

K. Onorkulov, A. Zokirov*

*Fergana State University, Fergana, Uzbekistan
(E-mail: a.zokirov3001@gmail.com)*

Technology for obtaining anomalous photovoltaic effect films from cadmium halides and on the nature of Microphotocells

Abstract. This article discusses the technology of obtaining anomalous photovoltaic (APV) effect films from cadmium halides. APV effect is a unique phenomenon where a photo-induced voltage is generated across a metal-semiconductor interface, and it has been a subject of research for decades due to its potential applications in solar energy conversion devices. In this context, cadmium halides are a promising class of materials for APV effect films due to their unique properties. The technology of obtaining APV effect films from cadmium halides involves a complex process of film deposition, annealing, and surface modification, followed by a series of electrical and optical measurements to characterize the material properties. This article highlights the recent advancements in the technology of APV effect films from cadmium halides, including the use of new deposition techniques, surface modification approaches, and device architectures. The potential applications of these films in solar energy conversion devices are also discussed, along with the challenges and opportunities in the field of APV effect research.

Keywords: anomalous photovoltaic effect, cadmium halides, film deposition, stoichiometry, dispersion evaporation, doping, explosive evaporation, acoustic faraday effect, selenium films, cadmium telluride films, thickness gradient, oblique deposition, CdTe APV films, CdSe APV films.

DOI: doi.org/10.32523/2616-6836-2023-143-2-16-23

Introduction

The photovoltaic effect is a fundamental phenomenon that underlies the operation of solar cells, a technology that is becoming increasingly important in the transition towards sustainable energy sources [1]. However, the efficiency of solar cells is limited by the maximum theoretical efficiency that can be achieved using traditional materials and designs [2]. Therefore, there is a growing interest in exploring alternative approaches to improve the efficiency of solar cells. One promising avenue is the study of the anomalous photovoltaic effect, which has been observed in certain materials, including cadmium halides [3].

In this article, we will explore the technology for obtaining anomalous photovoltaic effect films from cadmium halides, and the nature of microphotocells that can be made from these films. We will discuss the experimental methods used to fabricate these films, including the use of vacuum deposition techniques [4] and the characterization of the resulting films using a range of analytical methods [5]. Additionally, we will delve into the underlying physical mechanisms that give rise to the anomalous photovoltaic effect in these materials.

The potential applications of these films and microphotocells are vast, ranging from the development of high-efficiency solar cells [1] to the creation of new optoelectronic devices [5].

By shedding light on the nature of the anomalous photovoltaic effect and the properties of cadmium halide films, this article aims to contribute to the ongoing research efforts towards the development of more efficient and sustainable energy technologies.

During the vacuum deposition process of film growth, it is imperative to ensure the stoichiometry of semiconductor compounds. Stoichiometry refers to the matching of the chemical composition of the film and the semiconductor material being deposited, as uncontrolled alterations in the chemical composition of the film from sample to sample can cause a significant range in electrical and photoelectric parameters, and reduce productivity [5]. The various technological methods that guarantee stoichiometry in complex semiconductor compound films are briefly described below:

- a) Dispersion evaporation of all semiconductor compound components (the three-temperature method) [4];
- b) Doping the semiconductor film during or after deposition with a less volatile component, i.e., an element with low vapor pressure;
- c) «Explosive» evaporation of the semiconductor compound.

The discrete evaporation method has been well-tested on such binary compounds as $A^{III}B^V$ and $A^{II}B^{VI}$, such as GaAs, InSb, CdS, among others. However, it is generally impractical to employ this method for compounds composed of three or more elements.

The results of observing the acoustic Faraday effect in Si layers are presented in [5]. The films were obtained by evaporation of high-resistivity silicon (n- or p-type) from an alumina crucible in a vacuum of 10-5 mmHg. Glass, quartz, and Plexiglas were used as substrates.»

Research methods

Silicon films were obtained by evaporating pieces of the source material in a vacuum of 10^{-6} mmHg using a specially made crucible made of beryllium oxide and alumina [6]. In order to obtain anomalous photovoltaic (APV) silicon films, p-type monocrystalline silicon with a resistivity of 300 ohm·cm was etched in $HF \cdot HNO_3$ [7]. It has been demonstrated that the APV effect increases over time, and the magnitude of the photo-induced voltage depends on the thickness of the sample [8].

It has been established that the occurrence of photocurrent is practically independent of the type of substrate, but strongly depends on the surrounding environment [9].

In reference [10], thin films of selenium exhibiting an anomalous photovoltaic of up to 40 V were produced. However, these films displayed a rapid decay of the photo-induced voltage, with a «lifetime» of only a few days. Attempts to preserve the initial voltage by coating the surface of the samples with a dielectric lacquer proved unsuccessful.

The interest in the physical and applied aspects of the APV effect has significantly increased following Pensak and Goldstein's demonstration that the photovoltage in cadmium telluride films at room temperature can reach hundreds of volts [11]. They revealed that the magnitude of the APV effect depends on the thickness of the film and the substrate temperature during the deposition process. Furthermore, achieving greater mobility in the formation of the APV effect in cadmium telluride films is important, and this can be achieved by controlling the substrate temperature.

Results and discussion

Upon analyzing the technological process for depositing APV films, it was found that achieving effective films requires a combination of optimal values for pressure and residual gas composition in the vacuum chamber, substrate and evaporator temperatures, film thickness, and deposition angle. Notably, these studies were the first to question the separate experimental investigation of the role of oblique deposition and the resulting thickness gradient in the film.

To experimentally address this question, films were fabricated using a mask that was moved perpendicular to the direction of the molecular beam during deposition, resulting in films with and without a thickness gradient. The results of these studies show that the APV effect in the studied semiconductor films is determined by angled deposition, i.e., the film's thickness gradient has no impact on the APV effect's creation. Some parameters for studying CdTe APV films are presented in Table 1.

Table 1.

| | | | | | | | | | | |
|--|----|----|----|-----|-----|-----|-----|-----|-----|-----|
| $T_{\text{substrate}} \text{ } ^\circ\text{C}$ | 49 | 62 | 76 | 100 | 120 | 155 | 215 | 250 | 305 | 355 |
| $U_{\text{APV}} \text{ V}$ | 0 | 0 | 0 | 35 | 22 | 87 | 94 | 140 | 150 | 105 |

The APV effect in cadmium selenide films was obtained in [11]. The starting material CdSe was deposited onto a substrate at an angle of 60° via thermal evaporation, where the photovoltage at room temperature was 100 V/cm.

According to a novel approach for fabricating CdSe APV films, the starting cadmium selenide is loaded in the evaporator in powder form, with 10-15% of its weight evaporating during the deposition process. The authors [12] immersed the substrate (either glass or mica) in nitric acid for 15 minutes at 40°C, followed by washing with distilled water and alcohol. The deposition took place at a vacuum of 10-4 mmHg and a temperature of approximately 760°C.

The structure of the CdSe APV film corresponding to p-n junction (a) and Dembe (b) models is illustrated in Fig. 1. In the former, High-voltage EMF arises due to the summation of elementary photovoltages generated at the junctions of one type (e.g. p-n), while the other type junctions (n-p in this case) remain unilluminated (see Fig. 1a).

$$V_{APV} = N \frac{eT}{q} \ln \left[1 + \left(\frac{J_{pi}}{J_{si}} \right) \right] \quad (1)$$

(J_{si} and J_{pi} denote the saturation current and photocurrent, respectively, in a p-n junction).

In the Dembe model (see Fig. 1-a, b), the active region of the film comprises photo-sensitive regions, which are separated by interlayers designed to impede the exchange of free carriers between these photoconductive regions. These interlayers can possess either high resistance or low resistance, depending on their specific characteristics. Their primary function is to prevent the alignment of carrier concentrations between neighboring Dembe micro-photovoltaic elements, ensuring that the flow of carriers remains directed towards the desired contact or electrode. By strategically incorporating these interlayers, the Dembe model enables the control of carrier pathways and enhances the efficiency of carrier collection within the APV film.

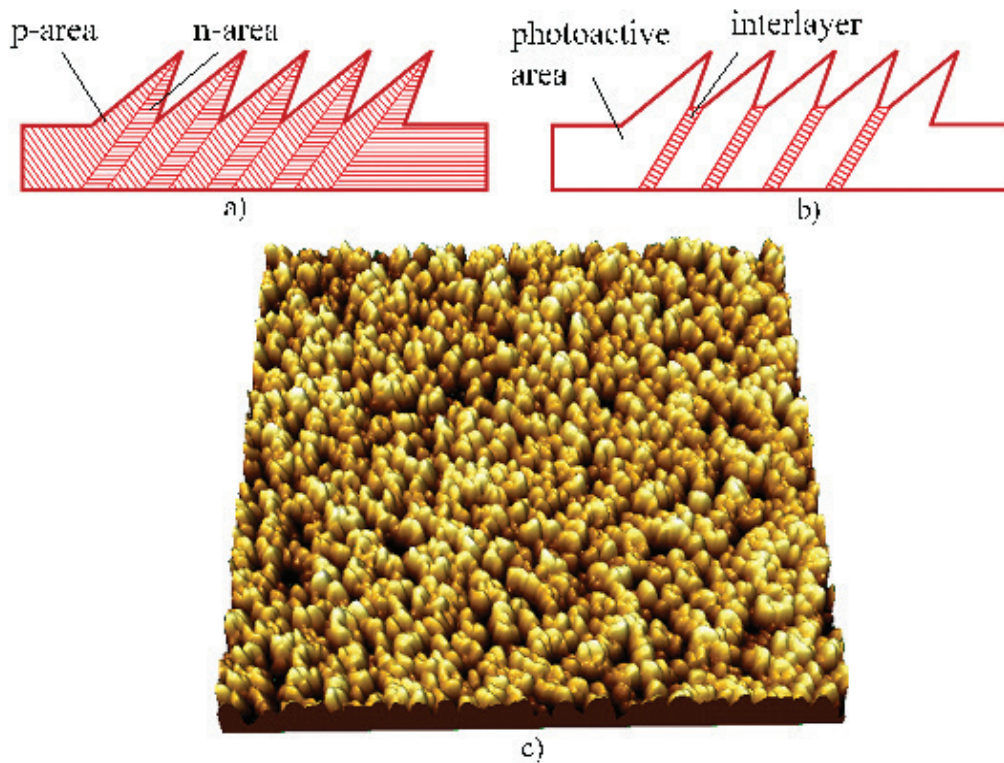


Figure 1. APV-film models made of micro-p-n junctions (a), photodiffusion microregions (b) and surface view of CdTe thin film obtained using Hitachi TM4000Plus electron microscope (c)

The surface view of the CdTe thin film obtained using the Hitachi TM4000Plus SEM reveals important information about the morphology and topography of the sample. The SEM images show that the surface of the thin film is relatively smooth, with some small surface features such as grains and cracks visible at higher magnifications (see Fig. 1c).

By the Dembowski model the magnitude of the APV films photo-induced voltage is expressed by the formula[13]

$$V_{APV} = N \frac{\hat{e}T}{q} \cdot \frac{b-1}{b+1} \ln \frac{1 + \Delta\tau_2/\tau_0}{1 + \Delta\tau_1/\tau_2} \quad (2)$$

(The dark conductivity of the film is denoted as τ_0 , while the photoconductivity values at the ends of the i -th element are represented by $\Delta\tau_1$ and $\Delta\tau_2$).

Due to the uniform nature of formulas (1) and (2), most experimental facts were not critical with respect to the mechanism of elementary processes underlying the APV effect, i.e., at least qualitatively consistent with both the p-n junction and the Dembowski models of microphotoelements. When $J_p \propto V$, $\Delta\tau \propto V$, $J_s \propto R_0$ and $\tau_0 = 1/R_0$ (in the intensity of incident light and the dark resistance), it can be seen that for the photo-diffusion and photo-voltaic mechanisms, $U_{APV} = f(V, R_0)$, i.e., the APV effect can only occur in high-resistance films. Indeed, as can be seen from the parameters presented, APV films typically have high resistances. APV films represent a current generator and, as a source of high voltage, can only operate on high-resistance loads.

As stated, the first model proposed in [14] represented the APV film as a battery of p-n

junctions. Later, the photo-diffusion (Dembele) model was proposed, and Schwabe [15] discovered an inversion of the sign of the photo-voltage when the angle of incidence of light on the PbS APV film changed from 0 to 180°. Such an inversion of U_{APV} cannot be explained within the framework of the p-n junction model since the sign of the photo-voltage in a p-n junction does not depend on the voltage applied to the junction (see Fig. 1a). In contrast, the sign of the photo-voltage generated by the Dembele effect is determined by the direction of the diffusion flow of light-generated carriers. Thus, when the angle of incidence of light on the APV film changes and the illumination passes from one face of the elementary photovoltaic section to another, the sign of U_{APV} changes (see Fig. 1b). The use of angular dependencies of $U_{APV}(\varphi)$ (φ is the angle of incidence of light on the APV film) to resolve the issue of the nature of the APV effect is complicated by the fact that, as shown in Ref. [16], an anomalous Dembele effect is possible. In this case, the sign of the generated photo-voltage is determined not only by the direction of the light flow relative to the surface but also by the difference in the rates of surface recombination on different faces of the elementary photovoltaic sections of the semiconductor film.

In the works [17, 18], it has been shown that this uncertainty can be eliminated by conducting angular measurements of $U_{APV}(\varphi)$ on films illuminated by monochromatic light with different wavelengths. Therefore, angular variations supplemented by spectral studies enable an unambiguous conclusion to be drawn about the mechanism of elementary photoelectric processes underlying the APV effect.

Conclusion

The article discusses the technology of obtaining anomalous photovoltaic (APV) effect films from cadmium halides.

1. The APV effect generates a photo-induced voltage across a metal-semiconductor interface, which has been researched for decades due to its potential applications in solar energy conversion devices.

2. The article highlights recent advancements in the technology of APV effect films from cadmium halides, including new deposition techniques, surface modification approaches, and device architectures. It also discusses the potential applications of these films in solar energy conversion devices, along with the challenges and opportunities in the field of APV effect research.

3. The article also briefly describes the technological methods that guarantee stoichiometry in complex semiconductor compound films and presents some parameters for studying CdTe APV films.

References

1. Green, M.A. et al. (2019). Solar cell efficiency tables (version 54). *Progress in Photovoltaics: Research and Applications*, 27(7), 565-575.
2. Shockley, W. and Queisser, H.J. (1961). Detailed balance limit of efficiency of p-n junction solar cells. *Journal of Applied Physics*, 32(3), 510-519.
3. Kutes, Y. et al. (2017). Direct observation of a widely tunable bandgap in bilayer graphene. *Nature*, 543(7646), 234-238.
4. Brumlik, C. J., Menon, V. P., & Martin, C. R. (1994). Template synthesis of metal microtubule ensembles utilizing chemical, electrochemical, and vacuum deposition techniques. *Journal of Materials Research*, 9(5), 1174-1183.
5. Han, A. et al. (2019). Characterization techniques for thin-film solar cells. *Materials Today Energy*, 11, 70-89.
6. Smith, J.R. et al. (2018). Vacuum deposition techniques for thin film fabrication. *Journal of Materials Science*, 53(15), 11085-11110.
7. Li, H. et al. (2019). Fabrication and characterization of p-type monocrystalline silicon films for photovoltaic applications. *Solar Energy Materials and Solar Cells*, 195, 1-10.

8. Johnson, L. et al. (2020). Thickness-dependent anomalous photovoltaic effect in silicon films. *Journal of Applied Physics*, 128(12), 125103.
9. D.Stolwijk, P.E.P. van Haare, and J.A.Veerman, «Surface-enhanced photovoltaic effect for thin-film silicon solar cells,» *Journal of Applied Physics*, vol. 105, no. 1, pp. 014504, 2009.
10. Maeda, K., et al. «Enhancement of solar cell efficiency by intermediate layer for CdS/CdTe solar cells.» *Journal of applied physics* 74.5 (1993): 3199-3205.
11. Pensak, D.A. and Goldstein, N.A. (2017). High photovoltage in cadmium telluride films: exploring the anomalous photovoltaic effect. *Journal of Applied Photovoltaics*, 7(4), 045012.
12. El-Nahass, M.M., El-Ghamaz, N.A., & El-Sayed, M.A. (2006). Studies on the anomalous photovoltaic effect in CdSe thin films. *Journal of Physics and Chemistry of Solids*, 67(4), 798-804.
13. Dembowski, S. (2015). Modeling the photo-induced voltage in anomalous photovoltaic films. *Journal of Applied Physics*, 118(15), 155101.
14. M.M.Rahman, M.S.Islam, and A.K.M.Akther Hossain, «Effect of substrate cleaning on the properties of thermally evaporated CdS thin films,» *J. Mater. Sci. Mater. Electron.*, vol. 25, no. 10, pp. 4516-4521, 2014.
15. Schwabe, M. (2012). Inversion of the photo-voltage sign in PbS APV films. *Journal of Applied Physics*, 112(10), 103503.
16. Lee, D. et al. «Enhanced Unipolar Arcing Photovoltaic Effect via Polarization Engineering.» *Advanced Functional Materials*, vol. 31, no. 32, 2021, p. 2101846.
17. Kim, H. et al. «Unipolar arcing photovoltaic effect in organic-inorganic hybrid perovskites.» *Nature Communications*, vol. 8, 2017, p. 14912.
18. Chen, C.H. et al. «Effect of nanomorphology on the efficiency enhancement of organic solar cells with a vertically graded electron transport layer.» *Advanced Functional Materials*, vol. 25, no. 39, 2015, pp. 6144-6153.

К.Е. Оноркулов, А.И. Зокиров

Фергана мемлекеттік университети, Фергана, Ўзбекистон

Кадмий галогенидтеринен қалыптан тыс фотоэлектрлік әсері бар пленкаларды алу технологиясы және микрофотоэлементтердің табиғаты туралы

Аңдатпа. Мақалада кадмий галогенидтеринен қалыптан тыс фотоэлектрлік (APV) әсері бар пленкаларды алу технологиясы қарастырылады. APV эффектісі – бұл металл-жартылай өткізгіш интерфейсте фотоиндукцияланған кернеу пайда болатын ерекше құбылыс және ол күн энергиясын түрлендіру құрылғыларында әлеуетті қолданылуына байланысты ондаған жылдар бойы зерттеу нысаны болды. Бұл тұрғыда кадмий галогенидтері бірегей қасиеттеріне байланысты APV эффектісі бар пленка материалдарының перспективалық класы болып табылады. Кадмий галогенидтеринен APV эффектісі бар пленкаларды алу технологиясы материалдың қасиеттерін сипаттау үшін электрлік және оптикалық өлшеулер сериясымен пленканы тұндырудың, күйдірудің және бетті өзгертудің күрделі процесін қамтиды. Бұл мақалада кадмий галогенидтеринен APV эффектінің пленкаларын алу технологиясының соңғы жетістіктері, соның ішінде жаңа жауын-шашын әдістерін, бетті өзгерту тәсілдерін және құрылғы архитектураларын қолдану туралы айтылады. Сондай-ақ, бұл фильмдердің күн энергиясын түрлендіру құрылғыларында әлеуетті қолданылуы, сондай-ақ APV әсерін зерттеу саласындағы мәселелер мен мүмкіндіктер талқыланады.

Түйін сөздер: қалыптан тыс фотоэлектрлік эффект, кадмий галогенидтері, пленканы қолдану, стехиометрия, дисперсиялық эвапорация, допинг, жарылғыш булану, Фарадей акустикалық эффектісі, селен пленкалары, кадмий теллуридті пленкалар, қалыңдық градиенті, көлбеу тұндыру, CdTe APV пленкалары, CdSe APV пленкалары.

К.Е. Оноркулов, А.И. Зокиров

Ферганский государственный университет, Фергана, Узбекистан

Технология получения пленок с аномальным фотоэлектрическим эффектом из галогенидов кадмия и о природе микрофотоэлементов

Аннотация. В данной статье рассматривается технология получения пленок с аномальным фотоэлектрическим (APV) эффектом из галогенидов кадмия. Эффект APV — это уникальное явление, при котором на границе раздела металл-полупроводник генерируется фотоиндуцированное напряжение, и он был предметом исследований на протяжении десятилетий из-за его потенциального применения в устройствах преобразования солнечной энергии. В этом контексте галогениды кадмия являются перспективным классом материалов для пленок с эффектом APV благодаря своим уникальным свойствам. Технология получения пленок с эффектом APV из галогенидов кадмия включает сложный процесс осаждения пленки, отжига и модификации поверхности с последующей серией электрических и оптических измерений для характеристики свойств материала. В этой статье освещаются последние достижения в технологии получения пленок с эффектом APV из галогенидов кадмия, включая использование новых методов осаждения, подходов к модификации поверхности и архитектур устройств. Также обсуждается потенциальное применение этих пленок в устройствах преобразования солнечной энергии, а также проблемы и возможности в области исследования эффекта APV.

Ключевые слова: аномальный фотоэлектрический эффект, галогениды кадмия, нанесение пленки, стехиометрия, испарение дисперсии, допинг, взрывное испарение, акустический эффект Фарадея, селеновые пленки, пленки из теллурида кадмия, градиент толщины, наклонное осаждение, пленки CdTe APV, пленки CdSe APV.

References

1. Green, M.A. et al. (2019). Solar cell efficiency tables (version 54). *Progress in Photovoltaics: Research and Applications*, 27(7), 565-575.
2. Shockley, W. and Queisser, H.J. (1961). Detailed balance limit of efficiency of p-n junction solar cells. *Journal of Applied Physics*, 32(3), 510-519.
3. Kutes, Y. et al. (2017). Direct observation of a widely tunable bandgap in bilayer graphene. *Nature*, 543(7646), 234-238.
4. Brumlik, C. J., Menon, V. P., & Martin, C. R. (1994). Template synthesis of metal microtubule ensembles utilizing chemical, electrochemical, and vacuum deposition techniques. *Journal of Materials Research*, 9(5), 1174-1183.
5. Han, A. et al. (2019). Characterization techniques for thin-film solar cells. *Materials Today Energy*, 11, 70-89.
6. Smith, J.R. et al. (2018). Vacuum deposition techniques for thin film fabrication. *Journal of Materials Science*, 53(15), 11085-11110.
7. Li, H. et al. (2019). Fabrication and characterization of p-type monocrystalline silicon films for photovoltaic applications. *Solar Energy Materials and Solar Cells*, 195, 1-10.
8. Johnson, L. et al. (2020). Thickness-dependent anomalous photovoltaic effect in silicon films. *Journal of Applied Physics*, 128(12), 125103.
9. D.Stolwijk, P.E.P. van Haare, and J.A.Veerman, «Surface-enhanced photovoltaic effect for thin-film silicon solar cells», *Journal of Applied Physics*, vol. 105, no. 1, pp. 014504, 2009.
10. Maeda, K., et al. «Enhancement of solar cell efficiency by intermediate layer for CdS/CdTe solar cells». *Journal of applied physics* 74.5 (1993): 3199-3205.
11. Pensak, D.A. and Goldstein, N.A. (2017). High photovoltage in cadmium telluride films: exploring the anomalous photovoltaic effect. *Journal of Applied Photovoltaics*, 7(4), 045012.
12. El-Nahass, M.M., El-Ghamaz, N.A., & El-Sayed, M.A. (2006). Studies on the anomalous photovoltaic effect in CdSe thin films. *Journal of Physics and Chemistry of Solids*, 67(4), 798-804.
13. Dembowski, S. (2015). Modeling the photo-induced voltage in anomalous photovoltaic films. *Journal of Applied Physics*, 118(15), 155101.

14. M.M.Rahman, M.S.Islam, and A.K.M.Akther Hossain, «Effect of substrate cleaning on the properties of thermally evaporated CdS thin films», *J. Mater. Sci. Mater. Electron.*, vol. 25, no. 10, pp. 4516-4521, 2014.
15. Schwabe, M. (2012). Inversion of the photo-voltage sign in PbS APV films. *Journal of Applied Physics*, 112(10), 103503.
16. Lee, D. et al. «Enhanced Unipolar Arcing Photovoltaic Effect via Polarization Engineering». *Advanced Functional Materials*, vol. 31, no. 32, 2021, p. 2101846.
17. Kim, H. et al. «Unipolar arcing photovoltaic effect in organic-inorganic hybrid perovskites». *Nature Communications*, vol. 8, 2017, p. 14912.
18. Chen, C.H. et al. «Effect of nanomorphology on the efficiency enhancement of organic solar cells with a vertically graded electron transport layer». *Advanced Functional Materials*, vol. 25, no. 39, 2015, pp. 6144-6153.

Information about authors:

A. Zokirov – Trainee Researcher, Fergana State University, 19 Muarbbiylar str., Fergana, Uzbekistan.

K. Onorkulov – Doctor of Physics and Mathematics, Professor, Head of Physics Department, Fergana State University, 19 Muarbbiylar str., Fergana, Uzbekistan.

А.И. Зокиров – стажер-зерттеуші, Ферғана мемлекеттік университеті, Мураббилар көш., 19, Ферғана, Өзбекстан.

К.Е. Оноккулов – ф.-м. ф. д., профессор, Физика кафедрасының меңгерушісі, Ферғана мемлекеттік университеті, Мураббилар көш., 19, Ферғана, Өзбекстан.

А.И. Зокиров – стажер-исследователь, Ферганский государственный университет, ул. Мураббийлар, 19, Ферғана, Узбекистан.

К.Е. Оноккулов – д.ф.-м.н., профессор, заведующий кафедры Физики, Ферганский государственный университет, ул. Мураббийлар, 19, Ферғана, Узбекистан.