PACS numbers: 81.05.Hd, 84.60.Jt, 88.40.fc, 88.40.jn

Third-generation Cu-In-Ga-(S, Se)-based solar inverters

G F Novikov, M V Gapanovich

DOI: https://doi.org/10.3367/UFNe.2016.06.037827

Contents

1.	Introduction	161
2.	History of $CuIn_{1-x}Ga_x(S, Se)_2$ application in solar cells	162
	2.1 Solar cell design; 2.2 History of synthesis technology development for $CuIn_{1-x}Ga_x(S, Se)_2$	
3.	Properties of $CuIn(S, Se)_2$ and $CuIn_{1-x}Ga_x(S, Se)_2$	163
	3.1 Crystal structure; 3.2 Phase equilibria in Cu ₂ Se-In ₂ Se ₃ system; 3.3 Optical properties and a bandgap energy;	
	3.4 Parameters characterizing solar cell efficiency; 3.5 Quantum efficiency of $CuIn_{1-x}Ga_x(S, Se)_2$ -base solar cells	
4.	Synthesis methods for $CuIn(S, Se)_2$ and $CuIn_{1-x}Ga_x(S, Se)_2$ thin films	167
	4.1 Vacuum methods; 4.2 Nonvacuum methods; 4.3 Features of selenization process	
5.	Graded elemental distribution in the $CuIn_{1-x}Ga_x(S, Se)_2$ layer	170
	5.1 Single-graded concentrations; 5.2 Double-graded concentrations; 5.3 Influence of recrystallization, bandgap and	
	elemental concentration grading on the characteristics of thin-film solar cells fabricated using three-stage method	
6.	Transport and lifetimes of excess charge carriers in polycrystalline $CuIn_{1-x}Ga_x(S, Se)_2$ layers	171
	6.1 Influence of intergrain boundaries on power conversion efficiency; 6.2 Influence of intercrystallite boundaries on	
	the transport and recombination of charge carriers and on the degradation of $CuIn_{1-x}Ga_x(S,Se)_2$ properties;	
	6.3 Influence of the sizes of X-ray coherent scattering regions on the electron lifetime and conductivity in	
	polycrystalline $CuIn_{1-x}Ga_x(S, Se)_2$ layers	
7.	Buffer layer materials and the design of contacts	174
	7.1 Buffer layer; 7.2 'Window' materials and the front electrode; 7.3 Bottom electrode and substrates	
8.	Conclusions	175
	References	176

<u>Abstract.</u> This paper reviews literature data on thin-film solar cells with absorber layers based on quaternary copper compounds Cu-In-Ga-(S, Se) (CIGS). The paper considers methods of preparation of CIGS layers and discusses the chemical composition, design features, and operating principles of CIGS-based solar cells. The bulk of the recent literature reveals how research in the field is starting to change: important results are being obtained by numerically simulating processes in thin-film solar cells; element concentration gradients in the CIGS structure, spatially nonuniform bandgap energy distribution, and layer grain boundaries are receiving increasing research attention for their respective roles, and the number of kinetic studies is increasing.

Keywords: photovoltaics, thin films, solar cells, chalcopyrites, CIGS

G F Novikov, M V Gapanovich Institute of Problems of Chemical Physics, Russian Academy of Sciences,

prosp. Akademika Semenova 1, 142432 Chernogolovka, Moscow region, Russian Federation

E-mail: ngf@icp.ac.ru

Received 23 March 2016, revised 3 June 2016 Uspekhi Fizicheskikh Nauk **187** (2) 173–191 (2017) DOI: https://doi.org/10.3367/UFNr.2016.06.037827 Translated by A L Chekhov; edited by A Radzig

1. Introduction

At the present time, the leading positions among different types of devices for direct conversion of solar energy into electrical energy are held by those based on crystalline silicon [1], which are attributed to first-generation solar energy cells. Power conversion efficiency η (PCE) of the best models of these devices amounts to about 25% [2] [this value is close to the theoretical limit (31% [3]) for single-junction solar cells (SCs)], and the device lifetime lasts more than 25 years. However, their price is high due to strict requirements in material purity and the complicated synthesis technology [4].

Second-generation solar cells are based on amorphous or polycrystalline silicon [5]. Their price is significantly lower due to cheaper technology; however, their PCE is lower as well. Lately, the price of crystalline silicon (on a peak power $W_{\rm p}$ basis) has significantly decreased, which has led to lower prices of modules based on it (less than 0.5 dollars per watt of peak power W_p). The most popular solar cells of this type are the ones fabricated using HIT (Heterojunction with Intrinsic Thin layer) technology, a two-cascade five-layer device, where crystalline silicon (one layer) and amorphous silicon (two intrinsic layers and two layers with p- and n-type doping) are utilized simultaneously [6]. Although these solar cells have a high efficiency (in some cases the PCE exceeds 20%), they exhibit not only the advantages but also the disadvantages of both types of solar cells based on amorphous and crystalline silicon. These include the large thickness of the crystalline silicon layers (100-200 µm) and degradation of intrinsic amorphous layers, which lowers the stability of such cells. The large thickness of the layers complicates the fabrication of the cell on a flexible substrate, which together with the large specific weight and low stability creates certain difficulties for the application of these devices in space systems.

Third-generation solar cells have different designs and are fabricated using various technologies; they are attributed by different authors to the category of thin-film solar cells (TFSCs). The absorber layers of these cells can be both inorganic [7, 8] and organic [9, 10] semiconductors. The cost of the power produced by the third-generation solar cells is potentially much lower than that of first-generation solar cells. For example, solar cells with absorber layers based on quaternary copper compounds with the structure of chalcopyrite Cu-In-Ga-(S, Se) (CIGS) [11, 12] are a very attractive and, most importantly, low-price alternative to SCs based on silicon and gallium arsenide. According to the data from paper [13], the price of CIGS-based cells in the USA amounts to 0.67 dollars per W_p , while their cost reaches 0.49 dollars per W_p .

Solar cells of this type are intensively studied in many laboratories around the world. The PCE of CIGS-based laboratory samples reached ~ 20% already in 2011 [14–16], while the commercial modules currently show only 10– 11.5% efficiency [17, 18]. However, unlike batteries based on cadmium telluride, which are also attributed to thin-film solar cells, this material is more ecologically friendly and, besides, the properties of CIGS barely change after long exposure to solar radiation. According to Ref. [14], the price depends on the production region and is defined by such factors as the cost of electrical power in the region and the price of materials (indium, gallium, glass). This fact is especially important for countries where the cost of electrical power is relatively low and there is a suitable resource base, which allows low-cost production of CIGS-based solar cells.

Despite the fact that the obtained record values of PCE for CIGS-based solar cells are still significantly lower than the theoretically possible level [3], the success in laboratory developments has already launched the application of the latest results achieved in carrying out the projects in several European companies (Solibro, Manz, Avancis (all German), Nexcis (France), and others [12]). In recent years there have also been many publications indicating a characteristic change in the research. Important results were obtained by numerically modeling the processes in TFSCs. The researchers started to investigate the role of elemental concentration gradients in the CIGS structure and of the inhomogeneous spatial distribution of the bandgap energy. New investigations are performed regarding the influence of intergrain boundaries in the layers and the kinetic properties. Thus, the review analyzes new results concerned with a promising and not yet fully realized direction of modern photovoltaics—solar cells based on the Cu-In-Ga-(S, Se) type semiconductor layers.

2. History of $CuIn_{1-x}Ga_x(S, Se)_2$ application in solar cells

2.1 Solar cell design

A typical design of an SC with absorber layers of $CuIn(S, Se)_2$ (CIS) or $CuIn_xGa_{1-x}(S, Se)_2$ (CIGS) (abbreviation from the first letters of the element names) semiconductors is shown in Fig. 1. The cell is usually assembled on glass substrates, metal foils, or polyimide films. The bottom (rear) contact of the cell is usually made of molybdenum layers (see Section 7). A 2–4-µm thick CIGS layer is then deposited. Methods of this deposition process can differ. The next layer, called the buffer one, has a typical thickness of 50–100 nm. The most common material for the buffer layer is CdS. The buffer layer is followed by a layer called the 'window'. For this purpose, wide bandgap ZnO type semiconductors with a layer thickness of 50–100 nm are most often applied. Ohmic contact is created using ZnO doped with aluminum. The typical thickness of the contact layer ranges 300–600 nm. A metallic contact grid is formed on the contact surface.

Table 1 shows some physical properties of the materials utilized in CIGS-based TFSCs [19–24].

The following notations are used in the table: band gap energy E_g , electron affinity χ , electron and hole concentration n, p, dielectric constants $\varepsilon/\varepsilon_0$, electron (μ_e) and hole (μ_h) mobilities, effective masses m_e , m_h of electrons or holes, typical acceptor concentration (midgap states [24]) N_a ,

Table 1. Properties of materials [18].

Bulk properties	ZnO	CdS	CIGS	Referen- ces		
$E_{\rm g}, {\rm eV}$	3.3	2.4	1.1 - 1.2			
χ, eV	4.7	4.7	4.64-4.74			
n, p, cm^{-3}	$n: 10^{18}, 10^{20}$	<i>n</i> : 6.0×10^{17}	$p: 2 \times 10^{16}$			
$\varepsilon/\varepsilon_0$	9	10	13.6			
$\mu_{ m e}$, cm ² V ⁻¹ s ⁻¹	25, 6.25	100	200; 1100*	[20]		
$\mu_{ m h}$, cm ² V ⁻¹ s ⁻¹	5, 1.25	25	25, 3-22	[21]		
			167 - 311, $439 - 1760^{**}$	[22]		
$m_{\rm e}/m_{\rm h}$	0.2/1.2	0.2/0.8	0.09/0.72			
Acceptor state concentration, cm ⁻³	N _a : 10 ¹⁶	N _a : 10 ¹⁶		[24]		
$\sigma_{\rm e}, \sigma_{\rm h}, {\rm cm}^2$	$10^{-16}, 10^{-13}$	$10^{-15}, 10^{-12}$				
$\tau_{\rm e}$, ns			100; 200-250	[23]		
$\tau_{\rm h}$, ns			0.1			
* Epitaxial layers on GaAs. Experimentally obtained maximum value						

of electron Hall mobility dependent on the Ga concentration; $T \sim 200$ K ^{**} Epitaxial layers on GaAs. Hall effect measurements at $T \sim 100$ K.



electron and hole cross sections σ_e , σ_h in ZnO and CdS, electron and hole lifetimes τ_e , τ_h in a CIGS layer.

2.2 History of synthesis technology development

for $CuIn_{1-x}Ga_x(S, Se)_2$

The history of CIGS fabrication technology [25, 26] began in 1991, when the EPV corporation (Energy Photovoltaics, Inc., USA) started its own research and now produces thin-film solar cells based on CuInSe₂ (CIS) and Cu(In, Ga)Se₂ (CIGS). In April 1998, EPV demonstrated a noncapsulated CIGS module with a complicated multilayer structure (PCE = 9.7%, area = 3100 cm²), which produced 24 W of power. EPV successively adhered to the vacuum fabrication technology for CIGS.

In the same year, a subcontractor organization NREL (National Renewable Energy Laboratory, USA) demonstrated a record value of PCE = 18.8% (for a module with an area of 0.44 m^2). Simultaneously, other methods for CIGS layer fabrication were developing: selenization of metallic precursors at atmospheric pressure, fast thermal process (annealing), and electrodeposition.

During the first phase of the subcontract, the EPV corporation fabricated a mini-module with an area of 34 cm², a 16-section CIGS with PCE = 10.2%. By applying a molybdenum rear electrode, EPV managed to get PCE = 17.1% for an area of 0.43 m².

During the last few decades, intensive investigations have been carried out in order to prepare SCs on a flexible substrate. The Japan National Institute of Advanced Industrial Science and Technology (AIST) created flexible solar cells with a relatively large PCE. AIST demonstrated a laboratory CIGS cell with PCE = 16.7%, which was fabricated on a low-cost metallic substrate. This very thin solar cell with layers of ceramics, metal, special glass, and semiconductors is only a laboratory sample, but due to its outstanding characterization it can achieve conveyor production.

One of the problems is to form a p-type conductor in the 'final' material with a certain charge carrier concentration. This is achieved by adding alkali metals, such as sodium in the form, in particular, of sodium selenide or sodium fluoride. However, several complications arise when including these elements in production, and the results become irreproducible. Therefore, AIST soon found a new method for manufacturing CIGS-based thin-film solar cells. First, an alkali–silicate glass thin layer (ASTL) is applied to a flexible substrate. Correspondingly, the method was named after this layer—the ASTL method. Then, all other layers are added to the future solar cell: the bottom electrode, light-absorbing CIGS layer, buffer layer, top transparent electrode, and antireflection layer.

AIST specialists believe that such a construction makes the process of alkaline metal addition to the cell main layer easier and allows a precise measurement of the additive amount. As the substrate for the new design of the solar cell, the Institute used three materials: flexible ceramics, thin transparent plastic, and titanium foil with a rough relief surface.

3. Properties of $CuIn(S, Se)_2$ and $CuIn_{1-x}Ga_x(S, Se)_2$

3.1 Crystal structure

CuInSe₂ compounds and CuIn_{1-x}Ga_xSe₂ solid solutions have the structure of chalcopyrite and sphalerite (zinc-



Figure 2. Unit cell: (a) sphalerite structure, and (b) chalcopyrite structure [27].

blende), respectively (Fig. 2). A unit cell of a chalcopyrite can be represented as a sphalerite unit cell with a doubled height. It contains eight atoms — that is, two formula units. Just as in the sphalerite lattice, the metal atoms (two atoms from group I and two from group III) form a regular tetrahedron with a chalcogen atom in the center [27].

The following lattice parameters are characteristic of a chalcopyrite modification: z = 4, a = 5.773 Å, and c = 11.55 [28]. This type of structure was verified in Ref. [29].

According to various data, the CIS density varies between 5.65 and 5.77 g cm⁻³ [28].

3.2 Phase equilibria in Cu₂Se-In₂Se₃ system

Figure 3 plots the phase diagram of the Cu₂Se–In₂Se₃ system [30]. It can be seen that, besides the CIS chalcopyrite modification (α), which is stable at temperatures below 750 °C, there is also a sphalerite modification (δ) in this







Figure 4. Pseudoternary diagram of $Cu_2Se - In_2Se_3 - Ga_2Se_3$ system with shaded region of $Cu_{1-z}(In_{1-x}Ga_x)_{1+z/3}Se_2$ existence at x = 0.5 [31].



Figure 5. Isothermal pseudoternary phase diagram of the $Cu_2Se - In_2Se_3 - Ga_2Se_3$ system at room temperature [32].

system at T = 750 - 1000 °C and 45–65 mol. % In₂Se₃, as well as a defect chalcopyrite modification (β) at *T* below 950 °C and 68–80 mol. % In₂Se₃; the In₆Se₇ modification (γ) is also observed. According to the data from Ref. [14], the CIS melting temperature is around 990 °C.

Figures 4, 5 show pseudoternary phase diagrams of the $Cu_2Se-In_2Se_3-Ga_2Se_3$ system. According to paper [31] (see Fig. 4), the region of CIGS existence with a general formula $Cu_{1-z}(In_{1-x}Ga_x)_{1+z/3}Se_2$ is quite wide (shaded area). However, as was discovered in paper [32], the region where precisely the chalcopyrite modification of the compound exists is quite narrow (region Ch in Fig. 5).

In the rest of the cases, the compound being formed has a sphalerite (Zb in Fig. 5), layered (P2), chalcopyrite derivative (P1), or mixed structure.

3.3 Optical properties and a bandgap energy

Figure 6 presents calculated absorption spectra for CIGS samples with different ratios x = Ga/(In + Ga) [33], and an absorption spectrum for CIGS films with 1.15-eV bandgap energy [12]. It is clear that the theoretically calculated and experimentally measured optical absorption coefficients are



Figure 6. Calculated absorption spectrum of CIGS films for different values of x = Ga/(In + Ga) [33]. The inset shows the absorption spectrum of a film with $E_{\text{g}} = 1.15$ eV [12] on a logarithmic scale.



Figure 7. CIGS bandgap energy versus content ratio Ga/(In + Ga) (solid [34] and dashed [35] curves).

slightly different. However, they are quite large and can exceed 10^5 cm⁻¹ in the visible range. According to data obtained by various authors, the values of the absorption coefficients falls in the range of $3 \times 10^5 - 6 \times 10^6$ cm⁻¹ [29, 36–38], so the thickness of the CIGS film should be on the order of several micrometers for an effective absorption of the solar radiation. Some difference in absorption coefficients of CIGS films obtained in different experiments is, most likely, caused by their different stoichiometry.

The CuIn_{1-x}Ga_xSe₂ solid solutions have the bandgap energy in the range of $E_g = 1.04 - 1.68$ eV [34]. Figure 7 plots the dependence of the CIGS bandgap energy on the content ratio between gallium and indium. It is seen that the bandgap energy smoothly changes from 1.04 eV (CuInSe₂) to 1.68 eV (CuGaSe₂). Moreover, the E_g value can be changed by adding other elements of group III (for example, Al) or elements of group VI (for example, S) [39, 40].

The CIGS bandgap energy is usually determined from the spectra of optical absorption or reflection and analyzing the dependence of the absorption coefficient on the energy of a light quantum close to the red edge. For direct gap semiconductors, such a dependence assumes the following form [41]:

$$\alpha^2 = A(hv - E_{\rm g}), \qquad (1)$$

where α is the absorption coefficient [cm⁻¹], *hv* is the photon energy [eV], E_g is the bandgap energy [eV], and *A* is a



Figure 8. An $(\alpha hv)^2 - hv$ plot of the CIGS film absorption spectrum [38].

constant. The segment which is cut off on the x-axis for the graph of $(\alpha hv)^2$ versus hv indicates the bandgap energy for such semiconductors.

For an example, Fig. 8 demonstrates dependences of $(\alpha hv)^2$ versus hv, obtained for CuIn_{0.6}Ga_{0.4}Se₂ films on a soda-lime glass (SLGTF) with different thicknesses (according to data from Ref. [38]). It can be seen from the figure that $E_{\rm g} = 1.21$ eV for this sample.

3.4 Parameters characterizing solar cell efficiency

The efficiency of radiation energy conversion is the most important parameter characterizing the solar cell (and, consequently, cell performance), and it is equal to the ratio of the maximum power output to the incident light power [42].

In order to compare different solar cells, testing is performed under standard conditions: the cell temperature is 25 °C and it is illuminated by light with a simulated spectrum of solar radiation AM1.5 with power $P_s = 83.5$ or 100 mW cm⁻². The standard simulated solar spectrum AM1.5 corresponds to the average power and spectral characteristics of sunlight near Earth's surface for zenith angles of 41.5° or 48.2°. As an illustration, Fig. 9 shows the



Figure 9. Example of a solar cell *I*–*V* curve.

current–voltage characteristic (I-V curve) of a solar cell under illumination; the inset demonstrates its simplified equivalent circuit. Tilt angles α_1 and α_2 of the curve characterize the effective parallel (R_p) and series (R_s) resistances.

When the load is connected, an electric current starts to flow in the external circuit. As the load resistance R_L increases, the cell potential changes from zero (for $R_L = 0$) to the potential of an open circuit (open circuit voltage):

$$V_{\rm oc} = \frac{k_{\rm B}T}{q} \ln\left(1 + \frac{J_{\rm ph}}{J_0}\right). \tag{2}$$

Here, $J_{\rm ph}$ is the photocurrent density, J_0 is the dark current density, $k_{\rm B}T/q$ is the 'thermal potential', $k_{\rm B}$ is the Boltzmann constant, and T is the temperature. At the same time, the current density changes from maximal (short circuit current density $J_{\rm sc}$) to zero. Short circuit current is defined as the product of photogenerated (excess) charge carrier density (n), drift mobility of carriers (μ_d), and the strength of the electric field (E) acting on the charge carriers: $J_{\rm sc} = q\mu_d nE$. The current density $J_{\rm sc}$ characterizes the maximum number of photogenerated charge carriers which create current in the external electric circuit and, consequently, this quantity depends on the absorption spectrum of the photoactive layer.

The power conversion coefficient (PCE) is calculated from the I-V curve as the ratio of the maximum specific power P_m to incident radiation power P_s :

$$\eta = \frac{P_{\rm m}}{P_{\rm s}} = FF \, \frac{V_{\rm oc}|J_{\rm sc}|}{P_{\rm s}} \,, \tag{3}$$

where the filling factor, equal to

$$FF \equiv \frac{P_{\rm m}}{J_{\rm sc} V_{\rm oc}} \,, \tag{4}$$

indicates how strongly the I-V curve shape differs from a rectangular one.

For a thin-film solar cell with one heterojunction, the limiting solar power conversion efficiency depends on the bandgap energy of the semiconductor in the active layer and is defined by the Shockley–Queisser limit [3].

The influence of the absorber layer thickness and bandgap energy on the performance of a TFSC with a CIGS absorber layer was studied by numerical modeling using the SCAPS program [33]. First, the bandgap energy and electron affinity were defined as mathematical functions of the argument x=Ga/(In + Ga). Then, these functions were used to model and study the operation of the cell. Numerical modeling results are given in Fig. 10. It can be seen that the optimal bandgap energy $E_g = 1.2$ eV is reached at x = 0.3.

The influence of the absorber layer thickness on SC characteristics was studied in paper [32]. As can be seen from Fig. 10, the response in the range of $1.4 < E_g < 1.7$ exhibits different behaviors as the absorber layer is varied. In other words, in a cell with an absorber layer with high E_g , the PCE value decreases as the absorber layer thickness is increased. This happens due to stronger recombination in a solar cell with large E_g . In these solar cells, the depletion layer has a smaller thickness and the photons are partially absorbed far from the depletion layer, so the photogenerated current carriers recombine before they are collected at the electrodes. Optimal thickness lies in the range of 2–3 µm.

Numerical modeling results agree with the dependence of the limiting power conversion efficiency on the bandgap energy predicted in 1961 [3]. The dependence of a limiting



Figure 10. (Color online.) Solar cell power conversion efficiency versus the bandgap energy and the thickness of the absorber layer. The efficiency scale is specified by the colors [33].



Figure 11. Solar cell limiting PCE versus bandgap energy of the absorber layer [3].

solar cell PCE on the bandgap energy of a semiconducting absorber layer is depicted in Fig. 11. The optimal value E_g falls in the range of 1.2–1.5 eV. By comparing the E_g value with the data in Fig. 7, we find that the CuIn_{1-x}Ga_xSe₂ samples with x = 0.3-0.7 are optimal in composition, because their bandgap energies correspond to the specified range.

3.5 Quantum efficiency of $CuIn_{1-x}Ga_x(S, Se)_2$ -based solar cells

Photon absorption in an active layer of solar cells is accompanied by a band-band transition with the generation of excess charge carriers. Diffusion processes together with bulk and surface carrier recombination tend to revert the system involving a conduction band and valence band to the equilibrium state, which is characteristic in the absence of irradiation and electroneutrality conservation. In effective solar cells, the majority of excess charge carriers has to diffuse in the direction of the transition region where they are separated by the electric field [42].

An energy diagram of a typical CdS/CIGS heterojunction is demonstrated in Fig. 12. The diagram was constructed



Figure 12. Energy diagram of a CdS/CIGS heterojunction [43]. ODC— Ordered Defect Compound.

using the standard notation: E_c and E_v as the energies of the conduction band bottom and the valence band top. Since CIGS is a p-type semiconductor, the Fermi level is located in it near the top of the valence band. The buffer layer in the heterojunction is made up from CdS—an n-type semiconductor with a larger bandgap energy $E_g = 2.4$ eV. As a window, the diagram shows a ZnO semiconductor having a large bandgap energy $E_g = 3.4$ eV. It can be seen from the diagram that ZnO also represents a heavily doped n-type semiconductor.

Quantum efficiency (QE) or the quantum yield (equal to the ratio of the number of electrons that reach the electrodes to the number of incident photons) equals 100% if all created excess charge carriers reach the electrodes. However, the QE value in real devices is significantly lower than 100% due to losses caused by reflection of incident photons and charge carrier recombination [44].¹

Figure 13 plots the calculated results for the behavior of CIGS solar cell quantum efficiency concerning different values of x = Ga/(In + Ga). These results can be interpreted in the following way. A decrease in the thickness of the depletion layer leads to a shift of the open circuit voltage towards the saturation threshold. On the other hand, the carrier collection probability lowers in a thinner depletion layer, especially for those carriers that are produced by photons with a larger wavelength. In other words, a part of the photogenerated charge carriers is created far from the depletion layer in a cell with a larger Ga/(Ga + In) ratio. These carriers cannot be collected during their lifetime due to their longer distance from the depletion layer, which results in increasing the role of recombination. Consequently, the reason for a quantum efficiency decrease in a cell with x > 0.3 is the smaller thickness of the depletion layer. According to numerical modeling results, the optimal value of the ratio Ga/(Ga + In) (that is, the x value) in $CuGa_xIn_{1-x}Se_2$ is $x \sim 0.3$, which corresponds to the bandgap energy 1.2 eV. Summing up, simulated results [33], experimental data, and theoretically predicted dependences of the limiting PCE on E_g [33] are in good agreement.

¹ This value can exceed 100%, for example, in devices where one absorbed photon creates more than one electron–hole pair, particularly due to the process of charge carrier multiplication (in the case of PbS, see, for example, Ref. [44]).



Figure 13. Quantum efficiency of a CIGS-based solar cell for different values of x = Ga/(In + Ga) [33].

The solar cell power conversion coefficient can be described as a function of x with the following expression [33]:

$$\eta(\%) = 9.01513 + 36.39558x - 72.34684x^2 + 31.05642x^3.$$
(5)

This expression can be used to predict the PCE of a solar cell with different *x*, but at constant values of other parameters.

4. Synthesis methods for $CuIn(S, Se)_2$ and $CuIn_{1-x}Ga_x(S, Se)_2$ thin films

The synthesis of ternary and quaternary compound films, such as CIS and CIGS, with specified properties is a quite complicated process. Almost all synthesis methods described in the literature consist of at least two stages. At the first stage, the precursor film is obtained, and at the next stages this film is annealed in an active and/or inert atmosphere. The composition of the precursor film can be different: successively deposited metals, their alloys, intermetallic compounds, binary selenides, CIGS nanoparticles, and others.

4.1 Vacuum methods

4.1.1 One-stage methods for CIGS film synthesis. One-stage methods include:

- co-evaporation from different sources,
- magnetron sputtering from CIGS targets,
- thermal evaporation of powders.

The co-evaporation method (simultaneous thermal evaporation from different sources of In, Ga, Cu, and Se) with variable deposition rates and a special three-stage process of substrate heating allows the fabrication of CIGS films with the highest PCE values. Using this method, the glass/Mo substrate is heated in a specific way, while metals and selenium are deposited on it and the rate of this process is controlled with high precision. The disadvantages of this method are its low scalability (currently, record efficiency has been obtained only for devices with area $S < 1 \text{ cm}^2$), high cost, and complications pertaining to reproducibility. Solar cells with $S = 0.419 \text{ cm}^2$ were produced applying the co-evaporation method in paper [17] and their PCE reached 19.9% under AM1.5 illumination. Figure 14 shows the



Figure 14. Deposition rates of In, Ga, Cu (left-hand axis) and Se (right-hand axis) (a) and substrate temperature (b) versus time [17].

temporal dependences of the elemental deposition rates and the substrate temperature. It is seen that during the synthesis the selenium deposition rate was kept constant, while the deposition rates of indium, gallium, and copper varied.

In paper [45], the active layer of a solar cell was obtained using a similar method. For an area of about 0.5 cm², the power conversion efficiency reached 21.7% under AM1.5 illumination.

Solar cells on a flexible polyimide substrate with a PCE of $\sim 5\%$ were produced using a similar method in papers [46, 47].

The magnetron sputtering method was applied to obtain CIGS films in paper [48] using direct current pulses² at room temperature. It was found that the final composition of the sample greatly depends on the sputtering parameters, such as the operating voltage and magnetron current. Under different operating regimes, the content ratio between gallium and selenium in the film remains constant, while the indium content is varied. Moreover, by changing the magnetron operating power, the primary orientation of grains in a CIGS film can be changed.

The method of electron-beam evaporation of preliminary synthesized powders was exploited to grow CIGS films in paper [49]. The samples obtained were utilized to create a solar cell with $\eta = 10.6\%$ over an area of S = 0.25 cm² under AM1.5 illumination. CIGS films were synthesized adapting a special regime for substrate evaporation and heating (Fig. 15).

The authors of paper [50] studied the influence of synthesis conditions on the properties of CIGS films fabricated

² Pulsed heating method (when using a direct current magnetron) is applied to prevent target heating.



Figure 15. Electron beam current and substrate temperature (T_{sub}) versus time [49].

applying the method of vacuum electron beam evaporation of preliminary synthesized powders. The results demonstrated that this method can be used to obtain films with a primary orientation (112).

4.1.2 Multistage methods for CIGS film fabrication. These methods are built around annealing and selenization of CIGS precursors obtained through various processes. The methods include various types of vacuum evaporation:

- thermal [51–55],
- atomic beam [56],
- hybrid [57],
- pulsed laser [58, 59],

• electron beam with subsequent treatment in sulfur and selenium vapors [60, 61],

• magnetron [53, 62–64].

Thermal and magnetron sputtering are the most popular. These methods allow the fabrication of large-area films with a well-controlled composition and thickness [65]. The methods include two stages: successive deposition of metallic layers followed by annealing of obtained layers in Se or H₂Se vapors (Fig. 16). At the first stage, the layers of Cu, Ga, In, and sometimes Se are successively deposited. At the second stage, the sample interacts with Se or H₂Se vapors at a high temperature (around 550 °C) in order to form CIGS. A screen is placed between the metal sources to decrease cross contamination [66].

Any excess In and Ga, when the deposition shifts along the surface during the selenization, can lead to the wrong deposition along the grain boundaries. One of the methods to compensate for such an excess is to add an additional amount of Cu during the selenization thereby contributing to CIGS formation.

In paper [66], two types of precursors with different temperature profiles were selenized. Precursors were



Figure 16. Two-stage CIGS fabrication process.

obtained in a vacuum chamber with two valve-isolated chambers at a temperature of $275 \,^{\circ}$ C. The first chamber contained Cu and Ga, while the second In and Se. This ruled out an excess amount of Se on the surface subjected to deposition. The deposition rate for Cu was 0.6 Å s⁻¹, Ga – 0.7 Å s⁻¹, In – 5.3 Å s⁻¹, and Se – 9.0 Å s⁻¹.

The physical properties and phase composition of CIS films prepared by two-stage selenization of Cu–In layers were studied in Ref. [29]. Cu–In layers were produced by simultaneous sputtering in a vacuum and the ion-plasma sputtering method in an argon atmosphere. CIS films formed after selenization were polycrystalline, and their phase composition and structural characteristics were determined by the content ratio Cu/In in the initial layer. It was shown in paper [28] that the physical properties of CIS films obtained by two-stage selenization in a closed volume depend on the composition of initial metallic layers.

It was reported in paper [65] that a change in the In/Ga ratio during film fabrication leads only to insignificant changes in the film growth kinetics, while a change of the Cu content has significant influence.

It was suggested in paper [54] that CIGS films be synthesized from precursor films consisting of intermetallic compounds Cu_2In , $CuGa_2$, and metallic indium. This method allows the stoichiometry of synthesized samples to be controlled and photosensitive films with a gallium gradient to be obtained [67].

The considered group of methods also includes the method of CIGS film synthesis by selenization of Cu–In–Ga metallic precursors in a hydrogen selenide H_2Se atmosphere [68, 69]. However, H_2Se is quite toxic and its usage is harmful to the ecology and human health. Moreover, hydrogen selenide is less stable than hydrogen sulfide.

4.2 Nonvacuum methods

Chemical bath deposition (CBD) [73] and electrodeposition pertain to the most popular methods [70–72].

4.2.1 Chemical bath deposition method. CIS deposition proceeds from the following reactions:

$$SO_3^{2-} + 2OH^- \to SO_4^{2-} + H_2O + 2e^-,$$
 (6)

$$Cu^{2+} + 2e^{-} \rightarrow Cu^{+}, \qquad (7)$$

$$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^-, \qquad (8)$$

$$\mathrm{HSe}^{-} + \mathrm{OH}^{-} \to \mathrm{H}_{2}\mathrm{O} + \mathrm{Se}^{2-} \,, \tag{9}$$

$$Cu^{+} + In^{3+} + 2Se^{2-} \rightarrow CuInSe_2.$$
⁽¹⁰⁾

In paper [73], CIS films were obtained applying the CBD method. Their thickness was determined gravimetrically, and the study of structural characteristics was performed by the X-ray diffraction method and scanning electron microscopy. The following structural parameters were estimated: lattice constants, the axial ratio, tetragonal distortion, crystallite sizes, the dislocation density, and the number of crystallites per unit area. Optical properties were studied in the wavelength range of 4000-14,500 Å, and the optical band gap was discovered and measured. In paper [73], the films were deposited in a solution of indium diselenide through the reaction of Cu²⁺ with In³⁺ and Se²⁻. CIS was precipitated from a solution containing copper sulfate, sodium citrate, sodium selenosulfate, and indium chloride.

4.2.2 Electrochemical deposition methods. Electrochemical deposition methods can be conditionally separated into two large groups: single-stage and multistage depositions.

In the first case, it is anticipated that a CIGS film is obtained without the stage of additional annealing. In all cases, however, during this synthesis an amorphous or nanocrystalline CIS (CIGS) film is formed, which needs annealing to be recrystallized [74].

Methods in the second group are based on the deposition at the first stage of metallic copper, indium, and gallium or their alloys, as well as binary selenides, are deposited. The sample is then annealed in an active environment. The main problem with CIGS film synthesis by electrochemical deposition from aqueous solutions is the complicated process of cathodic reduction of gallium [76]. Therefore, in order to obtain films with specified stoichiometry, one uses such techniques as the application of complexing agents (most often sodium citrate [75, 76]), adaptation of a special pulsereverse deposition regime [78], and deposition from nonaqueous solutions [77, 79].

Single-stage electrochemical deposition. Nanocrystalline CIGS films were prepared in paper [78] using the method of electrochemical deposition from aqueous solutions containing copper and indium chlorides and gallium nitrate. As a selenium precursor, the authors made use of H_2SeO_3 . Deposition was performed in the pulse-reverse regime (Fig. 17). The precursors obtained using this method were annealed, which resulted in the fabrication of CIGS films with high crystallinity and satisfactory adhesion on glass/Mo substrates.

CIS and CIGS nanocrystalline films were obtained in paper [79] using the method of cathode deposition in a potentiostatic regime on glass/Mo substrates from ethanolic solutions containing CuCl₂, InCl₃, GaCl₃, LiCl, and H₂SeO₃. Lithium chloride was added in order to increase the solubility of chlorides of other elements.

In the experiments, a potential of -0.6 V was applied when depositing CIS films, and -1.6 V when depositing CIGSs. The solution pH was kept in the range from 1.9 to 2.2. The results gave evidence that the annealed CIS or CIGS



Figure 17. Time dependences of (a) deposition potential (with respect to a saturated calomel electrode), and (b) current density [78].

films have phases with a good degree of crystallinity and a homogeneous and dense morphology.

The general scheme of the synthesis was represented in the following way [79]:

$$Cu^{2+} + In^{3+} + 2H_2SeO_3 + 13e^- + 8H^+ \rightarrow CuInSe_2 + 6H_2O$$
, (11)

$$Cu^{2+}$$
 + (1 − X) In³⁺ + XGa³⁺ + 2H₂SeO₃ + 13e⁻ + 8H⁺
→ Cu(In, Ga)Se₂ + 6H₂O. (12)

It was observed [72, 80] that the structure of nanocrystalline CIS and CIGS precursor films, as well as the adhesion during electrochemical deposition from ethanolic solutions, depend on the deposition potential: the potential range for films with plausible properties is narrow and does not exceed 100 mV. It was also revealed that the film structure depends on the solution steering speed during the synthesis.

CIS films were obtained in paper [77] by cathode deposition from ethylene glycol solutions containing CuCl₂, InCl₃, GaCl₃, LiCl, and H₂SeO₃. Synthesis was performed in the temperature range of 25-150 °C. By increasing the synthesis temperature, the authors achieved a slight enlargement of the film grains.

Samples from paper [81] were synthesized by annealing and selenization of films, which were obtained through a combination of two methods: single-stage electrochemical deposition from solutions containing Cu, In, Ga, and Se precursors, and vacuum sputtering. These samples were utilized to create a solar cell with $\eta = 15.4\%$ under AM1.5 illumination.

Multistage electrochemical deposition. In paper [75], CIGS films were prepared by annealing Cu–In–Ga alloys grown using the method of potentiostatic cathode deposition from aqueous solutions containing copper, indium, and gallium sulfates, sodium citrate, NaCl, and/or Na₂SO₄. Precursor films were annealed in two steps: in an inert atmosphere, and in selenium vapor. Solar cells fabricated using these films had an area of 0.1 cm² and $\eta = 9.3\%$ under AM1.5 illumination.

In paper [71], CIGS films were produced by selenization of precursors consisting of successively electrochemically deposited Cu/In/Cu/Ga/Cu layers. During the annealing and selenization, the film's composition variation was studied. It was established that during these processes the intermediate products are Cu-Ga, Cu-In, and CIS intermetallic compounds, as well as CIGSs enriched with indium and depleted with gallium. It was demonstrated in paper [82] how the Se concentration influences the growth of crystals and formation of defects in the CIGS layer if a low-cost method of Cu/In/Cu/Ga/Cu layer electrodeposition is utilized with subsequent selenization during rapid heating by lamps (rapid thermal process, RTP). Different crystal growth modes were observed for different Se concentrations. It was shown that the crystal growth strongly depends on the Se concentration at the initial selenization stage at temperatures from 250 to 350 °C, which can lead to variations in film composition and structure, including separation of CuGaSe and CuInSe phases, and the formation of hole defects in CIGS films at higher selenization temperatures.

In paper [83], the films were prepared by selenizing successively deposited Cu–In–Ga layers from chloride solutions. Using these films, the researchers fabricated a solar cell with $\eta = 10.7\%$ over an area of 0.4 cm² under AM1.5 illumination.

4.2.3 Other nonvacuum methods. These methods include the sol-gel method [84] and ink jet printing [87, 88].

Sol-gel method. The idea of this method consists in firstly applying a layer of paste from Cu, In, Ga hydroxides with an organic cohesive and then reducing the paste with hydrogen and selenizating.

A schematic of the synthesis is displayed in Figs 18 [85] and 19 [86]. In order to obtain the precursor gel, the authors of paper [85] dissolved calculated amounts of copper, indium, and gallium chlorides in water to achieve the needed concentration and content ratio of 1/0.8/0.5 between Cu, In, and Ga metals, respectively. The obtained hydroxides were mixed with cellulose paste fabricated from polyvinyl alcohol (PVA) with addition of triton-100. After that, the paste was applied to molybdenum glass.

During the desiccation, the water and solvent were removed. After that, the metal oxides were reduced with hydrogen (with the separation of bound oxygen in the form of water) and selenization.

The authors of paper [86] used polymethylmethacrylate as an organic cohesive.

Ink jet printing method. This method assumes usage of CIGS nanoparticles. The potential advantage of this method is its scalability and low cost. Currently however, the PCE of solar cells created using CIGS nanoparticles is significantly lower than that of classic solar cells.

Paper [87] describes CIS nanoparticle synthesis from oleylamine containing copper and indium chlorides, as well as elemental selenium. These nanoparticles were utilized to create a solar cell with $\eta \sim 3\%$.

In paper [88], CIGS nanoparticles were produced from the In_2Se_3 , Ga_2Se_3 and CuSe binary sulfides using a ball mill. The particle composition corresponded to $Cu_{0.976}In_{0.811}Ga_{0.277}Se_{1.935}$ stoichiometry; the size of CIGS grains was less than 100 nm.



Figure 18. Production process for CuInGa gel [85].



Figure 19. CIGS fabrication using sol-gel method [86]. CIGS production stages: 1 — paste formation, 2 — paste application to the substrate, 3 — desiccation for solvent removal, and 4 — selenization in oven to transform precursors into CIGS.

4.3 Features of selenization process

It has been established that in some cases the selenization of a precursor film leads to formation of a mixture of CIS, CIGS, or CGS phases [89–91]. However, the study of reaction mechanisms in the film is complicated [92–94], and there is not yet room for such questions as how the reaction goes and how the diffusion processes proceed for every element in CIGS during solid-state selenization. Due to this fact, the study of the processes of phase separation and the formation of a single-phase end product in the form of CIGS type quaternary copper compounds is a key moment in the fabrication of high-quality thin-film CIGS type absorber layers.

The annealing of precursor films in an active environment (Se, H_2Se) can be carried out in a quasiclosed volume or in a flow reactor. The two main problems that appear in the case of such annealing are the selenium aggregation on grain boundaries and the precursor film component's loss in the form of volatile In_xSe_y and Ga_xSe_y selenides.

The formation of a thin Se layer at the CIGS grain boundaries can lead to degradation of CIGS/CdS heterojunction characteristics [95], while the change in film stoichiometry influences its electrophysical and optical properties.

In order to remove the excess selenium and copper selenides, the films undergo a chemical treatment — etching in KCN [75, 96] and $H_2O/HBr-Br_2$ [97] solutions. The data on film composition changes during selenization, which may be found in the literature, are very contradictory. It was shown in paper [98] that during the annealing of a film consisting of metals in elemental selenium vapor in a closed volume a loss of gallium in the form of selenides takes place. However, this effect was not observed in paper [99]. In paper [54], a film composition change was observed during its selenization in a flow reactor. Apparently, contradictions in the literature data are caused both by the distinctions in precursor film selenization methods and by different sensitivities of experimental techniques employed for their composition analysis.

5. Graded elemental distribution in the $CuIn_{1-x}Ga_x(S, Se)_2$ layer

5.1 Single-graded concentrations

As was noted before, a power conversion efficiency of 21.7% was reached in paper [100] for small-area solar cells, and around 20.3% in paper [101]. The PCE of commercial modules was observed to increase up to 12% or higher [102]. It was also revealed that the specific distribution of Ga in the absorber layer has a positive influence on the PCE of the device [103, 104]. Therefore, there is a belief that gallium concentration gradient is one of the key factors which influences the PCE of CIGS-based solar cells. However, there is not yet complete clarity about this matter and in order to further improve the TFSC parameters a detailed investigation of CIGS film synthesis features is needed, together with a deeper understanding of film's complex structure and composition.

One approach to the improvement of solar cells based on $Cu(In, Ga)Se_2$ (CIGSe) is to vary the absorber layer bandgap energy. This can be achieved by incorporating and/or controling the spatial distribution of gallium or sulfur (in $Cu(In, Ga)Se_{2-x}S_x$ films) for creating a graded bandgap. Comprehensive investigations of the influence of E_g on solar

cell efficiency were already performed in previous decades. There are several reviews on this topic [105–107]. Moreover, using computer modeling [108] and theoretical analysis [109], it was shown that such grading should improve the solar cell characteristics.

In the specified papers, several factors were emphasized as the ones that have a positive effect on the characteristics of TFSCs with such films as an absorber layer:

(1) potentially better matching with the solar spectrum;

(2) an increase in photon absorption and charge carrier diffusion by optimizing the bandgap energy, and

(3) an increase in solar cell efficiency by improving the I-V curves of the device (V_{oc} and J_{sc}) [110, 111].

5.2 Double-graded concentrations

Experience working with single-graded concentrations allowed efforts to be focused on the study and analysis of solar cells with a more complicated active layer-based on $Cu_{1-\delta}In_{1-x}Ga_xSe_{2-y}S_y$ films with a double grading of elemental gallium and sulfur [15, 112-117]. It was reported in paper [118] that the presence of a gallium-rich layer near the bottom contact electrode and gallium deficiency near the heterojunction are the main features of films obtained by successive sputtering of metallic precursors with annealing in an H₂Se/H₂S atmosphere. This leads to the unintended creation of gallium grading in the chalcopyrite layer. Moreover, in order to increase the bandgap energy in the spatial charge region, the authors of Ref. [118] introduced sulfur at the last stage, which led to variations in the film composition profile throughout the depth: it was enriched with sulfur on the surface but contained almost no sulfur in the bulk. The existence of such double grading in CIGS films resulted in an increase in the PCE of solar cells based on this film.

Modeling the properties of real solar cells with a doublegraded structure was performed using the SCAPS 1D program [119]. It was shown that in such a structure the processes of recombination and absorption are segregated, which increases the open circuit voltage (V_{oc}) without influencing the short circuit current (J_{sc}) of the devices [111]. Moreover, it was shown that the gallium-rich GGI (Ga/(Ga + In) > 0.4) layer near the rear contact prevents the transfer of electrons to this contact.

Some details concerning the influence of Ga doublegrading on the photovoltaic characteristics of solar cells were studied in work [120]. The authors investigated the influence of the GGI content ratio near the back (C_b) and front (C_f) part of the absorber layer. According to calculations, for constant C_b and C_f concentrations, the increase in GGI in the middle of the CIGS absorber layer (C_m) decreases the short circuit current and increases the open circuit voltage, independent of the distance to the back contact (X_m). For $C_m < C_f$, the value of J_{sc} increases and V_{oc} decreases, when X_m reaches the front of the absorber layer. The behavior of J_{sc} and V_{oc} becomes the opposite if $C_m > C_f$. In almost all of the structures, the efficiency and filling factor showed similar behavior. The highest efficiency was achieved at $C_m = 0.8$ and $X_m = 200$ nm.

Let us note that cathodoluminescence (CL) microscopy [121] represents a powerful tool which allows a deeper understanding of processes that lead to radiative and radiationless recombination and which correlate with film morphology as the size reaches the nanometer scale. Lowtemperature CL investigations show that the defect layers change insignificantly, while the bandgap energy changes significantly [122, 123]. Thus, CL microscopy can provide an efficient approach to the study of the bandgap grading in films along both the longitudinal and transverse directions.

5.3 Influence of recrystallization, bandgap and elemental concentration grading on the characteristics of thin-film solar cells fabricated using three-stage method

As we have noted before, the maximum efficiency of laboratory solar cell samples with a CIGS/CdS heterojunction was achieved by preparing chalcopyrite films using precisely the three-stage method. Solar cells based on $Cu(In, Ga)Se_2$ and obtained using this synthesis technology have a high value of the short circuit current, mainly due to the bandgap grading, which improves the charge carrier sink.

The high open circuit voltage of these devices is attributed to the phenomenon of recrystallization after completing the second stage of the process (see Fig. 14). Recrystallization improves the quality of the absorber layer, because the grain size significantly increases and the region of grain boundaries becomes smaller. Moreover, the grains become strictly oriented along the crystallographic directions (112) or (220)/(204), which is due to the diffusion of sodium ions from the glass [124]. The profiles of indium and gallium distributions in the film are associated with the transition from a Cu-depleted to Cu-rich compositions during the recrystallization process [125]. Therefore, it is hard to distinguish which one is the reason for the positive influence on the absorber layer properties: the graded bandgap or the recrystallization process itself.

A number of publications present data on the numerical modeling investigations of the bandgap energy influence on the photovoltaic characteristics of solar cells. However, there is still a lack of papers which investigate real systems with a bandgap grading, but without repeated film recrystallization [111, 126]. Regarding electron defects, both factors are important, namely, the absolute position of the conduction band changed by the indium and gallium content ratio and the 'purifying effect' of the film recrystallization. Defect activation energies depend on the positions of the valence and conduction bands, so even a small variation in the energy can significantly change the charge density, which, in turn, will influence the electrical parameters of the end device; in other words, metastable defects are created [127]. One can assume that one of the recrystallization consequences is the decrease in electron density near the defects.

6. Transport and lifetimes of excess charge carriers in polycrystalline $CuIn_{1-x}Ga_x(S, Se)_2$ layers

6.1 Influence of intergrain boundaries on power conversion efficiency

The 'destiny' of photogenerated charge carriers in CIGSs after the thermalization process is either to be trapped by acceptors (traps) and recombine in the bulk or on the surface of the microcrystal, without reaching the electrodes during their lifetimes, or to overcome the intergrain boundaries and 'make it' to the electrodes [42]. Recombination processes have a negative influence on the efficiency of the photovoltaic conversion in TFSCs; therefore, an important task is to study the processes of photogenerated current carrier recombination and to understand the role of intergrain boundaries (IGBs).

In the English-language literature, the terms 'crystallites' and 'grains' are almost always used as synonyms. However, it is known that in polycrystalline films the sizes of regions with an ideal lattice can be smaller than the grain sizes. For example, CIGS films synthesized by CBD and electrodeposition methods usually consist of nano-sized crystallites [79, 80, 128, 129]. In this case, the crystallite and grain are the same formations. After annealing some crystallites sinter into larger conglomerates, usually micrometer-sized [80, 129]. The latter are called grains in some papers, regardless of the nature of such grains (see, for example, report [79]). Annealing was traditionally applied to polycrystalline CIGSs in order to increase grain sizes and improve the efficiency of photovoltaic conversion in TFSCs for any synthesis method, including physical vapor deposition (PVD) [79, 128–130].

There are a large number of publications regarding the influence of IGBs on TFSC efficiency. At the same time, there is no agreement not only concerning the nature (and the heights) of barriers located at the boundaries (charged or neutral barriers), but also regarding the role itself of IGBs: whether it is negative or positive. For example, according to the classical 'electron' model, IGBs in polycrystalline semiconductors contain defects (due to the segregation of impurities from the grain bulk to IGBs [131]), which can trap the charge carriers and create on the IGB an electrical potential barrier for the transport of electrons between adjacent grains [132]. The authors of Ref. [133] suggested a theoretical model for IGBs in CuInSe₂, which act as barriers for the primary charge carriers (holes). The model was experimentally confirmed for CuGaSe₂ in paper [134].

Moreover, there is a series of facts indicating the presence of an inhomogeneous inner structure of grains. Potential fluctuations observed in Refs [135, 136] mean that there is disordering in the grain bulk. The role of such fluctuations was considered as a factor which lowers the photoelectric conversion efficiency even in solar cells with record-high PCEs [136]. The authors of Ref. [137] have experimentally observed chemical composition fluctuations which lead to the formation of Cu-depleted or Cu-rich nanodomains (with respect to stoichiometric amounts). It is assumed that such domains have different conduction types (Cu-rich-p-type, and Cu-depleted — n-type). This means that it is possible to form a p-n junction inside the CIGS absorber layer, described by the model constructed in Ref. [138], in which CIGS films are considered a grid of nano-sized p-n junctions that can connect with each other. Such a model in a slightly modified version was confirmed in paper [139], in which the authors revealed the Maxwell-Wagner polarization effect at the temperature of 35 K.

Inhomogeneities can also be caused by incomplete recrystallization of small crystallites into larger grains — that is, the partial formation of conglomerates. This obviously means that it is necessary to take into account the inner structure of the grain [138, 139].

6.2 Influence of intercrystallite boundaries on the transport and recombination of charge carriers

and on the degradation of $\text{CuIn}_{1-x}\text{Ga}_x(\mathbf{S}, \mathbf{Se})_2$ properties There are not much data on charge carrier transport in polycrystalline CIGS films, and most of them were obtained using contact methods. For example, the lifetimes of minority charge carriers were estimated in Ref. [140] by the indirect numerical method from *I-V* curves; in Ref. [141], this was performed by an analysis of an electron beam-induced current (EBIC). A lifetime value of about 100 ns was obtained in paper [142] for a CIGS film in the structure ITO/ZnO/CdS(n-type)/Cu(In, Ga)Se₂(p-type)/Mo/glass using field-free time-of-flight method for conduction current measurement. The resulting interpretation of the measurements performed using contact methods in a polycrystalline (dispersive) medium encounters many difficulties due to the barriers at the IGBs discussed above [143, 144]. Moreover, additional difficulties in interpreting the data obtained using contact methods arise due to the features of near-electrode regions. At the same time, there is even less data on the application of contactless methods [145, 146].

In paper [23], the free-electron lifetime in a CIGS film was measured using a contactless method [147] of frequency-timeresolved microwave photoconductivity (FTRMC) at a frequency of ~ 9 GHz. The authors studied the kinetics of photogenerated electron loss in CIGS synthesized using a PVD method with a successive metal deposition and hightemperature annealing. Photoresponse decays $\Delta P(t)$ had an exponential form, did not depend on the incident light intensity, and agreed with the first-order kinetics. Therefore, the electron loss was related to the process when the electron is captured by the trap, and the free-electron lifetime τ_e turned out to be approximately 200 ns. This value is two times larger than the one reported in Ref. [142]. There are two reasons for such a difference. First, the number of charges registered during the conduction measurements is larger than in the case of luminescence, which registers only the acts of radiative recombination. Second, under the conditions of experiments [23], the contribution from recombination processes to the processes of electron losses is lower.

Bimolecular electron-hole recombination of free electrons and holes in CIGSs was investigated in paper [148]. The corresponding second-order loss kinetics, namely

CIGS
$$\xrightarrow{hv} e^- + p^+ + \dots$$
, (13)

$$e^- + p^+ \xrightarrow{K_r} \dots,$$
 (14)

manifested themselves in a nonlinear dependence of the microwave photoconductivity photoresponse on the incident light intensity and in a nonexponential form of photoresponse decays. Here, e^- and p^+ are photogenerated free (not captured by the traps) electrons and holes, and k_r is the bimolecular recombination rate constant $[cm^3 s^{-1}]$. According to the estimate made in Ref. [148], $k_r =$ 10⁻¹⁰ cm³ s⁻¹. Surprisingly, this value correlates very well with the dependence of the free-electron and hole recombination rate constant on the bandgap energy in a number of semiconductors, as presented in papers [149, 150] (Fig. 20). Apparently, the observed correlation between k_r and E_g is connected with the general 'problem' of bulk interband recombination in these semiconductors-the energy released during the recombination needs to be transferred to a 'third' body.

The interrelation between charge carrier lifetime and energy conversion efficiency and CIGS property degradation was studied in Refs [151–154, 19]. The CIGS elemental properties were analyzed depending on the action of water, free air, carbon dioxide, oxygen, nitrogen, and their combinations. It was established that the observed degradation of solar cell properties is mainly connected with the action of the agents used on the front ZnO:Al electrode and a decrease in the equivalent shunt resistance.



Figure 20. Bimolecular electron-hole recombination rate constant k_r versus the bandgap energy E_g [148–150].



Figure 21. Change in the solar cell PCE and electron lifetimes in CIGS under an identical action of an aggressive medium on the samples [19].

An investigation of the influence of the specified agents on the CIGS layer properties was attempted in paper [19] using the method of time-resolved photoluminescence (TRPL). A strong degradation of 'bare' Cu(In, Ga)Se₂ films was observed under exposure in air or after storage in closed chambers with dry nitrogen. Unexposed film samples in solar cells demonstrated good photovoltaic characteristics, small recombination rates of $< 10^3$ cm s⁻¹, and lifetimes of more than 50 ns. The influence of external factors on the films led to a decrease in both the solar cell PCE and the electron lifetimes measured with the aid of photoluminescence decay kinetics. The observed correlation between these values is shown in Fig. 21.

6.3 Influence of the sizes of X-ray coherent scattering regions on the electron lifetime and conductivity in polycrystalline $CuIn_{1-x}Ga_x(S, Se)_2$ layers

An attempt to study the inner structure of grains was made in papers [155, 156]. Samples were prepared using various methods with different sizes of the coherent scattering regions (CSRs) obtained from the data of X-ray phase analysis (XPA, Table 2). Figure 22 displays microwave photoconductivity decays ΔP measured for sample No. 5 under a 20-fold change in light intensity. One can see that characteristic decay times fall in the range of $\tau_{1/2} = 10-40$ ns, and at large exposures the values $\tau_{1/2}$ reach the limiting time

	Table 2. CSR	sizes in synthesized	polycrystalline	CIGS layers	[155].
--	--------------	----------------------	-----------------	-------------	--------

Sample number	Synthesis method	CSR size, nm
1	Ampoule method	117
2	Magnetron sputtering	65
3		28
4	Thermal deposition	27
5		24
6	×	25
7	Intermetallic precursors	18



Figure 22. Microwave photoconductivity decays in CIGS for three different light intensities: 4×10^{14} (1), 2.3×10^{14} (2), 2.1×10^{13} (3) photon cm⁻² [155].

of the device resolution, equal to 10 ns. Obtained values of $\tau_{1/2}$ for the samples from Table 2 are significantly smaller than those in Ref. [146]. This indicates that the lifetime of excess electrons depends on the size of the crystallites.

The temperature dependence of $\tau_{1/2}$ had an Arrhenius form with the activation energy $E \approx 0.028$ eV (for sample No. 5 in Table 2). This value is close to the thermal energy of $k_{\rm B}T \sim 0.025$ eV at room temperature, which is in good agreement with the calculated results [157] for the position of the acceptor level (0.03 eV), created by a copper vacancy near the valence band. These data are also in good agreement with the results of CIGS photoluminescence investigations at T = 20 K [158]. It is natural to associate the effect of a significant decrease in the photoconductivity decay characteristic time under a reduction in crystallite sizes with the effect of electron trapping near the CSR boundaries and following recombination of the trapped electron with a mobile hole.

In the case of a dispersive medium, at the moment when the charge carrier loses its mobility after falling into the acceptor trap (or after recombination) or after reaching the region boundary and stopping, the contribution of such a charge carrier to the electric current becomes zero. This property of the dipole moment was used in Refs [155, 156] for a qualitative description of the pulsed photoconductivity of a dispersive medium by applying the simplest molecularkinetic model in which the conductivity is expressed as

$$\sigma = q^2 \, \frac{n}{m} \, \tau \,. \tag{15}$$



Figure 23. Dependence of the product $\Delta P_{\max} \tau_{1/2}$ on the sizes of CSRs: dots — data from Ref. [156], dashed straight line — guide for the eye, and solid curve — data approximation result [159].

Here, q is the elementary charge, n and m the charge carrier concentration and mass, respectively, and τ is the carrier mean free path time. Processes of charge carrier losses with respect to their role in conduction can be characterized respectively by the bulk lifetime τ_b (trapping and recombination in the bulk) and by the charge carrier time-of-flight to the boundary of the dispersive medium region (τ_d). The loss rate for mobile current carriers can be expressed as

$$\frac{1}{\tau} = \frac{1}{\tau_{\rm b}} + \frac{1}{\tau_{\rm d}} \,. \tag{16}$$

Under the condition of $\tau_d \ll \tau_b$ (pure material, perfect crystal structure), we obtain

$$\sigma = q^2 \frac{n}{m} \tau_{\rm d} = q^2 \frac{n}{m} \frac{d}{\mu_{\rm d} E} \,. \tag{17}$$

It is clear from expression (17) that in the model with a constant electric field one should expect a linear dependence of the conductivity on the sizes of highly conductive regions of the dispersive medium (as shown in Fig. 23 by a dashed line). In Fig. 23, the ordinate corresponds to the product of the photoresponse amplitude and the half-decay time, $\Delta P_{\text{max}} \tau_{1/2}$, because the time resolution of the setup for the measurement of the photoresponse decay time was not large enough for the samples with small *d* sizes. Results obtained with a more precise time-of-flight model, which takes into account the alternating field [156, 159], are shown in Fig. 23 by a solid line.

In concluding this section, let us note that it is fundamentally important to take into account the roles of intergrain boundaries and CSR boundaries when developing CIGS-based solar cells. The role of the boundaries not only manifests itself in a decrease in the drift mobility and charge carrier lifetime due to the increase in the potential barrier heights for the carrier's motion and in the surface recombination rate, but also turns out to be fundamentally important for the photovoltaic characteristics and processes of solar cell property degradation under the action of external factors.

7. Buffer layer materials and the design of contacts

7.1 Buffer layer

As was already noted in the Introduction to the review, most often the buffer layer is made of thin CdS layers. Thin films of this compound are usually obtained by the chemical bath deposition method [160–162]. Despite the high popularity of such layers, they have several disadvantages [163], one of which is a relatively small value of the CdS bandgap energy $(E_{\rm g} = 2.4 \text{ eV})$. In order to solve this problem, there have been many investigations over the last decade aimed at the search for CdS layer replacement with a larger bandgap energy. Researchers have developed and investigated new types of buffer layers based on zinc and a series of alternative compounds [164-176], particularly ZnO and ZnS [177, 178], as well as ZnIn₂Se₄. Due to a large bandgap energy, these types of semiconductor films transmit light in the near UV region and allow a more efficient usage of the solar spectrum. In most papers, the CBD method is applied for the formation of the junction, but there are also ongoing experiments with other methods.

Another disadvantage of CdS buffer layers is their relatively high toxicity. Therefore, there are active investigations around the world into the possibility of using low-toxic alternatives — films of nonstoichiometric indium sulfide, zinc sulfide, and others [179–182]. More complicated buffer layer types based on Zn(S, O, OH)_x films are at the stage of laboratory development, and they are grown using CBD technology [183]. The process of high-quality ZnS-based film deposition on the CIGS surface is sensitive to a large number of factors and encounters many difficulties [184]. Therefore, when developing deposition methods for ZnS-based compounds, special control over the structural, optical, and photoelectric properties of the material is needed at all fabrication stages.

7.2 'Window' materials and the front electrode

The most popular material for the window layer (see Fig. 1) is undoped ZnO ($E_g = 3.30-3.52$ eV) [185, 186]. When the buffer layer is based on a compound with a larger bandgap energy, for example, ZnS ($E_g = 3.6$ eV), an acceptable efficiency of the solar cell can be achieved by making the windows from a film material with $E_g > 3.6$ eV, like solid ZnO–MgO solutions [187]. In order to prepare ZnO or Zn_{1-x}Mg_xO films, magnetron sputtering and reactive magnetron sputtering are usually employed [186, 188]. Moreover, the works are known where ZnO films are produced using liquid-phase methods like CBD or electrochemical deposition [189, 190]. The thickness of the window layer falls in the range of 50–150 nm. In order to create an efficient solar cell, one needs to match the buffer layer and window thicknesses [191].

ZnO containing approximately 2 mass % of Al₂O₃ (Aluminum–Zinc Oxide, AZO) is commonly used for the top contact of a solar cell. A thin (300–600 nm) film of this material transmits not less than 85% of the light in the visible spectral region [192], and its resistivity is on the order of $10^{-3} \Omega$ cm [193]. Solid ZnO–Ga₂O₃ solution films are adapted less often [194, 195]. In order to create the top contact, high-frequency magnetron sputtering is usually exploited [196]. Reactive magnetron sputtering or DC magnetron sputtering is used less often [193, 197].

After that, the solar cell is covered with a contact grid: 50-nm Ni/1-3 μ m Al. The grid configuration depends on the AZO layer resistance, which, in turn, is determined by the film thickness and the parameters of the fabrication method. The last layer of the solar cell is the antireflection coating — a thin layer of MgF₂.

For capsulation one takes advantage of the glass–glass vacuum lamination.

7.3 Bottom electrode and substrates

Fabrication of the CIGS-based solar cell begins with Mo deposition on glass or a flexible substrate [198–200]. The properties of the molybdenum layer and the substrate have a large influence on the properties of the resulting solar cell. The substrate needs to withstand temperatures up to 550 °C during precursor selenization and should react neither with Mo nor with CIGS [201]. It should be stable to the environment, be mechanically durable, and has a thermal expansion coefficient value close to that of Mo and CIGS ($4.6 \times 10^{-6} \text{ K}^{-1}$ [202]).

Glasses and flexible polymer or metallic films are utilized as substrates. When using Na-containing glasses, it is important to take into account that the Na diffusion into the absorber layer enhances the grain growth and increases the hole concentration. However, many companies adapt SiO₂ and Al₂O₃ blocking layers in order to provide stability of solar cell properties. Borosilicate glasses provide greater stability, but they increase the final cost of the solar cells.

It is of natural interest for TFSC developers to replace heavy and fragile glass substrates with more lightweight and flexible ones. Metallic substrates (Al, Ti, stainless steel, kovar alloy) are good for the means of thermal stability, but they need a formation of barrier layers in order to prevent metal atom diffusion into the absorber layer [203]. The molybdenum layer is less influenced by the titanium and kovar alloy. For titanium, the PCE values achieved are 17.4% [204] and 17.7–17.9% [205, 206], for zirconium 17.7% [204], and for stainless steel 17.5% [207]. In paper [208], a Ti/TiN barrier layer was applied in order to prevent Fe ions diffusing from the stainless steel into the absorber layer.

Polymer layers are less stable under the action of high temperatures, but they do not need the barrier layers to be present and have a smoother surface [209]. The PCE values achieved on a polyimide substrate are 14.1% [210], and 20.4% [211]. Molybdenum deposition on such a substrate slightly bends the layer, but this problem can be solved by several techniques, particularly by depositing Mo on the reverse side of the substrate [212]. In such TFSCs, Na is added either by evaporation of NaF during absorber layer deposition [213–216] or by depositing NaF over the absorber layer followed by additional annealing [217].

The main method of molybdenum layer preparation takes advantage of two-stage DC magnetron sputtering [218]. High-purity argon is used as the working gas. The first layer (Fig. 24), about 100 nm thick, is deposited under a residual pressure of $p \ge 10^{-2}$ mmHg and high magnetron power. These conditions result in the formation of porous molybdenum with high adhesion to glass. However, the resistivity of this layer is relatively high. In order to produce layers with low resistivity, the working pressure in the chamber is decreased to $1 \times 10^{-3} - 10^{-2}$ mmHg. Under these conditions, a layer with a column structure and low sheet resistance (0.2 Ω cm⁻²) is formed. Figure 24 displays the structure of such layers.



Figure 24. Molybdenum layer structure.

The authors of papers [219, 39] studied the influence of magnetron power and working gas pressure in the chamber on the Mo-film deposition rate. The deposition rate increased as the scattered power increased, but it decreased as the pressure in the chamber was increased. The highest rate of an Mo-film (15.1 nm min⁻¹) deposition was achieved at a power of 1200 W and working gas pressure of 0.15 Pa. The lowest resistivity of $3.7 \times 10^{-5} \Omega$ cm was explained by the close packing of large grains in the film. A high efficiency of 12.5% was obtained for CIGS-based solar cells with Mo-electrodes, obtained at a magnetron power of 1200 W and low working pressures. After further optimization of materials and device parameters, a power conversion efficiency of 15.2% was achieved.

There are reasons to believe that the success of Mo application as the bottom contact with respect to other alternatives [220, 221] is explained by the fact that, during the production of the Mo/Cu(In, Ga)Se₂ contact, the MoSe₂ layer is formed and it provides the ohmic contact [212, 222-224]. Regarding the fabrication of CIGS-based solar cells, the properties of molybdenum are unique. A molybdenum layer is thermally stable and is quite inert to the reactive environment used during the CIGS deposition and selenization processes. The molybdenum layer is also important for control over sodium diffusion from the glass substrate to the absorber layer [225]. Moreover, sodium, while diffusing towards the grain boundaries, catalyzes oxygenation and passivation of Se vacancies [226], contributes to MoSe₂ (or MoSe₂) layer formation, plays a specific role in the Cu(In, Ga)Se₂ growth, and provides high adhesion between the semiconductor and the substrate [228].

8. Conclusions

Based on the analysis of more than 200 literature sources, carried out in this review, one may conclude that the PCE of laboratory samples of CIGS/CdS heterojunction-based solar cells can exceed 20%. This is comparable to the efficiency of the best silicon-based devices. However, it should be noted that the PCE increase over the last decade has not been large, approximately 2–3%, although the theoretical limit for a single-junction solar cell is around 30%. This fact concerning parameter growth retardation, of course, did not remain unnoticed by researchers, which in recent years led to a relative increase in the fundamental research share with respect to applied research. In a number of cases, numerical modeling allowed the success of specific TFSC synthesis

techniques to be explained. Much attention was paid to the processes of excess charge carrier losses, to the role of a graded concentration of In, Ga, and S elements and Na diffusion from the substrate, to the influence of the MoS_2 boundary layer, and to other questions.

However, apparently, the most relevant question at this stage is the price of thin-film solar cells. It is also important because the mentioned record values are achieved by applying the expensive and poorly scalable vacuum synthesis method. Alternatives to this method are liquid-phase methods, particularly electrochemical deposition. Currently, the record value of solar cell PCE obtained employing nonvacuum technologies is approximately 10%, which is half the record values of samples fabricated with the aid of vacuum methods. However, when taking into account the fact that the expected cost of solar cell production using nonvacuum methods will be only a fraction of that for vacuum technology, it is no surprise that almost all the main solar cell production companies are carrying out research in this direction. This gives us hope that ground-breaking results in this research field will be obtained within the next decade.

Acknowledgments

The authors are thankful to S M Aldoshin for taking the constant interest in the work and important advice.

The work was carried out with the financial support of RFBR grant No. 16-08-01234.

References

- Green M A, in Solar Cell Materials: Developing Technologies (Eds G Conibeer, A Willoughby) (Chichester: Wiley, 2014) p. 84
- 2. Zhao J et al. Appl. Phys. Lett. 73 1991 (1998)
- 3. Shockley W, Queisser H J J. Appl. Phys. 32 510 (1961)
- Milichko V A et al. Phys. Usp. 59 727 (2016); Usp. Fiz. Nauk 186 801 (2016)
- Schropp R E, in Solar Cell Materials: Developing Technologies (Eds G Conibeer, A Willoughby) (Chichester: Wiley, 2014) p. 112
- Ghannam M, Abdulraheem Y, Shehada G Solar Energy Mater. Solar Cells 145 423 (2016)
- 7. Ekins-Daukes N J, in *Solar Cell Materials: Developing Technologies* (Eds G Conibeer, A Willoughby) (Chichester: Wiley, 2014) p. 144
- Rakitin V V, Novikov G F Russ. Chem. Rev. 86 99 (2017); Usp. Khim. 86 99 (2017)
- Nikolenko L M, Razumov V F Russ. Chem. Rev. 82 429 (2013); Usp. Khim. 82 429 (2013)
- Hoth C et al., in Solar Cell Materials: Developing Technologies (Eds G Conibeer, A Willoughby) (Chichester: Wiley, 2014) p. 282
- 11. Zaretskaya E P et al. *Tech. Phys.* **45** 1371 (2000); *Zh. Tekh. Fiz.* **70** (10) 141 (2000)
- 12. Paire M et al., in *Solar Cell Materials: Developing Technologies* (Eds G Conibeer, A Willoughby) (Chichester: Wiley, 2014) p. 215
- 13. Horowitz K A W, Fu R, Woodhouse M Solar Energy Mater. Solar Cells 154 1 (2016)
- 14. Baek E R et al. Current Appl. Phys. 11 S76 (2011)
- 15. Chirilă A et al. *Nature Mater.* **10** 857 (2011)
- 16. Dhere N G Solar Energy Mater. Solar Cells 95 277 (2011)
- 17. Repins I et al. Prog. Photovolt. Res. Appl. 16 235 (2008)
- von Roedern B, Ullal H S, in Proc. of the 33rd IEEE Photovoltaic Specialists Conf., 11–16 May 2008, San Diego, CA, USA Vol. 1 (Piscataway, NJ: IEEE, 2008) p. 161
- 19. Metzger W K et al. Thin Solid Films 517 2360 (2009)
- 20. Schumann B et al. Kristall Technik 16 71 (1980)
- 21. Lee J W, Cohen J D, Shafarman W N *Thin Solid Films* **480**-**481** 336 (2005)
- 22. Schroeder D J et al. J. Appl. Phys. 83 1519 (1998)
- 23. Novikov G F et al. J. Renewable Sustainable Energy 4 011604 (2012)
- 24. Metzger W K J. Appl. Phys. 103 094515 (2008)
- 25. Miles R W, Zoppi G, Forbes I Mater. Today 10 (11) 20 (2007)

- 26. Dhere N G Solar Energy Mater. Solar Cells 91 1376 (2007)
- Gremenok V F, Tivanov M S, Zalesskii V B Solnechnye Elementy na Osnove Poluprovodnikovykh Materialov (Solar Cells Based on Semiconductor Materials) (Minsk: Izd. Tsentr BGU, 2007)
- Novoselova A V, Lazarev V B (Exec. Eds) Fiziko-khimicheskie Svoistva Poluprovodnikovykh Veshchestv (Physical and Chemical Properties of Semiconductor Devices) (Moscow: Nauka, 1978) p. 339
- 29. Gremenok V F et al. Semiconductors **36** 340 (2002); Fiz. Tekh. Poluprovodn. **36** 360 (2002)
- 30. Park J S et al. J. Appl. Phys. 87 3683 (2000)
- 31. Souilah M et al. J. Solid State Chem. 183 2274 (2010)
- 32. Rudmann D, Thesis of a Dissertation for the degree of Doctor of Sciences (Zürich: Swiss Federal Institute of Technology, 2004)
- 33. Khoshsirat N et al. Optik 126 681 (2015)
- 34. Brown G et al. Appl. Phys. Lett. 96 022104 (2010)
- 35. Tsai W-T et al., in 23rd Photovoltaic Science and Engineering Conf., PVSEC-23, Taiwan, China, October 28–November 1, 2013, p. 21
- Shafarman W, Stolt L, in *Handbook of Photovoltaic Science and Engineering* (Eds A Luque, S Hegedus) (Hoboken, NJ: Wiley, 2006) p. 54
- 37. Wagner S, Bridenbaugh P M J. Cryst. Growth 39 151 (1997)
- 38. Ishizuka S et al. J. Appl. Phys. 106 034908 (2009)
- 39. Marudachalam M et al. J. Appl. Phys. 82 2896 (1997)
- 40. Bekker J et al. *Thin Solid Films* **431–432** 116 (2003)
- 41. Ukhanov Yu I *Opticheskie Svoistva Poluprovodnikov* (Optical Properties of Semiconductors) (Moscow: Nauka, 1977)
- Fahrenbruch A L, Bube R H Fundamentals of Solar Cells: Photovoltaic Solar Energy Conversion (New York: Academic Press, 1983); Translated into Russian: Solnechnye Elementy: Teoriya i Eksperiment (Moscow: Energoatomizdat, 1987)
- Sites J R, Subcontract Report NREL/SR-520-44811 (2009); http:// www.nrel.gov/docs/fy09osti/44811.pdf
- 44. Smith A, Dutton D J. Phys. Chem. Solids 22 351 (1961)
- 45. Jackson P et al. *Phys. Status Solidi RRL* **9** 28 (2015)
- Rud V Y et al. Semiconductors 46 221 (2012); Fiz. Tekh. Poluprovodn. 46 231 (2012)
- 47. Zachmann H et al. Thin Solid Films 517 2209 (2009)
- 48. Bai T R et al. J. Alloys Compounds 646 532 (2015)
- 49. Congkang X et al. Solar Energy Mater. Solar Cells 117 357 (2013)
- 50. Venkatachalam M et al. Solar Energy Mater. Solar Cells 92 571
- (2008)51. Moharram A H, Hafiz M M, Salem A *Appl. Surf. Sci.* 172 61 (2001)
- 52. Young M S et al. *Current Appl. Phys.* 15 18 (2015)
- Sunghun J et al. *Current Appl. Phys.* **10** 990 (2010)
- 54. Gapanovich M V et al. *Inorg. Mater.* **50** 775 (2014); *Neorg. Mater.* **50** 836 (2014)
- 55. Oishi K et al. Thin Solid Films 517 1449 (2008)
- 56. Ito K, Nakazawa T Jpn. J. Appl. Phys. 27 2094 (1988)
- 57. Tanaka T et al. J. Phys. Chem. Solids 66 1978 (2005)
- 58. Moriya K, Tanaka K, Uchiki H Jpn. J. Appl. Phys. 46 5780 (2007)
- 59. Moriya K, Tanaka K, Uchiki H Jpn. J. Appl. Phys. 47 602 (2008)
- 60. Katagiri H et al. *Solar Energy Mater. Solar Cells* **49** 407 (1997)
- 61. Katagiri H et al. Solar Energy Mater. Solar Cells 65 141 (2001)
- 62. Kang S et al. J. Alloys Compounds **563** 207 (2013)
- 63. Liao K-H et al. *Appl. Surf. Sci.* **263** 476 (2012)
- 64. Seol J-S et al. Solar Energy Mater. Solar Cells 75 155 (2003)
- 65. Singh U P, Patra S P *Int. J. Photoenergy* **2010** 19 (2010)
- 66. Pethe S, Thesis for the Degree of Master of Science (Tampa, FL: Univ. of South Florida, 2004)
- 67. Gapanovich M V, RF Patent No. 2567191 (2015)
- 68. Marudachalam M et al. Appl. Phys. Lett. 67 3978 (1995)
- 69. Nakada T, Kunioka A Jpn. J. Appl. Phys. 37 L1065 (1998)
- 70. Calixto M E et al. Solar Energy Mater. Solar Cells **59** 75 (1999)
- 71. Yeh M-H et al. Solar Energy **125** 415 (2016)
- Bocharova S I et al. Nanotechnol. Russ. 8 292 (2013); Ross. Nanotekhnol. 8 (5–6) 16 (2013)
- 73. Dhanam M et al. Phys. Status Solidi A 191 149 (2002)
- 74. Lincot D et al. Solar Energy 77 725 (2004)
- 75. Ribeaucourt L et al. Thin Solid Films 519 7241 (2011)
- 76. Lai Y et al. Electrochim. Acta 54 3004 (2009)
- 77. Bocharova S I et al., in 5th Photovoltaic Technical Conf., Aix-en-Provence, France, May 21-23, 2014, p. D-1-1

- Jadhav H S et al. Appl. Surf. Sci. 268 391 (2013) 78.
- Long F et al. J. Phys. Conf. Ser. 152 012074 (2009) 79.
- 80. Gapanovich M V et al. Kondens. Sredy Mezhfaznye Granitsy 13 413 (2011)
- Bhattacharya R N et al. Appl. Phys. Lett. 75 1431 (1999) 81
- 82. Yeh M-H et al. Solar Energy 132 547 (2016)
- Bhattacharya R N Solar Energy Mater. Solar Cells 113 96 (2013) 83.
- Tanaka K et al. Solar Energy Mater. Solar Cells 93 583 (2009) 84.
- Mitzi D B et al. Adv. Mater. 20 3657 (2008) 85.
- 86. Uhl A R, Romanyuk Y E, Tiwari A N Thin Solid Films 519 7259 (2011)
- 87 Ehrhardt M et al. Appl. Surf. Sci. 278 319 (2013)
- 88. Liu C P, Chuang C L Powder Technol. 229 78 (2012)
- 89 Marudachalam M et al. J. Appl. Phys. 82 2896 (1997)
- Chen J S et al. Solar Cells 30 451 (1991) 90.
- 91. Liu W et al. J. Phys. D 42 125303 (2009)
- 92. Kinoshita A et al. Phys. Status Solidi C 3 2539 (2006)
- 93 Liu W et al. Thin Solid Films 519 244 (2010)
- 94. Baek E R et al. Current Appl. Phys. 11 S76 (2011)
- 95. Chantana J et al. Renewable Energy 76 575 (2015)
- 96. Lin T-Y et al. Nano Energy 19 269 (2016)
- 97. Bouttemy M et al. Thin Solid Films 519 7207 (2011)
- 98. Liu W et al. Semicond. Sci. Technol. 24 035019 (2009)
- 99. Alberts V, Klenk M, Bucher E Solar Energy Mater. Solar Cells 64 371 (2000)
- 100. Jackson P et al. Prog. Photovolt. Res. Appl. 19 894 (2010)
- 101. Green M A et al. Prog. Photovolt. Res. Appl. 19 84 (2011)
- 102. Otte K et al. Thin Solid Films 511-512 613 (2006)
- 103. Gorji N E, Reggiani U, Sandrolini L Solar Energy 86 920 (2012)
- 104. Hayashi T et al. Solar Energy Mater. Solar Cells 93 922 (2009)
- 105. Lundberg O, Edoff M, Stolt L Thin Solid Films 480-481 520 (2005)
- 106. Gorji N E et al. Int. J. Eng. Technol. 4 573 (2012)
- 107. Dullweber T et al. Solar Energy Mater. Solar Cells 67 145 (2001)
- 108. Decock K, Lauwaert J, Burgelman M Energy Procedia 2 49 (2010)
- 109. Acevedo A M Energy Procedia 2 169 (2010)
- 110. Rockett A Thin Solid Films 361-362 330 (2000)
- 111. Song J et al. Solid-State Electron. 48 73 (2004)
- 112. Frisk C et al. J. Phys. D 47 485104 (2014)
- 113. Green M A Prog. Photovolt. Res. Appl. 17 57 (2009)
- 114. Pawlowski M et al. Thin Solid Films 535 336 (2013)
- 115. Murata M et al. Jpn. J. Appl. Phys. 53 04ER14 (2014)
- Kuo S-Y et al. Int. J. Photoenergy 2014 186579 (2014) 116.
- 117. Hirai Y, Kurokawa Y, Yamada A Jpn. J. Appl. Phys. 53 012301 (2014)
- 118. Knecht R et al. Phys. Status Solidi A 210 1392 (2013)
- 119. Burgelman M, Marlein J, in Proc. of References of the 23rd European Photovoltaic Solar Energy Conf. and Exhibition, 1-5 September 2008, Valencia, Spain, p. 2151
- 120. Saadat M, Moradi M, Zahedifar M Superlatt. Microstruct. 92 303 (2016)
- 121. Müller M et al. Thin Solid Films 535 270 (2013)
- 122. Rega N et al. Thin Solid Films 480-481 286 (2005)
- 123. Wei S-H, Zhang S B, Zunger A Appl. Phys. Lett. 72 3199 (1998)
- 124. Couzinié-Devy F, Barreau N, Kessler J Prog. Photovolt. Res. Appl. 19 527 (2011)
- 125. Drobiazg T et al., in 39th Photovoltaic Specialists Conf. IEEE, PVSC, Tampa, FL, USA, 16-21 June 2013, p. 2572
- 126. Orgis T, Maiberg M, Scheer R J. Appl. Phys. 114 214506 (2013)
- 127. Bosio A, Romeo A (Eds) Thin Film Solar Cells: Current Status and
- Future Trends (New York: Nova Sci. Publ., 2011) p. 103 128. Lincot D, Ortega-Borges R, Froment M Philos. Mag. B. 68 185
- (1993)129.
- Dhanam M et al. Phys. Status Solidi A 191 149 (2002)
- 130. Tseng B-H et al. J. Appl. Phys. 67 2637 (1990)
- 131. Möller H J Semiconductors for Solar Cells (Boston: Artech House, 1993) p. 339
- 132. Seto J Y W J. Appl. Phys. 46 5247 (1975)
- 133. Persson C, Zunger A Phys. Rev. Lett. 91 266401 (2003)
- 134. Siebentritt S et al. Phys. Rev. Lett. 97 146601 (2006)
- 135. Dirnstorfer I et al. Phys. Status Solidi A 168 163 (1998)
- 136. Siebentritt S Solar Energy Mater. Solar Cells 95 1471 (2011)
- 137. Yan Y et al. Appl. Phys. Lett. 87 121904 (2005)

138. Stanber B J, in Proc. of the 31st IEEE Photovoltaic Specialist Conf., 3-7 January 205, Lake Buena Vista, FL, USA, p. 355

177

- Reislöhner U, Ronning C Appl. Phys. Lett. 100 252111 (2012) 139.
- 140. Gray J L, Schwartz R J, Lee Y L, Subcontract Report NREL/TP-451-6398 (Golden, CO: National Renewable Energy Laboratory, 1994); http://nrel.ipac.dynixasp.com/
- 141. Scheer R, Wilhelm M, Lewerenz H J J. Appl. Phys. 66 5412 (1989)
- 142. Nishitani M et al. J. Appl. Phys. 82 3572 (1997)
- 143. Taretto K, Rau U J. Appl. Phys. 103 094523 (2008)
- 144. Gloeckler M, Sites J R, Metzger W K J. Appl. Phys. 98 113704 (2005)
- 145. Ahrenkiel R K, Keyes B M, Levi D L, in Proc. of the 13th E.C. Photovoltaic Solar Energy Conf., PVSEC, Florence, Italy, 1995, p. 917
- 146. Novikov G F et al. J. Renewable Sustainable Energy 4 011604 (2012)
- 147. Novikov G F, Marinin A A, Rabenok E V Instrum. Exp. Tech. 53
- 233 (2010); Prib. Tekh. Eksp. (2) 83 (2010) 148. Bocharov K V "Vliyanie khimicheskogo sostava i defektov kristallicheskoi reshetki na protsessy zakhvata i rekombinatsii izbytochnykh nositelei toka v poluprovodnikakh A^IB^{VII}, A^{II}B^{VI}, A^IB^{III}C^{VI}" ("Influence of chemical composition and crystal lattice defects on the processes of trapping and recombination of excess current carriers in AIBVII, AIIBVI, AIBIIICVI semiconductors"), PhD Thesis (Chernogolovka: IPCP RAS, 2012)
- 149. Golovanov B I "Issledovaniya rekombinatsionnykh protsessov v mikrodispersnykh galogenidakh serebra metodom SVCh-fotoprovodimosti" ("Investigations of recombination processes in microdispersive silver halogenides by microwave photoconductivity method"), PhD Thesis (Chernogolovka: IPCP RAS, 2002)
- 150. Radychev N A, Novikov G F Russ. Chem. Bull. 55 766 (2006); Izv. Ross. Akad. Nauk. Ser. Khim. 55 740 (2006)
- 151. Coyle D Prog. Photovolt. Res. Appl. 21 156 (2013)
- 152. Del Cueto J A et al., in Proc. of the 33rd IEEE Photovoltaic Specialists Conf., 11-16 May 2008 Vol. 1 (Piscataway, NJ: IEEE, 2009) p. 1
- 153. Theelen M et al. Thin Solid Films 565 149 (2014)
- 154. Theelen M et al. Solar Energy Mater. Solar Cells 141 49 (2015)
- 155. Bocharov K V et al. Semiconductors 47 335 (2013); Fiz. Tekh. Poluprovodn. 47 310 (2013)
- 156. Novikov G F, Bocharov K V Phys. Express 4 21 (2014)
- 157. Zhang S B et al. Phys. Rev. B 57 9642 (1998)
- 158. Medvedkin G A et al. Semiconductors 35 1329 (2001); Fiz. Tekh. Poluprovodn. 35 1385 (2001)
- Novikov G F J. Renewable Sustainable Energy 7 011204 (2015) 159
- 160. Salazar Y A et al. Brazilian J. Phys. 36 1058 (2006)
- 161. Contreras M A et al. Thin Solid Films 403 204 (2002)
- 162. Zinoviev K V, Zelaya-Angel O Mater. Chem. Phys. 70 100 (2001)
- 163. Schwartz C et al. Solar Energy Mater. Solar Cells 149 275 (2016)
- Bhattacharya R N, Ramanathan K Solar Energy 77 679 (2004) 164.
- 165. Nakada T, Mizutani M Jpn. J. Appl. Phys. 41 L165 (2002)
- 166. Bhattacharya R N, Contreras M A, Teeter G Jpn. J. Appl. Phys. 43 L1475 (2004)
- 167. Ahn B T et al. Pure Appl. Chem. 80 2091 (2008)
- Bayon R, Herrero J Appl. Surf. Sci. 158 49 (2000) 168.
- Kushiya K et al. Thin Solid Films 517 2108 (2009) 169.
- 170. Nakada T, Hongo M, Hayashi E Thin Solid Films 431-432 242 (2003)
- 171. Ennaoui A et al. Solar Energy Mater. Solar Cells 67 31 (2001)
- 172. Islam M M et al. Solar Energy Mater. Solar Cells 93 970 (2009)
- 173. Fang X S et al. J. Mater. Sci. Technol. 24 520 (2008)

Long F et al. Chem. Phys. Lett. 462 84 (2008)

Fang X S et al. J. Mater. Chem. 18 509 (2008)

179. Spiering S et al. Thin Solid Films 582 328 (2015)

182. El-Nahass M M et al. Physica B 425 23 (2013)

Energy Conf., Valencia, Spain, 2008, p. 2175

178. Fang X et al. Adv. Mater. 21 2034 (2009)

176.

177

180.

55 17 (2016)

143 159 (2015)

174. Bhattacharya R N et al. J. Phys. Chem. Solids 66 1862 (2005) 175. Ichiboshi A et al. Solar Energy Mater. Solar Cells 90 3130 (2006)

Ummartyotin S, Infahsaeng Y Renewable Sustainable Energy Rev.

181. Kobayashi T, Li Kao Z J, Nakada T Solar Energy Mater. Solar Cells

183. Nakada T et al., in Proc. of the 23rd European Photovoltaic Solar

- 184. Kushiya K et al. Jpn. J. Appl. Phys. 35 4383 (1996)
- 185. Sang B et al. Solar Energy Mater. Solar Cells 75 179 (2003)
- 186. Purohit A et al. *Opt. Mater.* **49** 51 (2015)
- 187. Witte W, Hariskos D, Powalla M Thin Solid Films 519 7549 (2011)
- 188. Rabotkin S V "Nanesenie prozrachnykh provodyashchikh pokrytii na osnove oksida tsinka metodom magnetronnogo raspyleniya" ("Deposition of transparent conductive coatings based on zinc oxide using magnetron sputtering method"), PhD Thesis (Tomsk: Inst. of High Current Electronics, Siberian Branch of the RAS, 2009)
- 189. Chu D et al. Phys. Status Solidi A 206 718 (2009)
- Chatman S, Ryan B J, Poduska K M Appl. Phys. Lett. 92 01203 (2008)
- 191. Sim H et al. J. Semicond. Technol. Sci. 15 267 (2015)
- 192. Islam M M et al. Appl. Surf. Sci. 257 4026 (2011)
- 193. Lee S et al. *Mater. Lett.* **85** 88 (2012)
- 194. Yilmaz M Mater. Sci. Semicond. Process. 40 99 (2015)
- 195. Hwang Y et al. J. Phys. Chem. Solids 87 122 (2015)
- 196. Yasui K et al. Mater. Sci. Eng. B 148 26 (2008)
- 197. Ji Z, Mao Q, Ke W Solid State Commun. 150 1919 (2010)
- Gordillo G, Grizalez M, Hernandez L C Solar Energy Mater. Solar Cells 51 327 (1998)
- 199. Yoon J H et al. J. Phys. D 44 425302 (2011)
- 200. Salome P et al. J. Phys. D 43 345501 (2010)
- 201. Kessler F, Rudmann D Solar Energy 77 685 (2004)
- 202. Brémaud D J L "Investigation and development of CIGS solar cells on flexible substrates and with alternative electrical back contacts", Doctoral and Habilitation Theses (Zürich: ETH, 2009)
- 203. Martínez M A et al. Surf. Coat. Technol. 148 61 (2001)
- 204. Ishizuka S et al. Appl. Phys. Lett. 93 124105 (2008)
- 205. Pianezzi F et al. Prog. Photovoltaics Res. Appl. 20 253 (2012)
- 206. Nakada T et al., in Proc. of the 24th European Photovoltaic Solar Energy Conf., Hamburg, Germany, 2009, p. 2425
- Tuttle J R, Szalaj A, Keane J, in Photovoltaic Specialists Conf., 2000. Conf. Record of the Twenty-Eighth IEEE, Anchorag, USA, 2000, p.1042
- 208. Liu W S et al. J. Alloys Compounds 631146 (2015)
- 209. Kessler F, Herrmann D, Powalla M *Thin Solid Films* **480-481** 491 (2005)
- 210. Rudmann D et al. J. Appl. Phys. 97 084903 (2005)
- 211. Chirilă A et al. Nature Mater. 10 857 (2011)
- 212. Wada T et al. Jpn. J. Appl. Phys. 35 L1253 (1996)
- 213. Powalla M, Dimmler B Thin Solid Films 361 540 (2000)
- 214. He X et al. J. Alloys Compounds 658 12 (2016)
- 215. Chen C C et al. Surf. Coat. Technol. 231 209 (2013)
- 216. Lee M et al. Appl. Surf. Sci. 346 562 (2015)
- 217. Rudmann D et al. Appl. Phys. Lett. 84 1129 (2004)
- 218. Scofield J H et al. *Thin Solid Films* **260** 26 (1995)
- 219. Zhou D et al. Appl. Surf. Sci. 362 202 (2016)
- 220. Kaelin M, Rudmann D, Tiwari A N Solar Energy 77 749 (2004)
- 221. Taunier S et al. Thin Solid Films 480-481 526 (2005)
- 222. Assmann L et al. Appl. Surf. Sci. 246 159 (2005)
- 223. Zhu X et al. Solar Energy Mater. Solar Cells 101 57 (2012)
- Shafarman W N, Phillips J E, in Photovoltaic Specialists Conf., 1996., Conf. Record of the Twenty Fifth IEEE, Anchorag, USA, 1996, p. 917
- 225. Bommersbach P et al. Prog. Photovoltaics Res. Appl. 21 332 (2013)
- 226. Guillemoles J F et al. Adv. Mater. 11 957 (1999)
- 227. Kohara N et al. Solar Energy Mater. Solar Cells 67 209 (2001)
- 228. Niki S et al. Prog. Photovoltaics Res. Appl. 18 453 (2010)