PHOTOELECTRICAL AND LUMINESCENT PROPERTIES COMPOSITES BASED ON SEMICONDUCTOR $CdIn_2S_4$ AND POLYMER

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The current-voltage and spectral characteristics of a composite based on the semiconductor $CdIn_2S_4$ and polypropylene have been studied. It has been established that the polypropylene composite exhibits photoconductivity and photoluminescence in the visible region of the spectrum.

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INTRODUCTION

The $CdIn_2S_4$ compound belongs to the class of ternary diamond–like semiconductor compound with the general formula $A^{II}B_2^{III}C_4^{VI}$, crystallizes in the cubic spinel structure Fd3m (O_h^7) space group, has an indirect band gap energy $E_g^{in}=2.28eV$ at 300K [1]. This compound has high photosensitivity and bright luminescence in the visible region of the spectrum. Interest in $CdIn_2S_4$ is associated with the possibility of practical application in optoelectronics [2–5]. Nowadays, there have been actively investigated $CdIn_2S_4$-based thin-film structures [6–12].

The creation of materials based on polymers and inorganic is a promising direction for organic electronics. Recently, polymer composite materials, in which the insulating polymer matrix contains semiconductor particles, have attracted considerable interest. In this work, the current-voltage and spectral characteristics of the $CdIn_2S_4$ semiconductor dispersed in a polymer matrix were studied in order to determine the effect of the of the polymer phase on the physical properties of $CdIn_2S_4$.

COMPOUND SYNTHESIS AND SAMPLE PREPARATION

The $CdIn_2S_4$ compound was synthesized from initial high-purity components In, Cd and S, which were loaded into a quartz ampoule in a stoichiometric ratio and pumped out up to 10^{-2} Pa. The obtained $CdIn_2S_4$ ingots were colored bright red. X-ray diffraction analysis revealed the spinel structure with a lattice constant: $a=10.79Å$.

We have developed a method for producing a composite in the polymer–semiconductor $CdIn_2S_4$ system. The preparation method we use consists of introducing pre-ground compound into the polymer. To do this, polycrystals of the $CdIn_2S_4$ compound are crushed in a ball vibrating mill for an hour. In this case, a powder is obtained, the particle size of which does not exceed 2-3 microns. The resulting powder is mixed with dissolved benzene polypropylene (*PP*). The weight fraction of $CdIn_2S_4$ particles in the composite was 90%. Stirring was carried out in a ball vibrating mill for an hour. This process provides a uniform distribution of $CdIn_2S_4$ particles in the polymer and partly further grinding. The composite was applied to horizontal substrates (glass). The working area of the samples is determined by the size of the substrate on which the material is applied. In the manufacture of structures with a conductive SnO_2–$CdIn_2S_4$–SnO_2 coating, the resulting emulsion was deposited on a conductive SnO_2 glass.

Then glass with a conductive SnO_2 coating was pressed against the emulsion. In this case, benzene, which is part of the emulsion, quickly evaporated, and the other components of the emulsion $CdIn_2S_4$ particles in the polymer matrix are fixed between the conductive glasses. After that, the resulting structure was dried. During measurements, the samples were placed in a cryostat with an optical window. A vacuum of 0.1*Pa* was maintained in the cryostat. Experiments were carried out in constant electric field mode. Samples were illuminated with unmodulated monochromatic light. The photoconductivity spectra were taken on a setup formed by the system «incandescent lamp *SI*–6–300 - spectrometer *SF*–4*A*». The current was recorded by a direct current recorded. The graph is plotted point by point in sequential excitation mode. The measurements were carried out according to a stationary technique in the wavelength range of 400÷2000*nm.*

The photoluminescence (*PL*) spectra were recorded on a *DFS*–12 setup. During luminescence studies, the samples were irradiated with a 365*nm* line of a *DRSH*–1000 mercury lamp.

EXPERIMENTAL RESULTS AND DISCUSSION

On figure 1 shows the dark and light current–voltage characteristics (*CVC*) of the *PP*–$CdIn_2S_4$ composite. It can be seen that the I–V characteristics are nonlinear and the resistance of the composite decreases with increasing electric field strength. The spectral distribution of the photoconductivity of the *PP*–$CdIn_2S_4$ composite at temperatures of 77 and 300*K* was also studied (fig.2). As can be seen from the figure, at room temperature, the structure has

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photosensitivity in a wide wavelength range of 450÷1200*nm* (fig.2, curve 1), with an impurity centers to the conduction band of $CdIn_2S_4$. At liquid nitrogen temperatures, the structure becomes sensitive in the wavelength range of 450÷800*nm*, and the photocurrent maximum shifts towards short wavelengths 540÷560*nm* (fig.2, curve2). This maximum in the photoconductivity spectrum is due to the transition of electrons from the valence band to the conduction band.

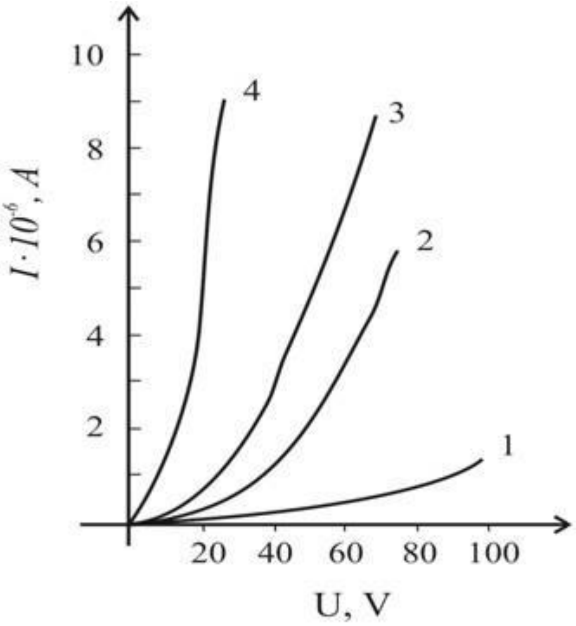

Fig. 1. Current-voltage characteristics of the PP–$CdIn_2S_4$ composite: 1-in the dark; 2, 3 and 4 at different intensities (*L*) o the exciting light (L_4>L_3>L_2).

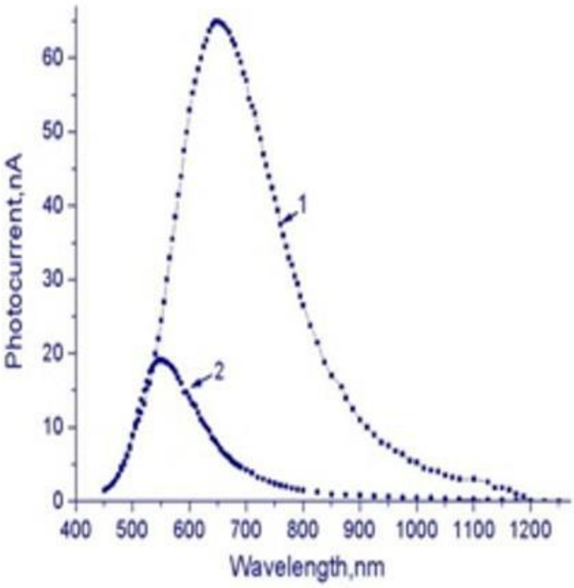

Fig. 2. Photoconductivity Spectrum of *PP*–$CdIn_2S_4$ composite at 300*K* (1) and 77*K* (2).

We studied the *PL* spectra of both polycrystalline $CdIn_2S_4$ samples and $CdIn_2S_4$ dispersed in polymer maximum in the range of 640÷660*nm*, due to the transition of electrons from the photosensitivity matrices (fig.3). Studies have shown that the obtained samples have *PL* in the visible region of the spectrum. *PL* spectrum polycrystalline $CdIn_2S_4$ has a wide maximum in the wavelength range of 655-660*nm*. It was established earlier that the *PL* spectrum of $CdIn_2S_4$ is complex and consists of four individual PL bands with maxima at about 1.89,1.67,1.45 and 1.35*eV*. *PL* spectrum $CdIn_2S_4$ dispersed in *PP* matrix has a maximum in wavelength of 640*nm*. As can be seen from the figure 3 *PL* spectra polycrystalline $CdIn_2S_4$ and $CdIn_2S_4$ dispersed in the polymer matrix are different. The luminescent characteristics of such materials are directly dependent on the nature of the semiconductor, particle size, and may have characteristic emission bands in a wide spectral region.

It should be noted that the polymer matrix and filler can actively interact. The degree of interaction depends on the concentration and size of the filler, the type of polymer, and the conditions for the formation of the composition. Potential barriers are formed between spherical semiconductor particles dispersed in a polymer [13, 14]. It is natural to assume that the value of the boundary potential barrier in composites is determined by the properties of the phases: polymer and semiconductor. The barrier height changes under the action of an electric field.

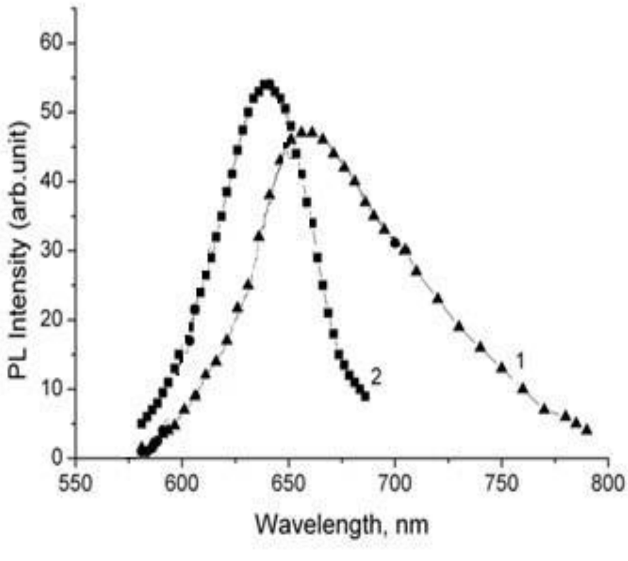

Fig. 3. Photoluminescence Spectrum of polycrystalline $CdIn_2S_4$ (1) and $CdIn_2S_4$ dispersed in a polymermatrix (2) at 100*K*.

Primary experimental results indicate the promise of *PP*–$CdIn_2S_4$ composite materials as photoactive and luminescent material. A good choice of component ratios can provide a sufficiently high photosensitivity of the specified composite. Considering also the technological simplicity of manufacturing materials based on semiconductor compound $CdIn_2S_4$ dispersed in a polymer matrix, one can count on their practical application in various photo- and optoelectronic devices.

[1] *H. Nakanishi.* Fundamental Absorption Edge in $CdIn_2S_4$. Jap. J. Appl. Phys., 1980, Vol.19. №1, pp.103-108.

[2] *Д.Т. Гусейнов, Т.Г. Керимова, Зафар Кадыроглы.* Эффекты, обусловленные отталкивающим барьером в соединении $CdIn_2S_4$. ФТП, 1996, т.30, в.6, стр. 974 -979.

[3] *З.Кадыроглы.* Оптическое гашение фототока в монокристаллов $CdIn_2S_4$. Transactions of National Academy of Science of Azerbaijan, series of physics-mathematical and technical sciences, Physics and Astronomy, 2021, т. XLI, №5, с. 121-127.

[4] *З. Кадыроглы.* Кинетика релаксации оптического гашения фотопроводимости в монокристаллах $CdIn_2S_4$ легированных Cu. Transactions of National Academy of Science of Azerbaijan, series of physics-mathematical and technical sciences, Physics and Astronomy, 2022, т.XLII, №2, с. 85-90.

[5] *Z. Kadiroğlu, T.G .Kerimova.* Photoelectronic and electrical properties of $CdIn_2S_4$ single crystals. Defects in Semiconductors ISDS-25, Book of abstracts, St Peterburg, Russia, 2009, pp.310-311.

[6] *A.V. Kokate, L.V. Gavalli, S.I. Mulla, P.P. Hankare, B.K. Chougull.* Photoelectrochemical properties of electrochemically deposited $CdIn_2S_4$ thin films. J. Phys. Chem. Solids, 2006, Vol.67, №11, pp.2331-2336.

[7] *Зафар Кадыроглы, Д.Т. Гусейнов, Т.Г Керимова., М.А. Алиев.* Фоточувствительная структура на основе соединения $CdIn_2S_4$. Fizika, 2008, т.14, №3, с.78-80.

[8] *Kwang Joon Hong.* Growth and optoelectrical properties of $CdIn_2S_4$ epilayers by hot wall epitaxy. Journal of Ceramic Processing Research, 2005, Vol.6, №3, pp. 201-204.

[9] *Alaa.-Al-jubory.* Structural and optical properties of $CdIn_2S_4$:Cu thin film prepared by shemical spray pyrolysis . J.of univercity of anbar for pure science, 2012, V.6, №3, pp.91-96.

[10] *Y. Li, R. Dellert, D. Bahnemann.* Preparation of porous $CdIn_2S_4$ photocatalyst films by hydrothermal crystal growth at solid/luquid/gas intervaces. Thin Solid Films, 2008, 516, pp. 4388-4392.

[11] *I. Zhao, X. Liu, P. Huo, J. Yan, L. Wang, Ch. Ltao, P. Huo, Ch. Liu.* Interface engeineering of Co958/ $CdIn_2S_4$ for efficient photocatalytic H evolution under visible light.Journal of Colloid and Interface Science, 2021, 600, pp.794-803.

[12] *L.K. Dhandole, M.A. Mahadik, H-S Chung, W.S. Chae, J.S. Jang.* $CdIn_2S_4$ chalcogenide / TiO_2 nanorod heterostructured photoanode: An advanced material for photoelectrochemical applications. Applied Surafce Science, 2019, 490, October, pp.18-19.

[13] *А.Д. Стадник, Г.К. Кирик.* Полимерные композиты и нанокомпозиты в магнитных полях, 2005, р. 239.

[14] *R.H. Bube.* Photoelectronic Properties of Semiconductors, Cambridge University Press, Cambridge, 1992, p.72.

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YARIMKEÇİRİCİ $CdIn_2S_4$ VƏ POLİMER ƏSASINDA KOMPOZİTLƏRİN FOTOELEKTRİK VƏ LÜMİNESSENSİYA XASSƏLƏRİ

$CdIn_2S_4$ yarımkeçiricisi və polipropilen polimeri əsasında alınmış kompozitlərin volt–amper və spektral xassələri tədqiq edilmişdir. Müəyyən olunmuşdur ki, $CdIn_2S_4$–polipropilen kompoziti spektrin görünən hissəsində fotohəssaslığa və fotolüminessensiyaya malikdir.

Зафар Кадыроглы

ФОТОЭЛЕКТРИЧЕСКИЕ И ЛЮМИНЕСЦЕНТНЫЕ СВОЙСТВА КОМПОЗИТОВ НА ОСНОВЕ ПОЛУПРОВОДНИКА $CdIn_2S_4$ И ПОЛИМЕР

Изучены волт-амперные и спектральные характеристики композита на основе полупроводника $CdIn_2S_4$ и полипропилен. Установлено, что композит $CdIn_2S_4$–полипропилен обладает фоточувствительностью и фотолюминесценсией в видимой области спектра.