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INVESTIGATION OF $CuIn_{1-x}Ga_xSe_2$ THIN FILMS FOR SOLAR CELLS OBTAINED BY THE MAGNETRON SPUTTERING METHOD FROM TWO MAGNETRONS SHIFTED TO EACH OTHER

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Abstract. It is shown the possibility of obtaining thin $CuIn_{1-x}Ga_xSe_2$ *(CIGS)* absorbing layers with the required ratio of gallium and indium content *(Ga/(Ga+In))* for solar cells *(SC)* by the method of simultaneous magnetron sputtering from two magnetrons with magnetic systems shifted to each other. This method makes it possible to obtain morphologically perfect and graded-gap layers in the direction of film growth, both with a decrease in the band gap and with an increase.

Keywords: *CIGS, chalcopyrite, thin layers, photovoltaic, solar cells,* $CuIn_{1-x}Ga_xSe_2$ *absorbing layer.*

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1. Introduction

$CuIn_{1-x}Ga_x(Se_{1-y}S_y)_2$ *(CIGSS)* films, as the most promising materials for solar cells *(SCs)*, have high optical absorbing properties ($3{\cdot}10^5$ - $6{\cdot}10^5$) cm^{-1}, are resistant to radiation and have a wide range of band gaps from 1.0 eV to 2.4 eV (Gremenok *et al.*, 2013; Khosroshahi *et al.*, 2022; Ishizuka *et al.*, 2022), depending on the composition (x and y values) (Figs. 1 and 2). They are used in the production of inexpensive third-generation solar converters.

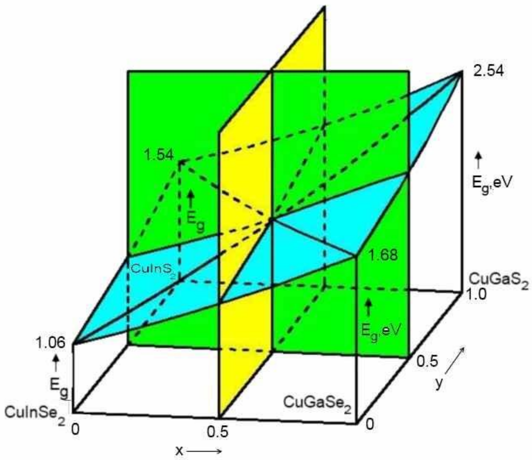

Fig. 1. Dependence of the band gap of complex materials $CuIn_{1-x}Ga_x(Se_{1-y}S_y)_2$ on the composition *(x, y)*

A large number of scientific works are devoted to the methods of obtaining the $CuIn_{1-x}Ga_xSe_2$ material, the study of its structure and physical properties (Gremenok *et al.*, 2013; Haug *et al.*, 2022; Murcia-López *et al.*, 2020; Omid *et al.*, 2020). At the same time, the creation of such a complex quaternary semiconductor with the necessary structural and physical properties is not an easy task. Therefore, various research groups are developing a wide range of methods for synthesizing chalcopyrite layers for solar cells on the surface of molybdenum, stainless steel or transparent conducting oxide layers and on glass substrates. Among physical methods, the method of obtaining metal precursors that are part of chalcopyrites by thermal evaporation in vacuum or magnetron sputtering and subsequent selenization of these metal layers in a selenium vapor atmosphere has become more widespread (Zaretskaya *et al.*, 2010; Mudryi *et al.*, 2010; Gremenok *et al.*, 2010; Zaretskaya *et al.*, 2012; Jackson *et al.*, 2015; Haug *et al.*, 2022).

$CuIn_{1-x}Ga_xSe_2$ based solar cells also have great potential as the bottom or top cells of tandem structure because of their controllable bandgaps (E_g) in the wide range of 1.0–1.7 eV. Eg is varied in CIGS by changing the compositional ratio of Ga to (Ga + In). Recently, an efficiency surpassing 28% has been achieved with III-V//CIGS three-junction solar cells (Kamikawa *et al.*, 2022; Green *et al.*, 2021; Makita *et al.*, 2021). Tandem solar cells of perovskite on $CuIn_{1-x}Ga_xSe_2$ have high potential, and their efficiencies have exceeded 24% (Green *et al.*, 2021, Jošt *et al.*, 2020).

As the technology improved, the technological regimes for obtaining $CuIn_{1-x}Ga_xSe_2$ films with a variable band structure were studied and improved. Thus, depending on the choice of the technological mode, the possibility of obtaining films with an increase or decrease in the band gap towards the thickening of the layer, i.e. acquisition of a graded-gap structure. The optical and photoelectric properties of the obtained layers and structures based on them have been studied.

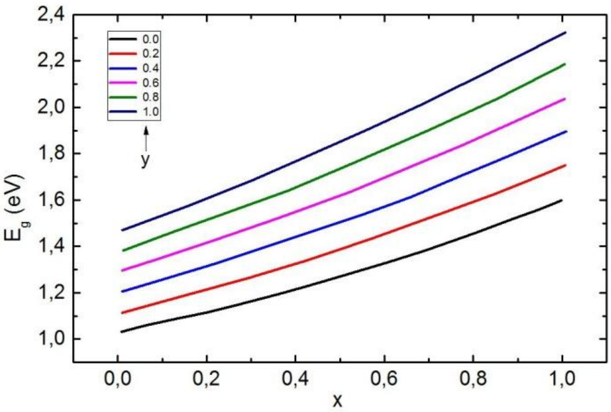

Fig. 2. Dependence of the band gap in $CuIn_{1-x}Ga_x(Se_{1-y}S_y)_2$ materials on the composition *(x, y)*

2. Technical methods of experience

Thin films of $CuIn_{1-x}Ga_xSe_2$ were obtained by simultaneous sputtering of $CuInSe_2$ and $CuGaSe_2$ targets from two magnetrons, the magnetic systems of which were moved to each other. Targets of $CuInSe_2$ and $CuGaSe_2$ materials with a thickness of ~3 mm and a diameter of 50 mm were obtained by pressing nanopowders of materials under a pressure of 16 tons. Magnetron sputtering of targets $CuInSe_2$ and $CuGaSe_2$ materials was carried out in a gaseous atmosphere of purified argon. The ratio of the amounts of gallium and indium *(Ga/(Ga+In))* in thin $CuIn_{1-x}Ga_xSe_2$ layers is determined by the ratio of the discharge current strength during simultaneous magnetron sputtering of targets of $CuInSe_2$ and $CuGaSe_2$ materials. The layer thickness is determined by the duration of the magnetron sputtering process (Fig.3). The $CuInSe_2$ and $CuGaSe_2$ thin films thickness dependence on the gas discharge current and sputtering time during magnetron sputtering is determined by the formula:

$$h = k \times I \times t \quad (1)$$

where k-factor, for $CuInSe_2$ *k= 0.28 nm/(mA.min), I=(120-140)mA, for* $CuGaSe_2$ *k=0.25 nm/(mA.min), I=(133-150)mA*, so-as the process of magnetron sputtering in both magnetrons occurred simultaneously, the time required to obtain a $CuIn_{1-x}GaxSe_2$ film with a thickness of *100 nm* was approximately *(30-60) min.*

Thin layers of $CuIn_{1-x}GaxSe_2$ were also obtained by magnetron sputtering from a target with a diameter of 100 mm. The material target was obtained by pressing under pressure 16 tons of crystalline $CuIn_{1-x}GaxSe_2$ powder, which were synthesized by us. It has been established that the surface morphology and the thickness of the layers depends on the modes of magnetron sputtering that is the chosen densities of the discharge current of the gaseous medium and the sputtering time (Fig.3).

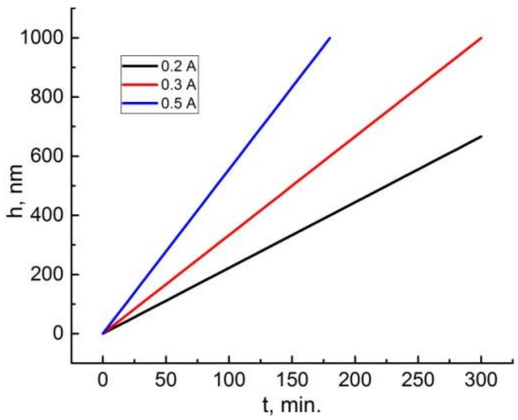

Fig. 3. The $CuIn_{1-x}Ga_xSe_2$ film thickness dependence on the sputtering time at current densities in the magnetron plasma: i=(2.7; 4.0 and 5.7) mA/cm^2

Since molybdenum forms an ohmic contact with the $CuIn_{1-x}Ga_xSe_2$ layer, as well as with the proposed upper *ZnO:Al* layer in the heterostructure, this contact was obtained by magnetron sputtering of the molybdenum target. In this study, *ZnO* was used as a buffer layer to create solar cells *(SCs)*. In our opinion, this material can become an alternative to *CdS* and *ZnCdS* materials with toxic technology. *ZnO:Al (ZnO* doped with aluminum) was used as a transparent and highly conductive top layer.

Thin layers of *ZnO* were obtained from metallic *Zn* by magnetron sputtering in an $Ar+O_2$ atmosphere. The upper *ZnO:Al* layer was obtained from two magnetrons by simultaneous magnetron sputtering of *Zn* and *Al* targets in the $Ar+O_2$ gaseous atmosphere. In this case, the concentration of aluminum in the *ZnO:Al* layer was determined by the ratio of the forces of current discharges during magnetron sputtering simultaneously with targets consisting of *Zn* and *Al* materials. The layer thickness was determined by the duration of the magnetron sputtering process. The dependence of the optical transmission of electromagnetic radiation of thin layers of *ZnO* and *ZnO:Al* on the wavelength of electromagnetic radiation is shown in Fig. 4.

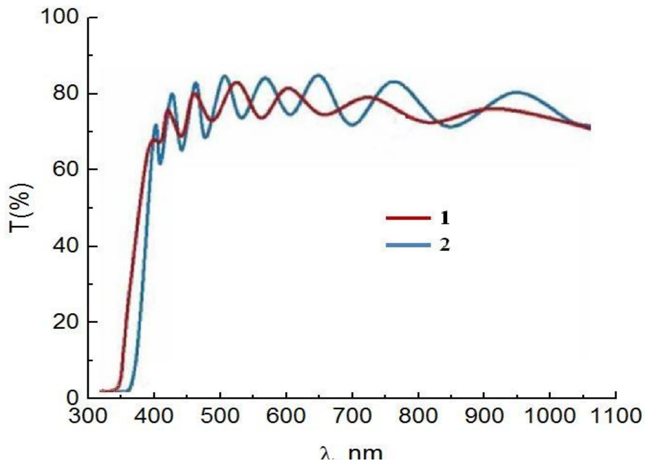

Fig. 4. Optical transmission spectra of thin *ZnO*(1) and *ZnO:Al* (2) layers obtained at different cathode potentials and discharge current

3. Experimental results and their discussion

The optical properties of thin $CuIn_{1-x}Ga_xSe_2$ layers deposited on glass substrates were studied by measuring the transmission *(T)* and reflection *(R)* spectra of light. At room temperature, from the radiation transmission spectrum, the transmission coefficient *T* of a thin layer of $CuIn_{1-x}Ga_xSe_2$ in the near infrared (IR) region is ~ 35-40%, and absorption in the intrinsic absorption region increases sharply towards short waves. With an increase in the *Ga/(In+Ga)* ratio in the $CuIn_{1-x}Ga_xSe_2$ material, the absorption band shifts to the short-wavelength region. The absorption coefficient of $CuIn_{1-x}Ga_xSe_2$ in thin layers was calculated from the spectra of rays transmitted and reflected from the material using expression (3) (Schroder *et al.*, 1990; Pankove *et al.*, 1971; Xueqiong *et al.*, 2015; Gremenok *et al.*, 2013):

$$\alpha = -\frac{1}{d} ln \frac{\sqrt{(1-R)^4 + 4T^2R^2} + (1-R)^2}{2T} \tag{3}$$

where α is the absorption coefficient, d is the layer thickness, T and R are the radiation transmission and reflection coefficients, respectively. The reflection spectra were studied in the photon energy range of 1-2 eV, and the value of the reflection coefficient R in this region is about 0.2 for a layer containing *Ga/(Ga+In)~0.2*. If the transition in the energy band of the semiconductor material is direct, the light absorption coefficient of the semiconductor is a function of the energy hν of the incident photon and is expressed by the following equation (4):

$$\alpha = A(h\nu - E_g)^{1/2} \tag{4}$$

Here Eg is the optical band gap of a direct-gap semiconductor, A is a constant value. Eg of the $CuIn_{1-x}Ga_xSe_2$ was determined by extrapolating the linear part of the spectral dependence $(\alpha\ (h\nu))^2$ from hν to the hν (eV) axis characterizing the photon energy. For layers with x = 0, the optical Eg is ~ 1.08 eV. Larger value of E_g of the film than E_g of the bulk sample is due to the small thickness of thin films (~100 nm). On Fig. 5 shows the dependences of the values $(\alpha \cdot h\nu)^2$ on the energy of photons in $CuIn_{1-x}Ga_xSe_2$ layers on a glass substrate on layers on their composition x = 0(1), 0.2 (2), 0.4 (3), 0.7 (4), 1.0 (5). It can be seen from the figure that E_g increases with increasing x, and this increase occurs linearly, as in expression (5):

$$E_g(CuIn_{1-x}Ga_xSe_2)=1.08+0.6x \qquad (5)$$

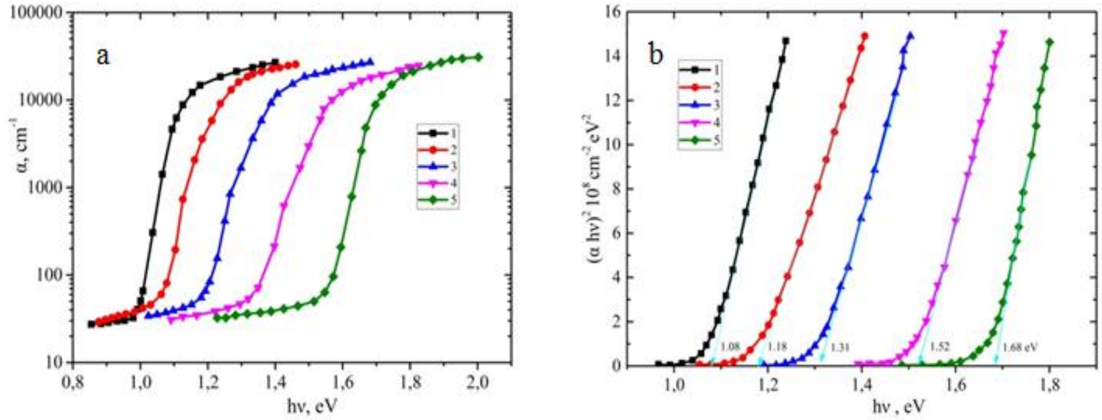

Fig. 5. Dependence of the absorption coefficient (a) and $(\alpha \cdot h\nu)^2$ (b) on the photon energy in thin $CuIn_{1-x}Ga_xSe_2$ films

Based on the results of studying the optical properties of thin $CuIn_{1-x}Ga_xSe_2$ layers obtained from two magnetrons by simultaneous magnetron sputtering, it can be concluded that the applied method allows one to obtain layers with the required properties and eliminate the disadvantages associated with the diffusion of gallium to the rear contact. In addition, there is no need to obtain *CuInGa* precursors and carry out their long-term treatment at high temperatures in the *Se* atmosphere.

4. Structure of a solar cell *(SC)*

A typical *SC* structure, the absorbing layer of which consists of a layer of $CuIn_{1-x}Ga_xSe_2$ material, is shown in Fig. 6. For the manufacture of solar cells, substrates made of glass, stainless steel metal foil, and polymer film (1) were mainly used. A molybdenum layer was used as the bottom contact (2). Active layer, i.e. $CuIn_{1-x}Ga_xSe_2$ (3) film is applied as the main absorbing material over the molybdenum layer. Next, a *ZnO* buffer layer (4) with a thickness of ~100 nm is deposited. A *ZnO:Al* layer with a low Al concentration, 50-100 nm thick, is deposited on the buffer layer. To form an ohmic contact, a top layer of *ZnO:Al* (5) was applied with a high *Al* concentration and a thickness of 200-500 nm. Finally, an ohmic contact layer is applied in the form of a molybdenum mesh (6).

As can be seen from the literature, in a heterostructural *SC*, a *CdS* or *CdZnS* layer is usually used as a buffer layer. It should be noted that Cd and its compounds are very toxic. In this work, we tried to use thin *ZnO* layers as an alternative to them as a buffer layer for SC, and the main reason for this is that thin *ZnO* layers are chemically stable, but the production technology is expensive and unreliable. One of the advantages of *ZnO* is that they have a large exciton binding energy (60 meV). Such a high exciton binding energy increases the emissivity of thin *ZnO* layers, which makes it possible to use them in optoelectronics. Despite improvements in technology, obtaining thin *ZnO* layers with the required conductivity remains a challenge. *Al*, *Ga*, and *In* are donors in *ZnO* due to the fact that the number of valence electrons of group III elements in *ZnO* with *N*-type conductivity is greater than in *Zn* atoms. In this work, aluminum was used as a donor. In some studies, despite the addition of various metals (Gremenok *et al*., 2013), thin films with the required parameters were not obtained. In our previous work, we managed to obtain both *ZnO* layers and aluminum-doped *ZnO:Al* layers using reactive magnetron sputtering (Zaretskaya *et al*., 2012). To ensure the necessary electrical conductivity in the layers obtained by this method, a long-term (10-12 hours) temperature treatment of the samples at 570 K is necessary.

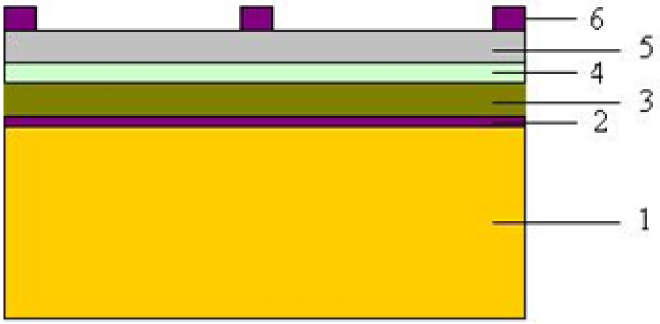

Fig. 6. Typical structure of a thin-film $Mo/CuIn_{1-x}Ga_xSe_2/ZnO/ZnO:Al/Mo$ solar cell

As mentioned above, the band gap E_g of the $CuIn_{1-x}Ga_xSe_2$ material varies from 1.04 eV to 1.68 eV depending on the value of x and is determined according to the law (6). It should be noted that the E_g value can be changed by adding other Group III elements (e.g. *Al*) or Group VI elements (e.g. *S* and *Te*) to the material. One of the ways to increase the efficiency of thin- film solar cells based on $CuIn_{1-x}Ga_xSe_2$ is to determine the optimal composition of the material by changing the band gap so that the *SC* efficiency with the corresponding E_g composition was the maximum for a given solar cells. The spectral dependence of the quantum efficiency of the obtained solar cells based on $CuIn_{1-x}Ga_xSe_2$ at different ratios *Ga/(In+Ga)* is shown in Fig. 7.

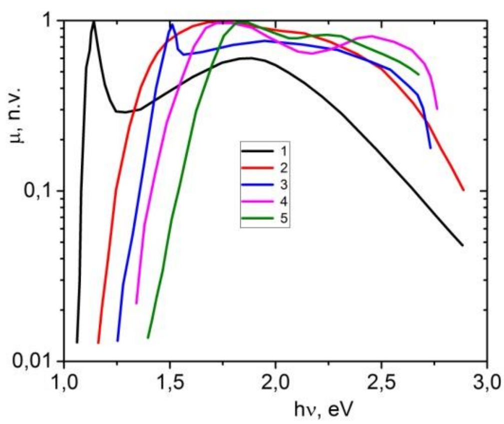

Fig. 7. Spectral dependence of the quantum efficiency of *Mo/CuIn1-xGaxSe2/ZnO/ZnO:Al/Mo* heterostructures

In the material $CuIn_{1-x}Ga_xSe_2$ E_g varies in the range (1.04-1.68) eV. Preliminary experiments have shown that the applied method can be used to obtain thin $CuIn_{1-x}Ga_xSe_2$ films with a variable band gap. By gradually adding sulfur and increasing the gallium content, a five-component active layer $Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ can be created in $CuIn_{1-x}Ga_xSe_2$ with the variable E_g increasing in the film growth direction. In a solar cell with such an active layer, the effect of a pulling field is added to the efficient separation of photo generated electron-hole pairs, and as a result, it becomes possible to create a more efficient structure for a solar cell.

5. Conclusion

A technology for obtaining thin layers has been developed $CuIn_{1-x}Ga_xSe_2$ from two magnetrons with magnetic systems shifted to each other. The optical properties of thin $CuIn_{1-x}Ga_xSe_2$ layers have been studied. It is shown that with the growth of gallium in the film, the edge of the absorption band shifts towards short waves of electromagnetic radiation. It has been shown that a thin *ZnO* layer can be used as a buffer layer, while the upper *ZnO:Al* layer can be used as a contact material, as well as an antireflection layer.

References

Green, M., Dunlop, E., Hohl-Ebinger, J.,Yoshita, M., Kopidakis, N., & Hao, X. (2020). Solar cell efficiency tables (version 57). *Progress in Photovoltaics: Research and Applications*. doi:10.1002/pip.3371.

Gremenok, V.F., Mudryi, A.V., Korotki, A.V., Zaretskaya, E.P., Ivanov, I.A., Abdulzade, N.N., Mursakulov, N.N., & Sabzaliyeva Ch.E. (2010). Characterization of $CuİnSe_2$ thin films from nanoparticle precursors. *The First International Scientific Conference Nano-technology and its use in Technique*, ATU, 132-137.

Gremenok, V.F., Zalessky, V.B., Mursakulov, N.N., & Tivanov, M.S. (2013). *Thin-film solar cells based on semiconductor materials Cu(In,Ga)(Se,S)2 with chalcopyrite structure*. Monograph, Elm, 250, (in Russian).

Haug, V., Klugius, I., Friedlmeier, T. M., Quintilla, A., & Ahlswede, E. (2011). Cu (In, Ga) Se2 thin-film solar cells based on a simple sputtered alloy precursor and a low-cost selenization step. *Journal of Photonics for Energy*, *1*(1), 018002.

Xueqiong, Su., Jiangbo W. Li,, Xiaojing W. Ch., Zh. Xin Ping. (2011). Role of cobalt in ZnO: Co ... thin films. *J. Phys. D: Appl. Phys*., 44, 265-267.

Ishizuka, S., Nishinaga, J., Beppu, K., Maeda, T., Aoyagi, F., Wada, T., ... & Terada, N. (2022). Physical and chemical aspects at the interface and in the bulk of CuInSe 2-based thin-film photovoltaics. *Physical Chemistry Chemical Physics*, 24, 1262-1265.

Jackson, P., Hariskos, D., Wuerz, R., Kiowski, O., Bauer, A., Friedlmeier, T. M., & Powalla, M. (2015). Properties of Cu (In, Ga) Se2 solar cells with new record efficiencies up to 21.7%. *Physica Status Solidi (RRL)–Rapid Research Letters*, *9*(1), 28-31.

Kamikawa, Y., Masuda, T., Nishinaga, J., & Ishizuka, S. (2022). Influence of argon pressure on sputter-deposited molybdenum back contacts for flexible Cu (In, Ga) Se2 solar cells on polyimide films. *Solar Energy*, *241*, 327-334.

Khosroshahi, R., Dehghani, M., Tehrani, N. A., Taghavinia, N., & Bagherzadeh, M. (2022). Optimization of selenization process to remove Ga-induced pin-holes in CIGS thin films. *Solar Energy*, *236*, 175-181.

Mudryi, A.V., Korotki, A.V., Gremenok, V.F., Zaretskaya, E.P., Zalesski, V.B., Mursakulov, N.N., ... & Sabzaliyeva, C.E. (2010). Growth and optical properties of Cu (In, Ga) Se 2 thin films on flexible metallic foils. *Fizika*, *16*(2), 408-413.

Mufti, N., Amrillah, T., Taufiq, A., Diantoro, M., & Nur, H. (2020). Review of CIGS-based solar cells manufacturing by structural engineering. *Solar Energy*, *207*, 1146-1157.

Murcia-López, S., Chakraborty, M., Carretero, N.M., Flox, C., Morante, J.R., & Andreu, T. (2020). Adaptation of Cu (In, Ga) Se 2 photovoltaics for full unbiased photocharge of integrated solar vanadium redox flow batteries. *Sustainable Energy & Fuels*, *4*(3), 1135-1142.

Ochoa, M., Buecheler, S., Tiwari, A.N., & Carron, R. (2020). Challenges and opportunities for an efficiency boost of next generation Cu (In, Ga) Se 2 solar cells: prospects for a paradigm shift. *Energy & Environmental Science*, *13*(7), 2047-2055.

Omid, M., Cora, Ö. (2020). State of the art review on the Cu (In, Ga) Se2 thinfilm solar cells. *Turkish Journal of Electromechanics and Energy*, *5*(2), 74-76.

Pankove, J.I. (1971). *Optical Processes in Semiconductors*. Prentice-Hall. New Jersey, *92*, 36.

Schroder, D.K. (2015). *Semiconductor Material and Device Characterization*. John Wiley & Sons.

Zaretskaya, E.P., Gremenok, V.F., Ivanov, I.A., Zalesski, V.B., Mursakulov, N.N., & Sabzaliyeva, C.E. (2010). Experimental study of $Cu(In_1\text{-}xGa_x)(S_1\text{-}ySe_y)$ thin film for solar cell applications, *Fizika*, 16.

Zaretskaya, E.P., Gremenok, V.F., Odrinsky, A.P., Mursagulov, N.N., Abdulzade, N.N., & Sabzaliyeva, C. E. (2012). Structure and electrical activity of structure defects of Cu (In, $Ga_1\text{-}x)(S_1\text{-}ySe_y)_2$ thin films. *Fizika*, *18*(2), 20-23.

Zaretskaya, E.P., Victorov, I.A., Goncharova, O.V., Leonova, T.R., Gartner, M., Mursakulov, N.N., Abdulzade, N.N., & Sabzaliyeva, Ch.E.. (2012). Deposition of Al-Doped ZnO films by DC magnetron sputtering. *Fizika*, *XVIII*(4), 26-30.