THE KINETICS OF THE RELAXATION OF NEGATIVE PHOTOCONDUCTIVITY IN $CdIn_2S_4$:Cu SINGLE CRYSTALS

ZAFAR KADIROGLU
Azerbaijan National Academy of Sciences, Institute of Physics,
H. Javid ave. 131, AZ-1143, Baku,
zafark@mail.ru

The discovery and study of negative photoconductivity in $CdIn_2S_4$:Cu single crystals reported. Were studied the kinetics of the relaxation of negative photoconductivity at different intensities of exciting monochromatic light and different values of the electric field strengths applied to the sample.

Keywords: semiconductor ternary compounds, $CdIn_2S_4$, negative photoconductivity, recombination and trapping, optical quenching, intrinsic defects, electronic states (localized).
PACS: 72.20.Jv, 72.80.Jc, 72.80.Tm, 72.40.+w,71.55.-i, 71.20.Nr

1. INTRODUCTION

The ternary $CdIn_2S_4$ belongs to the class of diamond-like semiconductor compounds with the general formula $A^{II}B_2^{III}C_4^{VI}$ and crystallizes in the cubic spinel structure Fd3m (O_h^7) space group. The indirect band gap energy of $CdIn_2S_4$ is E_g^{in}=2.28 eV at 300K [1]. $CdIn_2S_4$ has two kinds of atoms in cationic sublattice. It is possible formation of antistructural defects, due to substitution of cations (Cd_{In} and In_{Cd}), cadmium vacancies (V_{Cd}), sulfur vacancies (V_s), cadmium interstitials (Cd_{int}), sulfur interstitials (S_{int}), and complexes of these point defects. As a result, in the forbidden band of $CdIn_2S_4$ presence a lot of local levels.

This compound has high photosensitivity and bright luminescence in the visible region of the spectra [2-8]. The $CdIn_2S_4$ compound belongs to an interesting group of solids whose photoelectric properties can be changed over a wide range by doping and deviation from stoichiometry. The resistivity and photosensitivity of $CdIn_2S_4$ varies with the sulfur content S, as well as with doping with Cu, Ag, and Au. In $CdIn_2S_4$, the effect of switching and memory is observed at the $CdIn_2S_4$-metal contact, light memory, generation of current oscillations, photocatalytic properties, etc. Interest in $CdIn_2S_4$ is associated with the possibility of practical application as a photoresistor, solar cell, photocatalytyc material and light emitting diode [9-18]

One of the most interesting photoelectric effects observed in various semiconductor materials is negative photoconductivity [19-25]. The essence of the effect is to reduce the equilibrium dark conductivity of the semiconductor when illuminated. In this paper, we report the discovery and study of NPC in $CdIn_2S_4$ crystals doped with Cu impurity.

2. 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 and pumped out up to 10^{-2} Pa. The Cu impurity concentration in $CdIn_2S_{4.01}$ was 0.002 mol. The obtained $CdIn_2S_4$:Cu ingots were colored black. X-ray diffraction analysis revealed the spinel structure with a lattice constant: a=10.79Å.

$CdIn_2S_4$ single crystals have been grown by gas the transport method. Crystalline iodine was used as a carrier. During manufacture, the samples were given the form of plane-parallel plates with dimensions of about 3x2x1 mm^3.In this case, one of the sides always had a natural mirror face of the crystal. Metallic indium was used as ohmic contacts. The distance between the contacts was 2 mm. Investigated samples have a resistivity of about $10^6 \div 10^8$ Ω·cm, in the dark, and $R_{dark} / R_{light} = 10^2 \div 10^5$ ratio for a white light with 200 Lx intensity at T=300K. The samples had n-type conductivity.

During measurements, the samples were placed in a cryostat with an optical window. A vacuum of 0.1 Pa was maintained in the cryostat. The experiments were carried out at a sample temperature of 110 K, in the wavelength range of 400÷2000 nm, by steady state method.

3. EXPERIMENTAL RESULTS AND DISCUSSION

In experiments under various external conditions (strengths of an external electric field and illumination) were recorded spectral distributions and photoresponse kinetics of the negative and positive photoconductivity in $CdIn_2S_4$: Cu single crystals. As a result of the experiments performed, the following regularities were revealed in samples $CdIn_2S_4$: Cu in the absence of the background excitation (when the sample under study is illuminated with only one beam of monochromatic light with a varied wavelength).

1. Negative photoconductivity is observed at low strengths of the applied electric field. With an increase in the electric field strength, the negative photoconductivity effect decreases and passes into the usual positive photoconductivity. At electric field strengths greater than 50 V/cm, negative photoconductivity is not detected (Fig.1).

131, H.Javid ave, AZ-1143, Baku
ANAS, Institute of Physics
E-mail: jophphysics@gmail.com

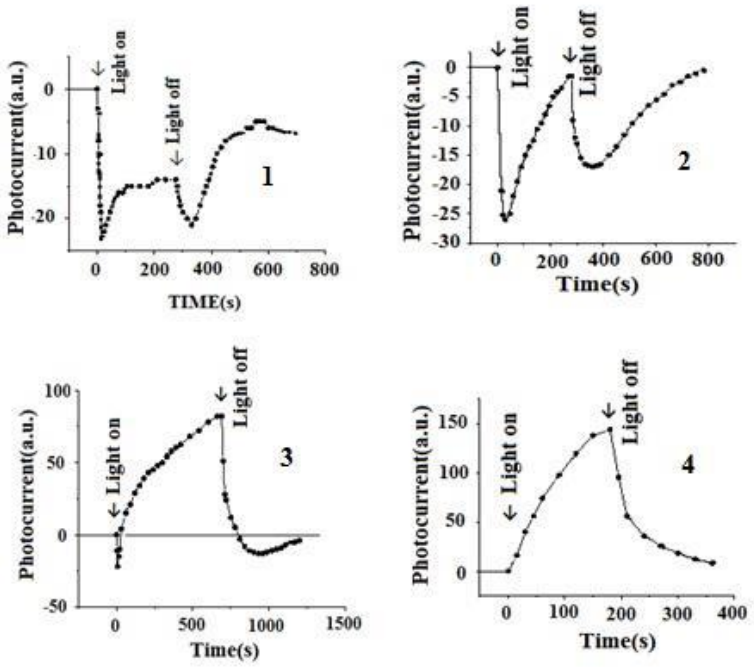

Fig.1. The kinetics of the relaxation of photoconductivity in $CdIn_2S_4$ crystals doped with Cu at various applied electric field strengths (λ =480 nm; T=110 K): 1. E = 5 V/cm; 2. E = 10 V/cm; 3. E = 30 V/cm; 1. E = 60 V/cm.

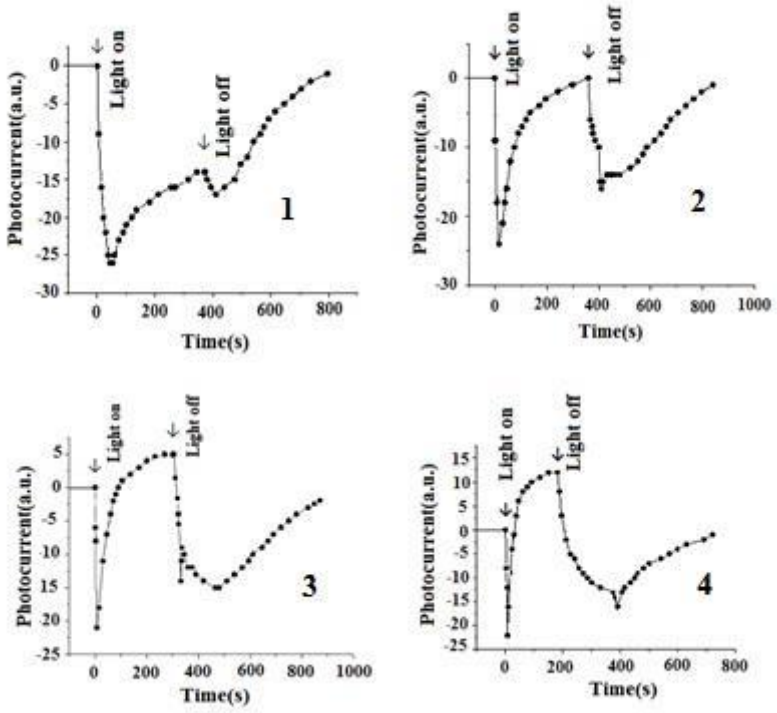

Fig. 2. The kinetics of the relaxation of photoconductivity in $CdIn_2S_4$:Cu single crystals at different intensities of exciting light from the intrinsic absorption region (λ=480 nm; T=110 K): 1. $I=I_0$; 2.$I =1.7\ I_0$; 1. $I =2\ I_0$; 1. $I=2.5\ I_0$.

2. Negatively photoconductivity is detected at rather low intensities of the exciting light. As the intensity of the exciting light increases, the negative photocurrent gradually decreases and transforms into the usual positive photoconductivity (Fig.2).

3. Negative photoconductivity is detected under illumination with both intrinsic and extrinsic light (Fig.3).

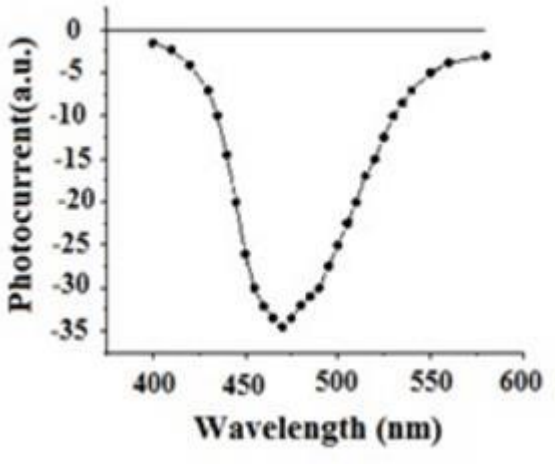

Fig.3. Spectral distribution of negative photocurrent in $CdIn_2S_4$:Cu single crystals (T = 110 K).

4. In $CdIn_2S_4$:Cu single crystals, at room temperatures, negative photoconductivity is not observed.

The interpretation of negative photoconductivity is currently difficult. In order to establish the nature of negative photoconductivity in $CdIn_2S_4$:Cu single crystals more detailed study will be necessary. Further investigations are now in progress.

[1] *H. Nakanishi.* Fundamental absorption edge in $CdIn_2S_4$, Japan J.of Appl. Phys., 1980, V.19, 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, стр. 974-979.

[3] *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.

[4] *Зафар Кадыроглы, Д.Т. Гусейнов, Т.Г. Керимова, М.А. Алиев.* Фоточувствительная структура на основе соединение $CdIn_2S_4$. Fizika, 2008, V.14, №3, стр. 78-80.

[5] *Зафар Кадыроглы, Т.Г. Керимова, Р.А. Гулиев, М.А. Алиев.* Электрические и фотоэлектрические свойства легированного примесью Fe. Transactions of National Academy of Science of Azerbaijan, series of physics-mathematical and technical sciences, Physics and Astronomy, 2012, V. XXXII, №2, pp.36-41.

[6] *З. Кадыроглы, Т.Г. Керимова, Д.Т. Гусейнов.* Влияние центров окруженных отталкивающим барьером на неравновесные процессы в $CdIn_2S_4$. Труды международной конференции «Fizika–2005», Баку, Элм, 2005, стр.849-852.

[7] *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, V. XLI, №5, pp.121-127.

[8] *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, 2022, V. XLII, №2, pp.85-90.

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

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

[11] *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, V.516, pp. 4388-4392.

[12] *A.V. Kokate, M.R .Asabe, S.B. Shelake, P.P. Hankare, B.K. Chougule*. Structural, optical and electrical studies on pulse electrodeposited $CdIn_2S_4$ thin films. Physica B, 2007, V.390, pp. 84-90.

[13] *Wanjun Wang, Tsz Wai Ng, Wing Kue Ho, Jianhui Huang, Shijing Liang, Taicheng An, Guiying Li, Jimmy C Yu, Po Keung Wong.* $CdIn_2S_4$ microsphere as an efficient visible–light–driven photocatalyst for bacterial inactivation: Synthesis, characterizations and photocatalytic inactivation mechanisms. Applied Catalysis B: Environmental, 2013, V. 129, pp. 482-490.

[14] *Ji-Peng Song, Peng-Fei Yin, JinyMao, Shi-Zhang Qiao and Xi-Wen Du*. Catalytically active and chemically inert $CdIn_2S_4$ coating on a CdS photoanode for efficient and stable water

splitting. Nanoscale, 2017, V. 9, №19, pp.6296-6301.
[15] *Xiao Shao, Wei-Yie Xin, Xiao-ong Yin and Shuai-Hua Ma*. Composite photocatalyst $CdIn_2S_4$-In $(OH)_3$ reducing carbon dioxide to methyl formate. Advanced Materials, Technology and Application, 2016, pp.121-127.
[16] *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, V. 490, №10, pp.18-19.
[17] *J. Chen, C. Mao, H. Niu and J. Song*. Synthesis of novel C-doped g-CsP_4 nanosheets coupled with $CdIn_2S_4$ for enhanced photocatalytic hydrogen evolution. J.Nanotechnology, 2019, V.19, pp.912-921.
[18] *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, 794-803.
[19] *C.H. Lui, A.J. Frenzel, D.V. Pilon, Y.-H.X. Ling, G.M. Akselrod, J. Kong, and N. Gedik.* Phys. Rev. Lett., Trion –Induced Negative Photoconductivity in Monolayer MoS_2, 2014, V.113, Iss.16-17 October, pp. 166801- 166807.
[20] *Ch. Biswas, F. Güneş, D.D. Loc, S.Ch. Lim, M.S. Jeong, D. Pribat, and Y.H. Lee*. Negative and Positive Persistent Photoconductance in Graphene. Nano. Lett., 2011, V.11, Iss.11, pp. 4682-4687.
[21] *Ф.Н. Джафаров, Э.Ф. Насиров, С.А. Мамедов.* Отрицательная фотопроводимость в пленках твердых растворов $A^{II}B_2^{VI}$, ФТП, 2014, Т.48, № 5, стр.590-596.
[22] *Sh. Kaushik, K. Kapour, R.K. Pant, S.B. Krupanidhi, R. Singh*. Observation of negative photoconductivity at bandgap and super bandgap excitations in GaN nanorods, Optical Materials, V.121, 2021, №11, pp. 11553-111561.
[23] *A.G. Milnes.* Deep impurities in semiconductors. 1973, New York, Wiley-Interscience Publishers, 526 p.
[24] *A. Rose*. Concepts in Photoconductivity and Allied Problems, 1963, New York, Interscience Publishers, 168 p.
[25] *R.H. Bube.* Photoelectronic Properties of Semiconductors, 1992, Cambridge, Cambridge University Press, 318 p.

Зафар Кадыроглы

КИНЕТИКА РЕЛАКСАЦИЯ ОТРИЦАТЕЛЬНОЙ ФОТОПРОВОДИМОСТИ В МОНОКРИСТАЛЛАХ $CdIn_2S_4$: Cu

Сообщается об обнаружении и исследовании отрицательной фотопроводимости в монокристаллах $CdIn_2S_4$: Cu. Изучена кинетика релаксации отрицательной фотопроводимости при различных интенсивностях возбуждающего монохроматического света и напряженностях электрического поля.

Zəfər Qədiroğlu

$CdIn_2S_4$: Cu MOHOKRİSTALLARINDA MƏNFİ FOTOKEÇİRİCİLİYİN RELAKSASİYASININ KİNETİKASI

$CdIn_2S_4$:Cu monokristallarında mənfi fotokeçiriciliyin aşkar və tədqiq olunması haqqında məlumat verilir.Həyəcanlandıran işığın müxtəlif intensivliklərində və nümunəyə tətbiq olunan elektrik sahəsinin intensivliyinin fərqli qiymətlərində mənfi qalıq fotokeçiriciliyin relaksasiyasının kinetikası öyrənilmişdir.