

# Optical Absorption and Luminescence Spectra of the Ag-CdI<sub>2</sub> Photosensitive Heterosystem

Vitaliy Lesivtsiv

dept. of Electronics and Computer Technologies  
Ivan Franko National university of Lviv  
Lviv, Ukraine

Serhiy Velhosh

dept. of Electronics and Computer Technologies  
Ivan Franko National university of Lviv  
Lviv, Ukraine  
velgosh@electronics.lnu.edu.ua

Iryna Novosad

Physics dept.  
Ivan Franko National university of Lviv  
Lviv, Ukraine  
irenanovosad@gmail.com

Stepan Novosad

Scientific-Technical and Educational Center of Low  
Temperature Studies  
Ivan Franko National university of Lviv  
Lviv, Ukraine

**Abstract**—This work deals with the study of absorption and luminescence spectra of Ag-CdI<sub>2</sub> photosensitive heterosystem and the influence of laser radiation on the spectral properties investigated system. In Ag-CdI<sub>2</sub>, additional absorption bands are found. Absorption with maxima at 400–500 nm is associated with surface plasmon resonance in silver nanoparticles, which are formed at the initial stages of metal sputtering. From the analysis of the parameters of the spectrum it is established, that silver particles have a spheroidal shape, with the ratio of the axes  $c/a \sim 1.43$ .

In Ag-CdI<sub>2</sub> heterosystem, the band of luminescence with maxima at 680 nm occurs, which intensity increase with time after deposition of metal. From the time dependence of the intensity of the light the value of the diffusion coefficient of silver in CdI<sub>2</sub> is determined:  $D = (3.0 \pm 0.5) \times 10^{-9}$  cm<sup>2</sup>/sec.

It is established that under the action of UV irradiation, the intensity of long-wave radiation of Ag-CdI<sub>2</sub> decreases over time to a certain minimum value of  $I_{\min}$ . A phenomenological model is proposed that describes the processes of attenuation of the emission and determines the parameters of the model.

**Index Terms**—heterosystem, cadmium iodide, luminescence spectra, absorption spectra

When spraying thin layers of metal halides on metal substrates, we obtain the structures of  $Me-BX_2$  ( $Me = Cu, Au, Ag, B = Pb, Cd$ ), which have high sensitivity to electromagnetic radiation. It is conditioned by photochemical transformations occurring in such systems under the action of light. Therefore, the study of ionic and electron processes occurring in a photo of sensitive se-deposits during their irradiation with light from the region of their own absorption of metal halides is important both from the scientific and the practical point of view.

In this article the absorption and luminescence spectra that occur in light-sensitive metal-iodine cadmium systems in the dark and when they are irradiated with light from the crystal's own absorption region are studied. The choice of the object of research is due, first of all, to the fact that the structure of the layered crystals of CdI<sub>2</sub> is rather fluffy, which contributes to the diffusion of atoms in the volume of the crystal, and the heterosystem of Ag-CdI<sub>2</sub> is practically not investigated. The optical properties of the Ag-CdI<sub>2</sub> heterostructures, obtained via silver metallic film evaporation, were partially investigated in [1, 2].

The cadmium and iodine atoms interaction causes the formation of triple ...I – Cd – I... layers, with ionic-covalent bonds inside. The neighboring layers are connected by relatively weak van der Waals forces, as a result the anisotropy of the Cd – I/I – I bonding is equal  $\sim 125$  [3, 4] and CdI<sub>2</sub> samples possess an excellent cleavage along the (0001) structural planes.

The Ag-CdI<sub>2</sub> heterostructures were obtained by thermal evaporation of a metallic silver film (thickness  $\sim 100$  nm) on the freshly cleaved surface (0001) of the crystalline CdI<sub>2</sub> samples, whose thickness was  $\sim 0.5 \dots 2.0$  mm. The results of the microscopic studies of the Ag-CdI<sub>2</sub> structures indicate that the metal atoms are localized primarily in areas associated with defects on the surface of the crystal: the steps associated with the breakdown of triple layers, the steps of growth, outlets of dislocations, pits, etc., which always exist on the surface [4–6] (fig. 1). Dark places that are caused by the localization of silver on the inhomogeneities of the surface in the ordinary illuminated light are luminescent.

This distribution of metal is explained by the ability of coagulation in the thin layers of silver, which results in the formation of a discrete nanoparticle system in the initial stages of deposition, which is further covered with a continuous metal film.

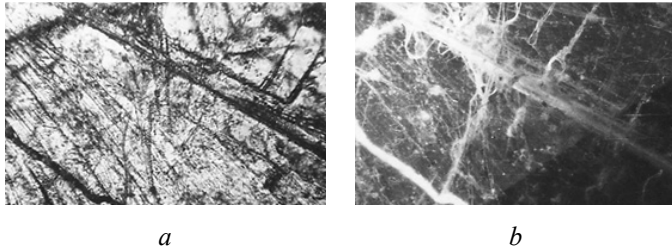


Fig.1. Microscopic image of the surface of Ag-CdI<sub>2</sub> in normal (a) and luminescent light (b).

In the absorption spectra of the Ag-CdI<sub>2</sub> structure, an intensive band with a peak at 569 nm and a short-wave component with a maximum at 460 nm are recorded (fig. 2).

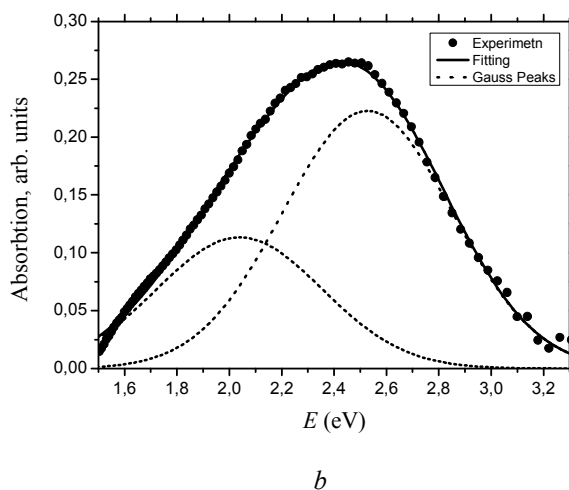
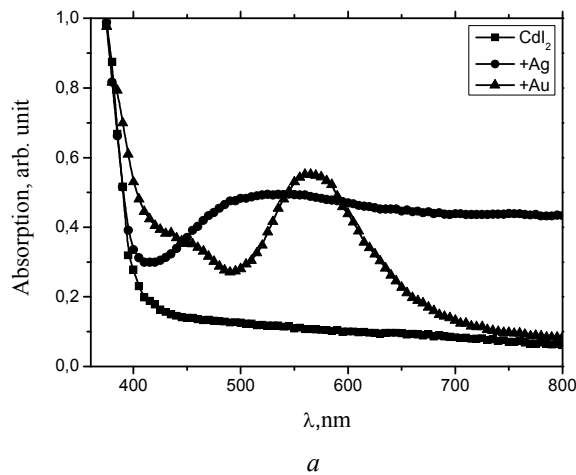


Fig. 2. Extinction spectra of the Ag-CdI<sub>2</sub> structure. For comparison, the absorption spectrum of the crystal before depositing a metal film (a) is given. Difference spectra of nanoparticles of Ag-CdI<sub>2</sub> heterostructures with allowance for continuous background absorption (b).

The analysis of literature data suggests, that additional absorption bands of Ag-CdI<sub>2</sub> structures are due to surface plasmon resonance in nanoparticles of metals, which are formed when sprayed onto a crystal surface [7, 8, 9].

The nature of the surface plasmon resonance is due to the fact that, under the action of external incident radiation, the conduction electrons are displaced relative to a stationary positively charged ionic core. This bias is a rather collective character, in which the motion of electrons is coordinated in phase. It is realized in the event that the radius of the particle  $R$  is smaller than the length of the optical path  $l$  of electrons:  $R < l$ . In the case when the frequency of external light coincides with the intrinsic frequency of electron oscillations, there is a resonance, that manifests itself in the appearance of an absorption band in the visible region of spectra of nanosized metal particles, which is absent in the spectra of massive specimens [7, 8].

The fig. 2 b shows the surface plasmon resonance band of silver nanoparticles in Ag-CdI<sub>2</sub> structures in the "pure" form with taking into account the continuous background. Those experimental data show at least two components with maxima at 491 and 608 nm are visible, which can be interpreted as the transverse and longitudinal modes of the spheroid. Therefore, the analysis of the surface plasmon resonances band structure of the investigated heterosystem shows [7], give evidence, that the form of silver nanoparticles in Ag-CdI<sub>2</sub> shaped like a disc. The ratio of the ellipsoid axes is  $\sim 1.43$  in the case  $c > a$ . The major axis of the silver nanoparticles flat disks lies in the plane of the CdI<sub>2</sub> crystal.

In the absorption spectra of the Ag-CdI<sub>2</sub> heterostructures, in addition to the bands of the nanoparticles of metals, there are shorter wave bands with maxima at 420 and 450 nm. These bands are caused by the centers that arise when localizing silver ions in the tetrahedral cavities of the van der Waals cadmium iodide slits and the occurrence of a chemical bond between the impurity metal atoms and the lattice iodine. In addition, in the spectral region adjacent to the edge of its own absorption of CdI<sub>2</sub>, there are bands due to defective centers, which can also contribute to the absorption of Me-CdI<sub>2</sub> structures.

In the luminescence spectra of the Ag-CdI<sub>2</sub> structure, in comparison with the pure crystal, a new band appears in the red spectrum with a maximum at 680 nm. The intensity of this glow increases with time that has passed from the spray-on of the film (fig. 3).

The long-wave emission of the heterostructure is observed only when samples are excited from the side of the metal. On the contrary, when samples are irradiated from the opposite side, the luminescence spectrum coincides with the spectrum of pure CdI<sub>2</sub>. That means the localization of the emission centers in the near-surface area of the CdI<sub>2</sub> crystal that is in contact with the evaporated metal. Such a conclusion is confirmed by the data of microscopic studies, which indicate the localization of centers of glow on the locations of metal.

The nature of the long-wavelength bands of the luminescence of the  $Me$ - $CdI_2$  ( $Me = Ag, Au$ ) heterostructures is associated with centers  $[Me^+I_4^-]^{3-}$  that arise when localizing silver and gold ions in the tetrahedral cavities of the van der Waals cadmium iodide slits and the occurrence of a chemical bond between the impurity metal atoms and the lattice iodine.

In the works [11, 12] by the method of MO LKAO the electronic structure of the centers formed by metal atoms with their localization in the tetrahedral cavities of van der Waals slit laminates was calculated. In the framework of the proposed model, the observed absorption bands and the  $Me$ - $CdI_2$  long-wave myomecativity are associated with electronic transitions between states of the valence band and the local level under the bottom of the conduction band.

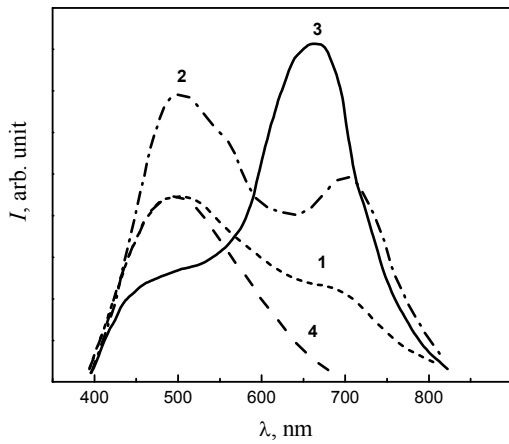


Fig. 3. Photoluminescence spectra of  $Ag$ - $CdI_2$  heterostructures (1-3), measured after 1 hour, (1), 20 hours, (2) and 70 hours (3) after evaporation a metal silver film. Curve 4 shown emission spectra of pure crystal  $CdI_2$  ( $T = 290$  K)

The time dependence of the intensity of the additional band of radiation,  $Ag$ - $CdI_2$ , is connected, obviously, with the increasing concentration of luminescence centers in the diffusion of silver into the  $CdI_2$  crystal. The process of silver diffusion into a matrix can be described by means of the second Fick law:

$$\frac{dC}{dt} = \frac{d}{dx} \left( D \frac{dC}{dx} \right), \quad (1)$$

where  $C$  is the concentration of diffusing ions,  $x$  is the diffusion distance,  $D$  is the diffusion coefficient.

The solution of equation (1) can be obtained in analytical form under the condition of a constant surface concentration of silver  $C_{surf}$ :

$$C(x, t) = C_0 + C_{nob.} \left[ 1 - \text{Erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right],$$

were  $C_0$  is the initial concentration of silver in  $CdI_2$ ,  $t$  is the time of diffusion and

$$\text{Erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-z^2) dz$$

Given that the intensity of the radiation is directly proportional to the concentration of the centers of luminosity, the time dependence of the intensity of the long-wave luminescence of  $Ag$ - $CdI_2$  can be described by the dependence

$$I(t) \sim 1 - \text{Erf} \left( \frac{x}{2\sqrt{Dt}} \right). \quad (2)$$

Thus, the diffusion coefficient  $D$  can be determined by substituting experimentally the obtained dependence  $I(t)$  into equation (2), provided that the diffusion distance  $x = 0,2$  mm is known (fig. 4).

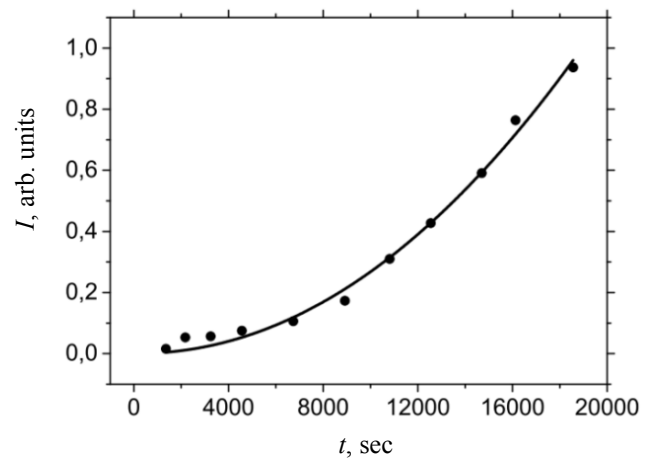


Fig. 4. Time dependence of the intensity of the glow of  $Ag$ - $CdI_2$  heterostructures. Points are an experimental curve, a solid line is an approximation of equation (2).

The comparison of the theoretical calculated (fig. 4, solid curve) and experimentally obtained (fig. 4, circles) of the dependences of the integral intensity of luminescence  $I(t)$  shows that the best coincidence is achieved at  $D = 3.2 \times 10^{-9}$   $cm^2/sec$ . Taking into account the fact that the estimation of the diffusion distance may contain an error, we have chosen the value  $D = (3,0 \pm 0,5) \times 10^{-9}$   $cm^2/sec$ . We shall further consider this veinchin as the coefficient of silver diffusion in the  $CdI_2$  matrix.

It is established that under the action of UV irradiation (laser LHY-21,  $\lambda = 337$  nm), the intensity of long-wave radiation of  $Ag$ - $CdI_2$  decreases over time to a certain minimum value of  $I_{min}$  (fig. 5).

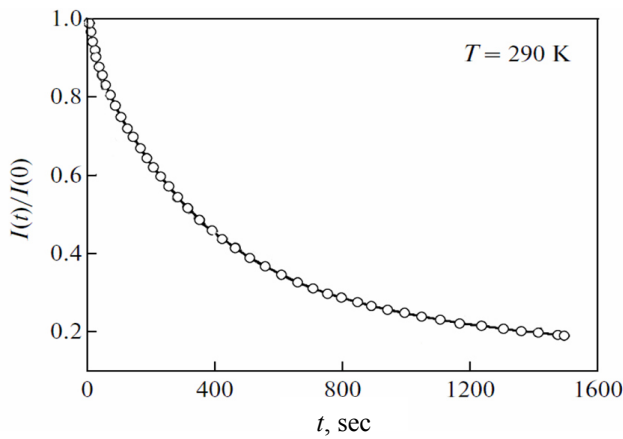


Fig.5. Time dependence of the luminescence intensity of Ag-CdI<sub>2</sub> at UV irradiation ( $\lambda = 337$  nm). Points – an experimental curve, a solid line – the calculation on formula 3.

Time variations in the luminescence intensity of the heterostructures are described within the framework of the model in which it is considered that under the action of UV irradiation a part of the centers of glow disappears [13,14]:

$$I(t) \approx \frac{\gamma \cdot S I_0 N}{\alpha} \left\{ (1-\beta) + \frac{\beta}{F I_0 t} \cdot [1 - \exp(-F I_0 t)] \right\} \quad (3)$$

Equation (3) can be used to find the intersection of the capture of the process of decaying the luminescence of Ag-CdI<sub>2</sub> under the action of UV irradiation. In this case, the value was determined from the experimental damping curve and for the investigated structures was  $\sim 0.60$  at  $T = 290$  K.

The intensity of the exciting light  $I_0$  varied from  $2.0 \times 10^{16}$  to  $1,1 \cdot 10^{18} \frac{\text{foton}}{\text{cm}^2 \cdot \text{sec}}$ , and the value  $\alpha$  for  $\lambda = 337$  nm was chosen equal  $5.0 \times 10^4 \text{ cm}^{-1}$ .

Approximation of the experimental damping curve by equation (3) allowed to determine the value of the intersection of the absorption of the process of "attenuation" of the light

$$F \approx 10^{-19} \frac{\text{cm}^2}{\text{foton}}.$$

Due to the decrease in the intensity of the luminescence of Ag-CdI<sub>2</sub> between the UV-irradiated and non-irradiated sections of the heterostructures, a contrast occurs in the luminescent image. It is possible to implement the medium for visualization of the field and the intensity of UV radiation [15, 16].

## REFERENCES

- [1] I.M. Bolesta, I.V. Kityk, V.I. Kovalisko, O.G. Syrбу, The Luminescence of Metal-Cadmium Iodide Heterostructures, Phys. Stat. Sol. (a), vol. 147, 1995, pp. K53–K56.
- [2] I. Bolesta, S. Velgosh, A. Kushnir, V. Lesivtsiv, I. Rovetsky, Plasmonic absorbance and luminescence of the Ag–CdI<sub>2</sub> heterostructures, Visnyk of Lviv University. Physics Series, is. 50, 2015, pp. 37–47 (in Ukrainian).
- [3] Q.-J. Liu, Z.-T. Liu, L.-P. Feng, Calculations of structural, elastic, electronic, and optical properties of trigonal CdI<sub>2</sub>, Phys. Status Sol. (b), vol. 248, 2011, pp. 1629–1633.
- [4] Wide-Gap Layered Crystals and Their Physical Properties, edited by A.B. Lyskovich, Vyscha Shkola, Lviv, 1982, 148 p. (in Russian).
- [5] R. Singh, S. Samanta, A. Narlikar, G. Trigunayat, A combined optical, SEM and STM study of growth spirals on the polytypic cadmium iodide crystals, Bull. Mater. Sci., vol. 23, № 2, 2000, pp. 131–133.
- [6] B. Kumar, N. Sinha, Micromorphology of pure and PbI<sub>2</sub>-doped CdI<sub>2</sub> dendritic single crystals, Cryst. Res. Technol., vol. 40, № 9, 2005, pp. 887–892.
- [7] R. Singh, S. Samanta, A. Narlikar, G. Trigunayat Influence of weak atomic bonding on the height of growth spiral steps on cadmium iodide crystals, Surface Sc., vol. 422, 1999, pp. 188–191.
- [8] V.V. Klimov, Nanoplasmonics, Pan Stanford, New York, 2014, 598 p.
- [9] S.A. Maier, Nanoplasmonics: Fundamentals and applications, Springer, New York, 2007.
- [10] U. Kreibitz, M. Vollmer, Optical properties of metal clusters, Springer-Verlag, Berlin, 1995, 532 p.
- [11] S. Velgosh, V. Lesivtsiv, Electronic structure of impurities centers, localized in van der Waals gaps of CdI<sub>2</sub> layered crystals, Inorganic Materials, vol. 32, № 10, 1996, pp. 1261–1264.
- [12] I.M. Bolesta, I.V. Kityk, V.I. Kovalisko, Electronic states of impurities localized in van der Waals gaps of CdI<sub>2</sub> layered crystals, Inorganic Materials, vol. 32, № 10, 1996, pp. 1261–1264.
- [13] I.M. Bolesta, S.R. Velgosh, I.D. Karbovnyk, V.N. Lesivtsiv, I.N. Rovetskii, Time dependence of the luminescence intensity in CdI<sub>2</sub>-Cd and CdI<sub>2</sub>-Ag crystals, Phys. of the Sol. State, vol. 54, is 10, 2012, pp. 2061–2065.
- [14] I.M. Bolesta, B.M. Kalivoshka, I.D. Karbovnyk, V.M. Lesivtsiv, I.S. Novosad, S.S. Novosad, I.M. Rovetsky, S.R. Velgosh, Time dependence of the luminescence intensity in CdBr<sub>2</sub>: AgCl, PbBr<sub>2</sub> crystals under N<sub>2</sub>-laser excitation at room temperature, Materials Science-Poland, vol. 32(4), 2014, pp. 604–609.
- [15] M.A. Shustov, E.P. Surovoy, G.V. Zinger, Thermographic recording of information on heavy metal iodides, J. of Sci. and Appl. Photography and Cinema, vol. 27, № 6, 1982, pp. 447–449 (in Russian).
- [16] M.T. Kostyshyn, Physical fundamentals of semiconductor electronics, Nauk. Dumka, Kyiv, 1985, pp. 192–200 (in Russian).