edu.ua*
[2]*Ivano-Frankivsk National Technical University of Oil and Gas, Ivano-Frankivsk, Ukraine, mazur@nung.edu.ua*
[3]*Yuri Fedkovich Chernivtsi National University, Chernivtsi, Ukraine, oksanakinzerska@gmail.com*

The optical absorption, reflection and luminescence of CdTe:Ca were studied. It was established that the obtained Ca doped surface layers are characterized by intense photoluminescence from $\eta =$ 8-10% in the edge region. Radiation is formed due to interband recombination of free charge carriers and the annihilation of excitons bound on isovalent impurities of Ca. The indicated components are observed in the differential optical reflection spectra R'_{ω} in the surface layer obtained by doping CdTe substrates with an isovalent Ca impurity. It is established that doping causes the formation of p-type conductivity.

Keywords: cadmium telluride, isovalent impurity, optical absorption and reflection, intense photoluminescence.

Received 13.02.2020; accepted for publication 15.03.2020

Introduction

Currently, one of the most promising materials for the manufacture of electronics devices is cadmium telluride. A unique set of its physicochemical parameters is a prerequisite for the manufacture of optoelectronic devices on its basis [1,2]. CdTe is direct-gap, can have both *n*-type and *p*-type conductivity, has a band gap (1.5 eV at 300 K), which is close to the optimal value for converting solar energy into electrical energy [3]. All this makes it attractive for use in solar energy. At the same time, technologies for creating radiation sources of the infrared region based on CdTe remain poorly studied. For their manufacture, it is possible to create barriers of various types using thin-film technology. However, despite the simplicity of fabrication and their cheapness compared to those obtained on crystals, manufacturing techniques are currently not sufficiently studied in the case of thin CdTe films [4,5]. In this regard, it is important to search for manufacturing technologies and the creation of thin near-surface layers on CdTe base crystals, which make it possible to provide important promising properties without affecting the basic parameters of the base material. In addition, such a technology could be used later with a small correction for the manufacture of structures based on other wide-gap II-VI compounds. It was shown [6, 7] that in the case of other II – VI compounds, in particular ZnSe, such promising developments can be alloying with isovalent impurities (IVI). They fundamentally affect the optical properties and cause highly efficient radiation. In addition, an inversion of the conductivity type is observed and a *p*-*n*-junction is formed. Therefore, research is relevant and important to study the effect of IVI on the optical properties of CdTe.

I. Objects and research methods

Cadmium telluride base crystals were grown according to the classical Bridgman method. They are characterized by *n*-type conductivity and resistivity of ρ ~ 100 Ohm·cm. For studies of their properties, substrates with a size of 4×4×1 mm^3 were cut out and their chemical-mechanical treatment was carried out according to the classical method. Doping with an isovalent admixture of Ca was carried out in an aqueous solution of $Ca(NO_3)_2$ [8].

The electrical, optical, and luminescent properties of undoped CdTe and specially doped surface layers of CdTe:Ca were studied. The optical processes of absorption, reflection, and luminescence were studied using a universal optical setup, which made it possible to carry out measurements both by the classical technique and using the λ-modulation method [9,10]. The optical spectra were studied on an MDR-23 diffraction monochromator, after which the optical signals were recorded by an FEU-79 or FEP-112 photomultiplier. Sources of diagnostic radiation were an ELC / C halogen lamp with a monotonic smooth spectrum and an LGN-21 nitrogen laser with exciting radiation with λ = 0.337 μm ($\hbar\omega$ ~ 3.68 eV). The latter was used to excite luminescence on the obtained CdTe:Ca layers. The measured signal was recorded using a synchrodetection system, which at the modulation frequency Ω the emitted signals also made it possible to measure the differential spectra of the first derivative of the optical signal. Electrical and current-voltage characteristics were studied by well-known classical methods [9] and also by the method developed in [11].

II. Research results and discussion

The optical properties of the CdTe base material were determined from studies of optical transmission T_ω and reflection R_ω. The transmission is characterized by a typical spectral distribution in the photon energy range $\hbar\omega$ = 1-1.55 eV. The monotonic nature of the dependence indicates the absence of uncontrolled impurities that can be introduced during cultivation. At the same time, in the range of ($\hbar\omega \geq 1.55$ eV, a sharp decrease in the transmission intensity is observed, the

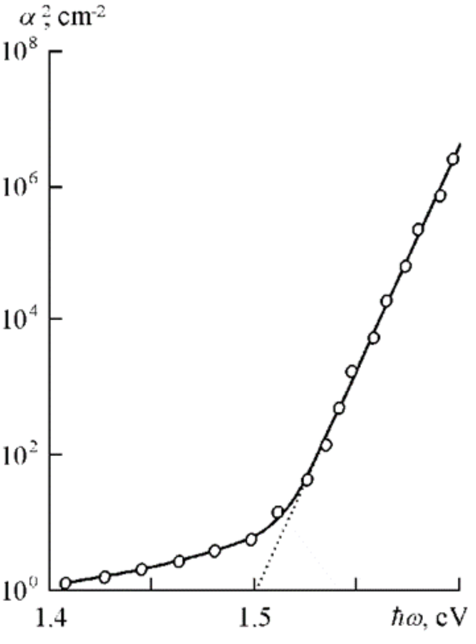

Fig. 1. Absorption spectra of the original cadmium telluride. T = 300 K.

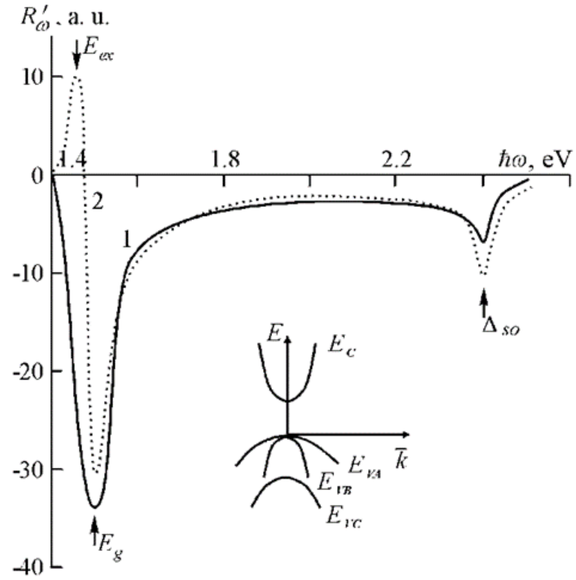

Fig. 2. Optical reflection spectra of the original (1) and doped Ca (2) CdTe. T = 300 K.

character of which is characteristic of the long-wavelength absorption edge. The absorption coefficient is well approximated by the well-known analytical expression for direct optical transitions, namely, $\alpha = A^*\left(\hbar\omega - E_g\right)^{1/2}$, where A^* is the known constant. This is also confirmed by the linear nature of the dependence constructed in coordinates using the widely used technique [9]. An approximation of the linear portion of this dependence to the energy axis for the measured absorption on freshly cleaved CdTe plates ~ 40 μm thick allows us to determine the band gap of $E_g = 1.5$ eV at 300 K, Fig. 1. The obtained value correlates well with published data [13].

Doping of CdTe plates and substrates with an isovalent Ca impurity does not affect the dependence of the optical absorption curves and the value of a certain basic material parameter of $E_g = 1.5$ eV. This indicates the formation of a thin Ca-doped surface layer and the absence of effects of doping processes on the properties of the volume of the base material. Under such circumstances, a study was made of λ-modulated optical reflection. The properties of base substrates and the resulting CdTe:Ca layers were studied. The corresponding differential curves R'_ω are shown in Fig. 2. The main maximum at ω ($\hbar\omega$ = 1.5 eV is observed for the starting material, which is explained by optical transitions of charge carriers through the band gap. A second feature was also found on the curves R'_ω at ($\hbar\omega$ = 2.4 eV. The difference between 2.4–1.5 = 0.9 eV correlates well with the values of the energy of optical transitions with the participation of the valence subband, split off due to spin – orbit interaction Δ_{so} [3, 13]. Thus, the discovered property is due to the features of the band structure of CdTe. They indicate the directness straightforwardness of the material and its rather high structural perfection, which is confirmed by the absence of additional extrema in the curves R'_ω and T_ω in the region $\hbar\omega$ = 1-1.55 eV.

At the same time, Ca doping of CdTe substrates leads to the formation of a thin layer, which is characterized by a decrease in the half-width of the curve maximum R'_ω at $E_g = 1.5$ eV and the formation of structurality, curve 2, Fig. 2. At energies of $E_g = 1.458$ eV, an intense maximum is observed. Its nature is well explained by studies of the luminescent properties of CdTe:Ca. Note that doping of cadmium telluride with an isovalent Ca impurity does not affect the position of the main features of the differential curves. This indicates that, as a result of chemical treatment, another substance is not formed on the surface of the base material.

Doping of CdTe with an isovalent Ca impurity leads to the formation of intense photoluminescence. Evaluation of its quantum efficiency η by a known method made it possible to determine the value η ~ 8-10% at 300 K [14]. We note that on unalloyed material it was not observed even at T=77 K. According to published data, η with possible doping with other types of impurities gives a maximum value of 0.05-0.1% [13].

The effective luminescence of CdTe:Ca is observed in the edge region at $\hbar\omega$ = 1.3–1.6 eV. Its spectral distribution is characterized by the presence of two components, curve 1, Fig. 3. They are clearly manifested in the case of Ca doped freshly cleaved plates, curve 2, Fig. 3. The properties of the bands are fundamentally different. Thus, the dominant band with a maximum at $\hbar\omega$ = 1.458 eV is characterized by a shift of the maximum to the high-energy region with a decrease in the excitation level L. Secondly, the intensity I depends L on the law $I \sim L^{1.5}$. Thirdly, the shape of the strip is

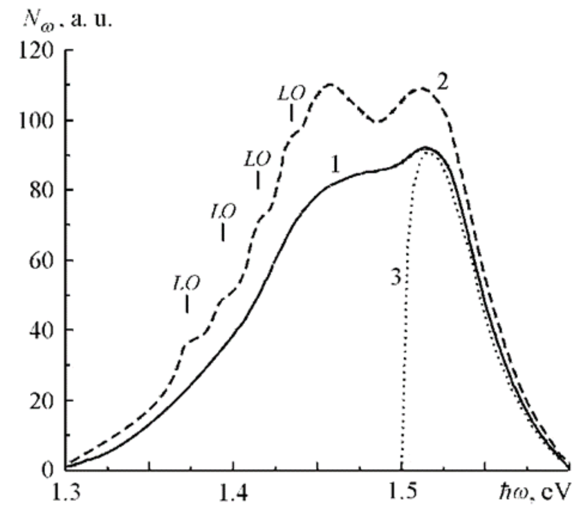

Fig. 3. Photoluminescence spectra of CdTe doped Ca surface layers (1, 2): 1 – appropriately treated surface of CdTe doped with Ca; 2 – freshly chipped CdTe surface doped with Ca; 3 – the calculated spectrum of interband radiation transitions. T = 300 K.

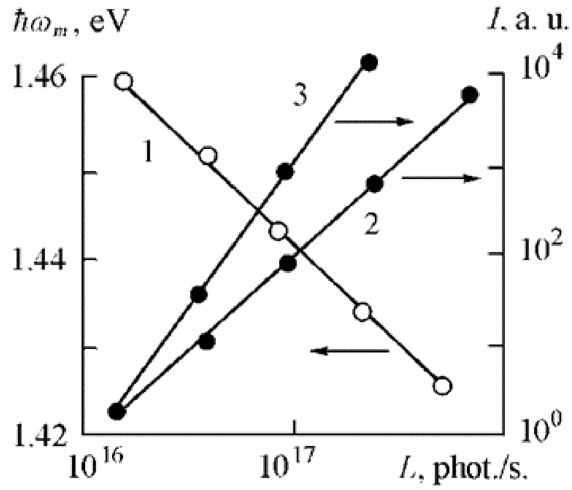

Fig. 4. Depending on the excitation level L, the position of the maximum $\hbar\omega_m$ (1) and the intensities I of the exciton (2) and interband (3) components of the radiation of the CdTe:Ca layers. T = 300 K.

characterized by asymmetry with a sharp decrease I in the region of high maximum energies and a slow decrease at $\hbar\omega < \hbar\omega_m$. The indicated properties are characteristic of exciton processes. In this case, annihilation of excitons bound by isovalent impurities takes place upon their inelastic scattering by free charge carriers [15]. In addition, equidistant kinks are observed in the low-energy region N_ω, which are consistent with the energy of the LO phonon for CdTe, namely, $\hbar\omega$ = 21 meV [13]. The above properties of the exciton band are shown in Fig. 4, curves 1 and 2.

In the photon energy range $\hbar\omega$>- E_g, a second band is observed with a maximumof $\hbar\omega$ = 1.51 eV. The position of its maximum is independent of L, and the half-width $\hbar\omega_{1/2}$ is ~ 1.5kT. The intensity at the maximum depends on L by law $I \sim L^2$. Such properties are inherent in interband recombination of free charge carriers [12]. Accordingly, the intensity distribution is in good agreement with the analytical expression, which approximates it [12, 16]

$$N_\omega \sim (\hbar\omega)^2 \sqrt{\hbar\omega - E_g}\, \exp\left(-\frac{\hbar\omega - E_g}{kT}\right) \qquad (1)$$

Where k is the Boltzmann constant, T is the temperature, N_ω is the number of photons in a unit energy interval. Note that it is these bands that are observed in the study of optical reflection, Fig. 2. On the curves given, they are indicated by the corresponding symbols E_g and E_{ex}. Their presence confirms the effect of "purification" of the starting material as a result of doping with an isovalent impurity, which is determined by the features of its interaction with atoms of matter [6, 17].

An important consequence of doping in an aqueous solution of $Ca(NO_3)_2$ is the creation of p-type conductivity of the surface layer. The study of the electrical characteristics of the ohmic contacts gives the corresponding linear dependence of the current when the voltage changes and the symmetry of the forward and reverse branches. In addition, the inversion of the conductivity type is also confirmed by studies of electrical conductivity with a thermal probe [11]. This indicates the prospects of the proposed technology for producing doped with isovalent impurity layers in the manufacture of solid state electronics devices based on CdTe.

Conclusion

Thus, doping of CdTe with an isovalent Ca impurity in an aqueous solution allows one to obtain intense edge luminescence with an efficiency of η = 8–10%. It is formed by interband recombination of free charge carriers and annihilation of bound excitons. The introduction of an isovalent impurity does not change the optical properties of the base material, which are determined by its direct-gap structure and are characterized by the corresponding parameters of E_g = 1.5 eV and Δ_{so} = 0.9 eV.

The proposed technological alloying regimes do not affect the properties of the base material and make it possible to obtain surface layers with inversion of conductivity from *n*-type to *p*-type.

Mazur T.M. – Ph.D student;
Prokopiv V.V. – Professor, Ph.D (Physics and Mathematics), Head of the Department of Physics and Chemistry of Solid State;
Slyotov M.M. **–** Professor, Doctor of Physics and Mathematics, Professor of the Department of Optics and Publishing and Printing;
Mazur M.P. **–** Associate Professor, Ph.D (Physics and Mathematics), Director of the Institute of Architecture, Construction and Power Engineering;
Kinzerska O.V. **–** Candidate of Physical and Mathematical Sciences, Assistant of the Department of Semiconductor Physics and Nanostructures;
Slyotov O.M. **–** Candidate of Physical and Mathematical Sciences, Assistant of the Department of Electronics and Energy.

[1] O. Ermakov, Applied optoelectronics (Technosphere, Moskva, 2004).
[2] V.P. Makhniy, M.M. Slyotov, N.V. Skrypnyk, Ukrainian Journal of Physical Optics 10(1), 54 (2009) (https://doi.org/10.3116/16091833/10/1/54/2009).
[3] D.V. Korbutyak, S.V. Melnichuk, E.V. Korbut, M.M. Borisyuk, Telluride cadmium: home-defective camps and detection authorities ("Ivan Fedorov", Kyiv, 2000).
[4] T. Mazur, V. Prokopiv, L. Turovska, Molecular Crystals and Liquid Crystals 671(1), 85 (2018) (https://doi.org/10.1080/15421406.2018.1542088).
[5] T.M. Mazur, V.P. Makhniy, V.V. Prokopiv, M.M. Slyotov, Journal of Nano- and Electronic Physics, 9(5), 05047 (2017) (https://doi.org/10.21272/jnep.9(5).05047).
[6] V.I. Fistul, Atoms of dopants in semiconductors (state and behavior) (Fizmatlit, Moskva, 2004).
[7] V.P. Makhniy, M.M. Sletov, N.V. Demich., A.M. Sletov, Transactions of Int. scientific conf. "Actual problems of solid state physics." (Ed. Center BSU, Minsk, 2005), 385.
[8] V.P. Makhniy, T.M. Mazur, M.M. Berezovsky, O.V. Kinzerska, V.V. Prokopiv, Physics and Chemistry of Solid State, 19(4), 313 (2018) (https://doi.org/10.15330/pcss.20.4.372-375).
[9] Yu.V. Vorobiev, V.I. Dobrovolsky, V.I. Stryha, Semiconductor research methods (Vyshcha schola, Kyiv, 1988).
[10] M.M. Slyotov, A.M. Slyotov, Journal IAPGOS, 4, 4 (2018).
[11] V.V. Prokopiv, B.S. Dzundza, O.B. Kostyuk, T.M. Mazur, L.V. Turovska, O.M. Matkivskyi, M.V. Deychakivskyi, Physics and Chemistry of Solid State, 20 (4), 372 (2019) (https://doi.org/10.15330/pcss.20.4.372-375).
[12] V.P. Gribkovsky, The theory of absorption and emission of light in semiconductors (Science and technology, Minsk, 1975).
[13] V.I Gavrilenko, A.M. Grekhov, D.V. Korbutyak, V.G. Litovchenko, Optical properties of semiconductors. Directory (Naukova Dumka, Kyiv, 1987).
[14] V. Khomyak, M. Slyotov, I. Shtepliuk, O. Slyotov, and V. Kosolovskiy, Acta Physica Polonica A, 122 (6), 1039 (2012).
[15] Era Koh, D.W. Langer, J. Luminescence, (1-2), 514 (1970).
[16] M.M. Slyotov, V.P. Makhniy, A.M. Slyotov, V.V. Kosolovskiy, Telecommunication and Radio Engineering, 73 (10), 909 (2014) (https://doi.org/10.1615/TelecomRadEng.v73.i10.50).
[17] I.V. Horichok, H.Ya. Hurhula, V.V. Prokopiv, M.A. Pylyponiuk, Ukrainian Journal of Physics, 61 (11), 992 (2016) (https://doi.org/10.15407/ujpe61.11.0992).

Т.М. Мазур[1,2] , В.В. Прокопів [1] , М.М. Сльотов [3], М.П. Мазур[2], О.В. Кінзерська[3], О.М. Сльотов[3]

Оптичні властивості CdTe, легованого Ca

[1]*ДВНЗ «Прикарпатський національний університет імені Василя Стефаника», Івано-Франківськ,Україна, volodymyr.prokopiv@pnu.edu.ua*
[2]*Івано-Франківський національний технічний університет нафти і газу, Івано-Франківськ, Україна, mazur@nung.edu.ua*
[3]*Чернівецький національний університет імені Юрія Федьковича, Чернівці, Україна, oksanakinzerska@gmail.com*

Досліджено оптичне поглинання, відбивання і люмінесценцію CdTe:Ca. Встановлено, що отримані леговані Ca поверхневі шари характеризуються інтенсивною фотолюмінесценцією з $\eta = 8$-10% у крайовій області. Випромінювання формується внаслідок міжзонної рекомбінації вільних носіїв заряду і анігіляцією зв'язаних на ізовалентних домішках Ca екситонів. Зазначені складові спостерігаються у диференційних спектрах оптичного відбивання R'_{ω} у приповерхневому шарі, отриманому при легуванні ізовалентною домішкою Ca підкладинок CdTe. Встановлено, що легування обумовлює утворення *p*-типу провідності.

Ключові слова: телурид кадмію, ізовалетна домішка, оптичне поглинання і відбивання, інтенсивна фотолюмінесценція.