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Effect of stoichiometry and synthesis conditions on the phase composition, structure, and electrophysical properties of thin films of $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ – chalcopyrites, promising electrodes for photoelectrochemical decomposition of water

© V. V. Rakitin^{1,*}, I. D. Kulemetyev^{1,2}, U. R. Baklanova^{1,2}, D. S. Lutsenko¹, A. V. Stanchik³, E. V. Rabenok¹, and M. V. Gapanovich^{1,2,4}

¹ Federal Research Center on Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences, Moscow, Region, Chernogolovka, 142432 Russia

* E-mail: domi-tyan@yandex.ru

² Faculty of Fundamental Physical and Chemical Engineering, Moscow State University, Moscow, 119991 Russia

³ Scientific-Practical Materials Research Centre, National Academy of Sciences of Belarus, Minsk 220072 Republic of Belarus

⁴ Moscow Institute of Physics and Technology, Moscow Region, Dolgoprudny, 141701 Russia

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The effect of stoichiometry and synthesis conditions on the phase composition, structure, and electrophysical properties of $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ chalcopyrite thin films on Mo/MoO_x substrates, promising electrodes for photoelectrochemical decomposition of water, is studied. It has been found that annealing in selenium vapor at $T = 650^\circ\text{C}$ for a period of 15 minutes to 30 minutes is most optimal for obtaining single-phase films. For the first time, for samples of the $\text{Ag}_{0.9}\text{Cu}_{0.1}\text{GaSe}_2$ composition synthesized at 550°C for 15 minutes, a record photocurrent density of $1.763\text{ mA}/\text{cm}^2$ (at $E = -0.517\text{ V}$ relative to 3M SSCE) was obtained under lighting conditions close to AM1.5 .

Keywords: thin films, electrodes, chalcopyrites CuGaSe_2 and AgGaSe_2 , phase composition, electrophysical properties.

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Introduction

Currently, one of the most relevant areas of photovoltaics development is the production of hydrogen through photoelectrochemical water splitting. A large number of different compounds are used for this purpose, such as $\text{NaTiO}_3\text{:La}$, TiO_2 , $\text{WO}_3\text{@BiVO}_4$, compounds of the $\text{A}^{\text{III}}\text{-B}^{\text{IV}}$ group, chalcopyrites $\text{A}^{\text{I}}\text{-B}^{\text{III}}\text{-C}^{\text{VI}}_2$, and others. All of them can act as photocathodes or photoanodes and have both certain advantages and characteristic disadvantages.

For instance, photocathodes based on $\text{NaTaO}_3\text{:La}$ exhibit one of the highest water

splitting rates ($9.7\text{ mmol}/\text{h}$) and a high quantum yield (about 57 % under 270–300 nm illumination). However, this requires the use of UV radiation, and the surface of the photocathode must be non-uniform to allow adsorption of the evolved hydrogen [1]. The use of a wide-bandgap n -type semiconductor TiO_2 with $E_g = 3\text{ eV}$ also requires illumination in the UV region. Furthermore, this system necessitates the presence of Pt or any p -type semiconductor as a counter electrode for the target hydrogen evolution reaction [1, 2]. Compared to TiO_2 , the compound BiVO_4 has a smaller bandgap ($E_g = 2.4\text{ eV}$) and extends into the visible part of

the solar spectrum [3]. Study [4] shows that photoanodes based on BiVO_4 thin films have an efficiency of $\eta = 5.2\%$ (AM1.5 illumination), and with the use of $\text{WO}_3@\text{BiVO}_4$ core-shell nanostructures, the efficiency of such devices can reach up to 8.2% [5, 6]. However, achieving such values and high photocurrent densities (6.56 mA/cm^2) requires a tandem structure in the form of $\text{WO}_3@\text{BiVO}_4$ (photoelectrochemical cell) – GaAs/InGaAsP (heterojunction), which significantly complicates the design and increases production cost. Photocathodes based on thin films of $\text{A}^{\text{III}}\text{-B}^{\text{IV}}$ compounds have efficiencies up to 14% , but they remain quite complex to manufacture and expensive. Furthermore, the long-term operational stability of such photocathodes in aqueous solutions is low [7]. Another type of semiconductor that could potentially be used for hydrogen production is $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ powders ($0.2 \leq x \leq 0.35$), which possess different bandgaps $E_g = 2.49\text{--}2.68 \text{ eV}$ depending on the zinc content in the films. Such systems can operate in the visible range of sunlight and generate hydrogen at a rate of $0.35 \text{ mmol/h} \cdot \text{g}_{\text{cat}}$. However, efficient photolysis of water requires the use of a consumable $\text{SO}_3^{2-}/\text{S}^2$ component, which acts as an electron donor and facilitates the reduction of hydrogen ions from the solution [8]. Currently, a more promising approach is the creation of a heterojunction with p -type semiconductors to increase photocurrent density and facilitate electron transfer to active sites on the surface.

To achieve this goal, an alternative to expensive photocathodes based on III-V group semiconductors can be used: compounds of the $\text{A}^{\text{I}}\text{-B}^{\text{III}}\text{-C}^{\text{VI}}_2$ type with a chalcopyrite crystal structure, specifically CuGaSe_2 (CGS) and AgGaSe_2 (AGS), as well as solid solutions based on them. The main advantages of these compounds are their variable bandgap ($E_g \sim 1.6\text{--}1.8 \text{ eV}$), close to the optimal value for efficient absorption of solar radiation and overcoming the thermodynamic threshold of water splitting (1.23 V), as well as their low cost compared to $\text{A}^{\text{III}}\text{-B}^{\text{IV}}$ group compounds [9, 10, 11]. Considering the high overpotentials for hydrogen and oxygen evolution reactions caused by the low surface activity of the semiconductor as a photoelectrode and a number of other losses, $E_g \sim 1.7 \text{ eV}$ is considered the optimal value for

water molecule splitting [12]. The most widespread method for producing high-efficiency photocathodes based on CuGaSe_2 is thermal evaporation of elements in vacuum. CGS films obtained by this method demonstrate high crystallinity and large grains ($1\text{--}2 \mu\text{m}$), and the efficiency of photoelectrochemical water splitting reaches $\eta \sim 10\%$ [13]. It is known that an important feature of this method is composition control, as the Cu/Ga ratio significantly affects the properties of the photocathodes. In study [14], devices based on films with different Cu/Ga ratios exhibited high photocurrent density values: -19.0 mA/cm^2 for $\text{Cu/Ga} = 0.85$ and -12.1 mA/cm^2 for $\text{Cu/Ga} = 0.33$ (at a potential of $E = -0.4 \text{ V}$ vs. reversible hydrogen electrode, RHE) and 0 mA/cm^2 for $\text{Cu/Ga} = 0.85$ and -8.2 mA/cm^2 for $\text{Cu/Ga} = 0.33$ (at a potential of $E = 0 \text{ V}$ vs. RHE) in $0.5 \text{ M H}_2\text{SO}_4$ ($\text{pH} = 0.4$). For a pure CuGaSe_2 single crystal in study [15], values of $j_{\text{ph}} = 0.3 \text{ mA/cm}^2$ were achieved (at a potential of $E = 0 \text{ V}$ vs. RHE, which corresponds to -0.517 V vs. 3M Ag/AgCl electrode).

Furthermore, the authors of many studies state that thermal annealing, especially in a selenium atmosphere, is a powerful tool for controlling the defect structure and, consequently, the photoelectrophysical properties. The main goal of this type of annealing is to compensate for selenium loss and eliminate selenium-deficient defects (V_{Se} vacancies), which are deep recombination centers. Annealing facilitates the passivation of acceptor levels associated with copper vacancies V_{Cu} and gallium vacancies V_{Ga} [16]. For example, annealing in a Se atmosphere drastically reduces the resistivity of p -type CGS films to $1\text{--}10 \Omega\cdot\text{cm}$ [17]. In some cases, the application of rapid thermal annealing to finished CGS-based solar cells has increased their efficiency from 10% to 11.46% due to grain boundary passivation and improved heterojunction quality [18]. For high efficiency of AGS-based photocathodes, annealing in a selenium atmosphere at 600°C is typically required [19], since at low annealing temperatures the samples are a mixture of Ag , Ga_2Se_3 , GaSe phases and the target AgGaSe_2 phase. Reference [20] describes the fabrication of AGS-based photocathodes without a heterojunction; the photocurrent density value was 0.2 mA/cm^2 (at a potential of $E = -0.1 \text{ V}$ vs. RHE) under

illumination with light of wavelength 420–800 nm (Xe lamp, power 300 W). Of particular interest are $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ solid solutions, as photocathodes based on them show higher photocurrent values. Reference [20] describes the production of films of mixed composition, in which ~6 % of the copper is substituted by silver atoms. The obtained photocathode with the structure $\text{FTO}/\text{Ag}_{0.06}\text{Cu}_{0.94}\text{GaSe}_2/\text{CdS}/\text{Pt}$ exhibited a photocurrent density of $8.1 \text{ mA}/\text{cm}^2$ (at a potential of $E = 0 \text{ V}$ vs. RHE). In turn, the photocathode without a heterojunction, $\text{FTO}/\text{Ag}_{0.06}\text{Cu}_{0.94}\text{GaSe}_2$, had photocurrent density values $j_{ph} \sim 1.4 \text{ mA}/\text{cm}^2$ (at a potential of $E = 0 \text{ V}$ vs. RHE).

In our previous studies [21, 22], it was established that in the powder system of $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ solid solutions, an increase in the silver fraction leads to an increase in the lifetime of photogenerated carriers, and the best photocurrent values were characteristic of powders with a higher silver content. This phenomenon is explained by the substitution of deep traps with shallower ones. However, such compositions have not been investigated as photocathodes for direct water splitting in photoelectrochemical cells.

Therefore, this paper studied the influence of synthesis conditions of $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ thin films on their phase composition, structure, and their applicability as photocathodes for direct water splitting in photoelectrochemical cells.

Experimental section

The synthesis of $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ thin films was carried out in several stages. In the first stage, intermetallics of various compositions, CuGa_2 and Ag_2Ga_3 , were obtained by high-temperature solid-state synthesis. In the next synthesis stage, metals and intermetallics of the required mass were thermally evaporated in vacuum onto a pre-heated Mo/MoO_x substrate. The final stage of the synthesis was annealing the obtained films in an active selenium atmosphere. This method for synthesizing chalcopyrite films of other compositions was developed by us earlier [23] and has proven successful.

The obtained films had the following structure: Mo ($500 \mu\text{m}$)/ MoO_x ($0.05 \mu\text{m}$)/ $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ ($1.50 \mu\text{m}$).

The phase composition of the films was studied by XRD (PANalytical Aeris, $\text{Cu-K}\alpha$ radiation). The applicability of the obtained films as photocathodes was investigated in a three-electrode electrochemical cell with a working electrode of $\text{glass}/\text{Mo}/\text{MoO}_{3-x}/\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ film, a graphite counter electrode, and a reference electrode, a 3 M silver/silver chloride electrode (AgCl), under pulsed illumination conditions close to AM1.5 (metal halide lamp, $P = 0.1 \text{ W}/\text{cm}^2$). To increase the shunt resistance, the edges of the sample were insulated. The electrolyte used was a solution containing CH_3COOH (0.1 M) + CH_3COOK (0.175 M) + K_2SO_4 (0.1 M) (acetate buffer with $\text{pH} = 5$), which helps reduce corrosion of the Mo/MoO_x substrates. The potential sweep rate was $5 \text{ mV}/\text{s}$.

Results and Their Discussion

Fig. 1a shows X-ray diffraction patterns of AgGaSe_2 films obtained under different conditions. For AgGaSe_2 films obtained at a temperature of 550°C , a decrease in the amount of impurity phases with increasing annealing duration was characteristic. The films contain an impurity cubic chalcopyrite phase Ag_9GaSe_6 ($P231$), enriched with silver, a hexagonal GaSe phase ($P63mc$), and some phases that could not be identified. The intensity of the lines of the main AgGaSe_2 phase decreased with increasing annealing time. This change in intensities can be associated with the thermal decomposition of AgGaSe_2 into Ag_9GaSe_6 and the volatile Ga_2Se_3 phase upon increasing the heat treatment time. AgGaSe_2 films obtained at 650°C contained the smallest amount of impurity phases compared to those obtained at 550°C . With increasing duration of heat treatment, the intensity of the lines of the main chalcopyrite phase increases and the amount of the impurity hexagonal GaSe phase ($P63mc$) decreases.

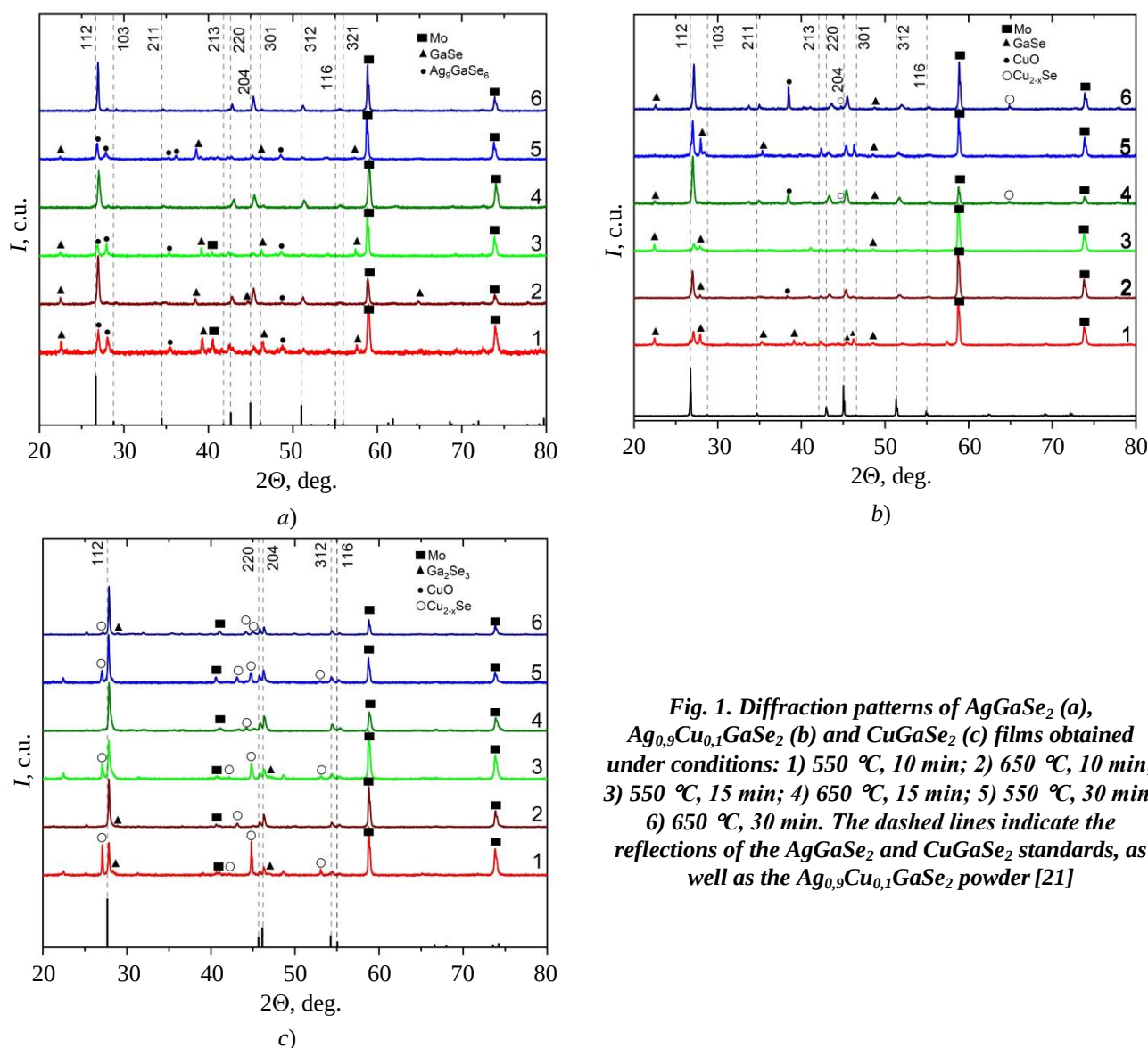


Fig. 1. Diffraction patterns of AgGaSe_2 (a), $\text{Ag}_{0.9}\text{Cu}_{0.1}\text{GaSe}_2$ (b) and CuGaSe_2 (c) films obtained under conditions: 1) 550 °C, 10 min; 2) 650 °C, 10 min; 3) 550 °C, 15 min; 4) 650 °C, 15 min; 5) 550 °C, 30 min; 6) 650 °C, 30 min. The dashed lines indicate the reflections of the AgGaSe_2 and CuGaSe_2 standards, as well as the $\text{Ag}_{0.9}\text{Cu}_{0.1}\text{GaSe}_2$ powder [21]

For $\text{Ag}_{0.9}\text{Cu}_{0.1}\text{GaSe}_2$ films (Fig. 1b) annealed at 550 °C, an increase in the intensity of the main phase and a decrease in the intensity of the impurity GaSe phase are observed. For films obtained at 650 °C, although an increase in the intensity of the lines of the main chalcopyrite phase is observed with increasing annealing time, impurity phases of cubic Cu_{2-x}Se ($F-43m$) and hexagonal GaSe ($P63mc$) are still present. This may be because, although the target $\text{Ag}_{0.9}\text{Cu}_{0.1}\text{GaSe}_2$ phase forms at elevated temperature, it begins to decompose with excessively long annealing times.

For CuGaSe_2 films (Fig. 1c) annealed at 550 °C, the presence of impurity phases of cubic ($F-43m$) Cu_{2-x}Se and Ga_2Se_3 was characteristic for different annealing durations. Probably, this time at this temperature is insufficient for the

formation of a single-phase film, since copper and selenium form a large number of intermediate selenides and equilibrium in the system does not have time to establish. For AgGaSe_2 films, for example, this is not observed, since only the Ag_2Se phase exists and less time is required to achieve equilibrium in the system. The higher annealing temperature of 650 °C, as well as increasing the duration of heat treatment, also does not significantly affect the composition of the obtained CuGaSe_2 films.

The crystal lattice parameters a , c and the unit cell volume V for $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ films obtained under different conditions varied nonlinearly. Moreover, for CuGaSe_2 samples, only films obtained at 650 °C with an annealing time of 30 min have the closest values of crystal lattice parameters $a = 5.611(6)$ Å, $c = 10.989(25)$ Å

and $V = 346.0(6) \text{ \AA}^3$ compared to powders of the same composition [21, 22]. Among the samples containing silver, only $\text{Ag}_{0.9}\text{Cu}_{0.1}\text{GaSe}_2$ films obtained at 650°C with an annealing time of 15 min, and AgGaSe_2 films obtained at 650°C with an annealing time of 30 min, had similar crystal lattice parameter values $a = 5.937(9) \text{ \AA}$, $c = 10.87(7) \text{ \AA}$ and $V = 380.0(21) \text{ \AA}^3$ and $a = 5.976(4) \text{ \AA}$, $c = 10.702(23) \text{ \AA}$ and $V = 382.3(5) \text{ \AA}^3$, respectively, compared to powders of the same composition [21, 22].

Fig. 2 shows the current-voltage characteristics under intermittent illumination, which best represent the electrophysical properties of $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ films obtained under different conditions. As can be seen from the figure, films of different compositions exhibit p -type dark conductivity, as evidenced by the increase in photocurrent amplitude upon shifting to the negative potential region. The increase in photocurrent density correlates with the increase in the lifetime of photogenerated charge carriers for powders of similar composition, described by us in [21, 22].

Based on the studied current-voltage curves, the photocurrent density values j_{ph} were obtained for films with the best photoelectrophysical characteristics. Furthermore, based on the studied current-voltage curves, the series (R_s) and shunt (R_{sh}) resistances were

calculated from the relations: $\frac{1}{R_{sh}} \sim \left[\frac{dI}{dE} \right]$ at

$E \rightarrow 0$, $\frac{1}{R_{sh}} \sim \left[\frac{dI}{dE} \right]$ at $I \rightarrow 0$, where I is current,

E is potential [24]. Based on the known thickness and area of the synthesized films, the resistivity values (ρ) were calculated. The table presents summary data with these values for $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ films obtained under different conditions. For comparison with data available in the literature [14, 20], the photocurrent density values recalculated relative to 3M Ag/AgCl are also given.

As can be seen from the table, for the CuGaSe_2 composition, the best photocurrent density values $j_{ph} = 0.066 \text{ mA/cm}^2$ (at $E = -0.517 \text{ V}$ vs. 3M Ag/AgCl) are exhibited by CuGaSe_2 samples annealed at 650°C for 10 min, which is in good agreement with literature data for this type of semiconductor material [14, 15]. For AgGaSe_2 -based samples, the best photocurrent $j_{ph} = 0.132 \text{ mA/cm}^2$ (at $E = -0.517 \text{ V}$ vs. 3M Ag/AgCl) was obtained for films annealed at 550°C for 30 min. The shunt and series resistance values are relatively low. The obtained photocurrent density data are in good agreement with [20]. For photocathodes with the structure $\text{Mo/MoO}_x/\text{Ag}_{0.9}\text{Cu}_{0.1}\text{GaSe}_2$, annealed at 550°C for 15 min, a record photocurrent density value of 1.763 mA/cm^2 (at $E = -0.517 \text{ V}$ vs. 3M Ag/AgCl) was achieved under illumination conditions close to AM1.5, compared to devices based on similar chalcopyrites described in the world literature [14, 15, 20]. The material of this sample exhibits low series resistance $R_s = 0.5 \text{ k}\Omega$ and resistivity $\rho = 0.2 \text{ M}\Omega\cdot\text{cm}$. Thus, based on the combination of our data and literature data [20], it can be concluded that the efficiency in $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ solid solutions varies nonlinearly. In the range $0 \leq x \leq 0.06$, a significant increase in photocurrent density is observed, then in the range $0.06 \leq x \leq 0.2$ a strong decrease in j_{ph} occurs, followed by another increase up to $x = 0.9$. The obtained electrophysical characteristics of the films correlate well with the lifetime data for powders of similar mixed composition $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$, in which the best values were obtained for samples with high silver concentrations [21, 22]. The observed phenomenon may be due to a change in the defect structure of the samples, namely, a decrease in the depth and number of traps for charge carriers. With an increase in the silver content in the samples, a sequential substitution of deep acceptor levels by shallow donor levels occurs.

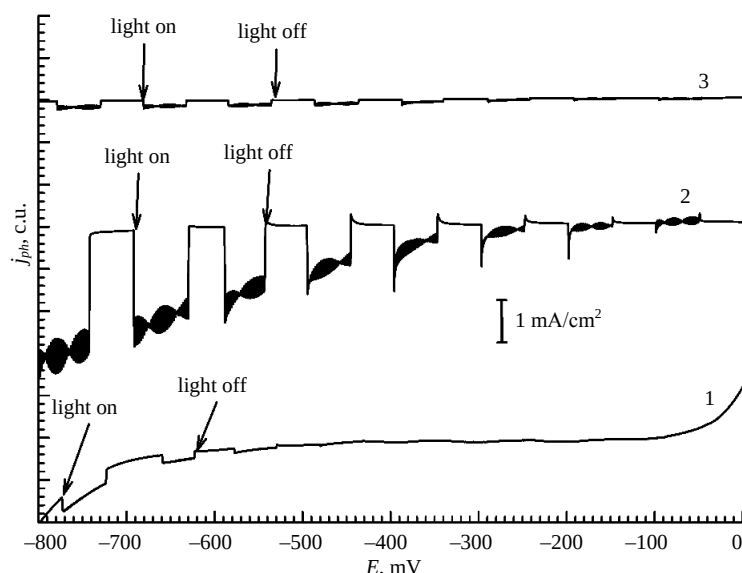


Fig. 2. Current-voltage characteristics (vs. 3M Ag/AgCl) under intermittent light illumination of $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ films obtained under different conditions: (1) – CuGaSe_2 (550 °C, 30 min); (2) – $\text{Ag}_{0.9}\text{Cu}_{0.1}\text{GaSe}_2$ (550 °C, 15 min); (3) – AgGaSe_2 (650 °C, 10 min)

Table

Photocurrent density j_{ph} , series R_s and shunt R_{sh} resistance values for $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ films obtained under different conditions

Film composition	Synthesis conditions	j_{ph} , mA/cm ² (at $E = -0.517$ V vs. 3M AgCl electrode)	R_s , kΩ	R_{sh} , kΩ	ρ , MΩ·cm
CuGaSe_2	550 °C 10 min	0.017	2.8	6.6	0.9
	550 °C 15 min	0.026	71.3	92.2	23.8
	550 °C 30 min	0.015	39.1	53.5	13.0
	650 °C 10 min	0.066	5.0	0.5	1.7
	650 °C 15 min	0.026	4.4	7.3	1.5
	650 °C 30 min	0.011	5.4	4.9	1.8
$\text{Ag}_{0.9}\text{Cu}_{0.1}\text{GaSe}_2$	550 °C 10 min	0.049	147.5	37.8	49.2
	550 °C 15 min	1.763	0.5	2.2	0.2
	550 °C 30 min	0.16	7.9	4.8	2.6
	650 °C 10 min	0.029	6.0	17.3	2.0
	650 °C 15 min	0.075	65.3	2.9	21.8
	650 °C 30 min	0.0074	8.2	5.8	2.7
AgGaSe_2	550 °C 10 min	0.014	1.2	12.3	0.4
	550 °C 15 min	0.029	0.7	16.2	0.2
	550 °C 30 min	0.132	0.5	7.4	0.2
	650 °C 10 min	0.012	26.2	59.7	8.7
	650 °C 15 min	0.035	0.5	2.6	0.2
	650 °C 30 min	0	–	–	–

Conclusion

A study was conducted on the influence of stoichiometry and synthesis conditions on the phase composition, structure, and electrophysical properties of $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ chalcopyrite thin

films on Mo/MoO_x substrates. It was established that for the synthesis of $\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ films ($x = 0, 0.9$, and 1) on Mo/MoO_x substrates, annealing in selenium vapor at $T = 650$ °C for a duration of 15 min to 30 min is most optimal. Under these conditions, films with a chalcopyrite

structure of the space group *I*-42d are formed, with crystal lattice parameters closest to those of powders of similar composition. At the same time, electrodes based on $\text{Ag}_{0.9}\text{Cu}_{0.1}\text{GaSe}_2$ chalcopyrite composition, obtained at $T = 550^\circ\text{C}$ and $t = 15$ min, possess the best electrophysical properties and the highest efficiency. In our opinion, the presence of small amounts of these impurity phases in the films does not significantly affect the photocurrent; a more significant contribution is made by the stoichiometry of the photoactive phase. On such samples, under pulsed illumination conditions close to AM1.5, a record photocurrent density $j_{ph} = 1.763\text{ mA/cm}^2$ (at $E = -0.517\text{ V}$ vs. 3M Ag/AgCl) was achieved. The efficiency of electrodes based on

$\text{Ag}_x\text{Cu}_{1-x}\text{GaSe}_2$ solid solutions varies nonlinearly across the entire range of x . The increase in j_{ph} correlates with the increase in the lifetime of photogenerated charge carriers for powders of similar composition, which may be due to a change in the defect structure of the samples, namely, a decrease in the depth and number of traps for charge carriers.

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REFERENCES

1. Kudo A. and Miseki Y., Chemical Society Reviews **38**, 253 (2009).
2. Eidsvåg H., Bentouba S., Vajeeston P., Yohi S., and Velauthapillai D., Molecules **26**, 1687 (2021).
3. Shafiq I., Hussain M., Shehzad N., Maafa I. M., Akhter P., Shafique S., Razzaq A., Yang W., Tahir M., and Russo N., J. Environmental Chemical Engineering **7** (4), 103265 (2019).
4. Abdi F. F., Han L., Smets A. H., Zeman M., Dam B., and Van De Krol R., Nature Communications **4** (1) 2195 (2013).
5. Pihosh Y., Turkevych I., Mawatari K., Uemura J., Kazoe Y., Kosar S., Makita K., Sugaya T., Matsui T., Fujita D., and Tosa M., Scientific reports **5** (1), 11141 (2015).
6. Kosar S., Pihosh Y., Turkevych I., Mawatari K., Uemura J., Kazoe Y., Makita K., Sugaya T., Matsui T., Fujita D., and Tosa M., Japanese journal of applied physics **55** (4S), 04ES01 (2016).
7. May M. M., Lewerenz H. J., Lackner D., Dimroth F., and Hannappel T., Nature Communications **6** (1) 8286 (2015).
8. Del Valle F., Ishikawa A., Domen K., De La Mano J. V., Sánchez-Sánchez M. C., González I. D., Herreras S., Mota N., Rivas M. E., Galván M. Á., and Fierro J. L. G., Catalysis Today **143** (1-2), 51–56 (2009).
9. Turner J. A., Science **305**, 972 (2004).
10. Barreto L., Makihiro A., and Riahi K., Int. J. Hydrogen Energy **28**, 267 (2003).
11. Leijtens T., Bush K. A., Prasanna R., and McGehee M. D., Nat. Energy **3**, 828 (2018).
12. Jacobsson J., Fjällström V., Edoff M., and Edvinssona T., Sol. Energy Mater. Sol. Cells **138**, 87 (2015).
13. Ishizuka Sh., Okamoto R., and Ikeda Sh., Adv. Mater. Interfaces **9** (25), 2201266 (2022).
14. Mahmoudi B., Caddeo F., Lindenberg T., Schneider T., Hölscher T., Scheer R., and Maijenburg A. W., Electrochim. Acta **367**, 137183 (2021).
15. Ikeda S., Fujita W., Katsube R., Nose Y., Suzuki H., Abe R., and Yoshino K., Electrochimica Acta **454**, 142384 (2023).
16. Ponomareva I. P., Serov A. Yu., and Bodnar I. V., Physics of the Solid State **49** (1), 23–27 (2007) [in Russian].
17. Ramakrishna Reddy K. T. and Jayarama Reddy P., Thin Solid Films **253**, 238–242 (1994).
18. Karthikeyan S., Hwang S., Sibakoti M., Bontrager T., Liptak R. W., and Campbell S. A., Appl. Surf. Sci. **493**, 105–111 (2019).
19. Jung S. and Kim J., J. Nanosci. Nanotechnol **16** (5), 5279–5284 (2016).
20. Zhang L., Minegishi T., Kubota J., and Domen K., Phys. Chem. Chem. Phys. **16**, 6167 (2014).
21. Rakitin V. V., Gapanovich M. V., Lutsenko D. S., Nazarov V. B., Stanchik A. V., Gremenok V. F., and Kabyliatski A. V., High Energ. Chem. **58** (5), 492–498 (2024).
22. Rakitin V. V., Gapanovich M. V., Rabenok E. V., Kalimullina D. R., Lutsenko D. S., Kulemetev I. D., Koltsov E. N., Stanchik A. V., and Gremenok V. F., Condensed Matter and Interphases **27** (3), 441 (2025) [in Russian].

23. Aldoshin S. M., Bocharova S. I., Novikov G. F., and Gapanovich M. V. Method of manufacturing photosensitive chalcopyrite films. Patent for invention № RU 2567191 C1 (RF). 2015 [in Russian].
Das D. and Damodare L., Mater. Chem. Phys. **56** (2), 116–124 (1998).

About authors

Rakitin Vladimir Valerievich, Candidate of Chemical Sciences, Senior Researcher, Federal Research Center on Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences (1 Ac. Semenov Ave., Chernogolovka, Moscow Region, 142432, Russia). E-mail: domi-tyan@yandex.ru SPIN code: 2273-0113, Author ID https://elibrary.ru/author_profile.asp?id=897817, Orcid ID 0000-0001-6582-5212

Kulemetyev Ivan Denisovich, Student, Federal Research Center on Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences (1 Ac. Semenov Ave., Chernogolovka, Moscow Region, 142432, Russia); Faculty of Fundamental Physical and Chemical Engineering, Moscow State University (1 Leninskie Gory, Moscow, 119991, Russia). E-mail: ivan-2002@bk.ru

Baklanova Ulyana Ruslanovna, Student, Federal Research Center on Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences (1 Ac. Semenov Ave., Chernogolovka, Moscow Region, 142432, Russia); Faculty of Fundamental Physical and Chemical Engineering, Moscow State University (1 Leninskie Gory, Moscow, 119991, Russia). E-mail: ulyana.baklanova@mail.ru

Lutsenko Denis Sergeevich, Junior Researcher, Federal Research Center on Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences (1 Ac. Semenov Ave., Chernogolovka, Moscow Region, 142432, Russia). E-mail: rylah161den@mail.ru Orcid ID 0009-0000-5788-7763

Stanchik Aliona Viktorovna, Candidate of Physical and Mathematical Sciences, Leading Researcher, Scientific-Practical Materials Research Centre, National Academy of Sciences of Belarus (19 Petrusya Brovki, Minsk, 220072, Republic of Belarus). E-mail: alena.stanchik@bk.ru Orcid ID 0000-0001-8222-8030, Scopus Author ID www.scopus.com/authid/detail.uri?authorId=57200500542

Rabenok Evgeniya Vitalievna, Candidate of Physical and Mathematical Sciences, Senior Researcher, Federal Research Center on Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences (1 Ac. Semenov Ave., Chernogolovka, Moscow Region, 142432, Russia). E-mail: jane.rabenok@yandex.ru SPIN code: 6923-7417, Author ID 123644, Orcid ID 0000-0002-3500-6918

Gapanovich Mikhail Vyacheslavovich, Candidate of Chemical Sciences, Head of Group of Semiconductor and Nanocomposite Materials, Federal Research Center on Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences (1 Ac. Semenov Ave., Chernogolovka, Moscow Region, 142432, Russia); Faculty of Fundamental Physical and Chemical Engineering, Moscow State University (1 Leninskie Gory, Moscow, 119991, Russia); Moscow Institute of Physics and Technology (9 Institutskiy per., Dolgoprudny, Moscow Region, 141701, Russia). E-mail: gmw1@mail.ru Orcid ID 0000-0002-9109-6532, Scopus Author ID www.scopus.com/authid/detail.uri?authorId=6506377278