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FABRICATION OF CdS/CdTe SOLAR CELLS BY QUASICLOSED SPACE TECHNOLOGY AND RESEARCH OF THEIR PROPERTIES

A quasiclosed space technology has been developed for the deposition of CdS and CdTe layers, while fabricating solar cells (SCs). Technological factors affecting the crystal lattice structure, the optical band gap width, and the conductivity in the CdS and CdTe layers are studied and analyzed. A technology to produce an ohmic contact with p-CdTe, by using the degenerate Cu_xS *semiconductor, is proposed. The characteristics of SCs fabricated on substrates covered with various conducting films (Mo, ZnO, ZnO : Al) are analyzed. The measurement results of light and dark voltage-current characteristics testify to the better characteristics of ZnO and ZnO : Al films obtained by the atomic layer deposition from the viewpoint of their application in SCs. The optimum thicknesses of the CdS (67 nm), CdTe (about 1 μm), and* Cu_xS *(30 nm) layers, at which the best SC efficiency (*$\eta = 1.75 \div 1.89\%$*) is obtained, are determined. The application of thin films in SC structures is shown to improve the characteristics of the latter.*

Keywords: vacuum quasiclosed space technology; CdS/CdTe solar cell; Cu_xS ohmic contact; Mo, ZnO, ZnO : Al conducting films.

1. Introduction

Search for alternative energy sources stimulates scientific developments that are aimed at the creation of highly efficient cheap solar cells (SCs). Solar cells based on thin films are of special interest. Thin-film solar cells (TFSCs) become competitive with silicon-based (mono- and polycrystalline) ones owing to their low cost and high efficiency values [1]. By the volume of their production, solar panels fabricated from cadmium telluride (CdTe) are next after silicon-based elements. In 2016, the efficiency of CdTe-based solar cells exceeded a value of 16.5%, which was a record within the last decade.

In work [2], the following values for the parameters of TFSCs based on the CdS/CdTe structure under the illumination of 1000 W/m^2 (AM1.5) and at a temperature of 25 °C were reported: an efficiency of $21.0 \pm 0.4\%$, an aperture area of 1.0623 cm^2, the open-circuit voltage $V_{\rm oc} = 0.8759$ V, the short-circuit current $J_{\rm sc} = 30.25$ mA/cm$_2$, and the filling factor $FF = 79.4\%$. For ground-based units with thin-film CdS/CdTe solar cells, the following data were obtained under the AM 1.5 illumination condition and at a temperature of 25 °C: the efficiency $\eta = 18.6 \pm 0.6\%$, an aperture area of 7038.8 cm^2, $V_{\rm oc} = 110.6$ V, $J_{\rm sc} = 1.533$ A, and $FF = 74.2\%$. The record values for CdS/CdTe solar cells are as follows: $\eta = 22.1 \pm 0.5\%$, an illuminated area of 0.4798 cm^2, $V_{\rm oc} = 0.8872$ V, $J_{\rm sc} = 31.69$ A, and $FF = 78.5\%$ (under the AM 1.5 illumination condition and at a temperature of 25 °C).

The fabrication technology of CdS/CdTe solar cells is suitable for the large-scale production owing to the following reasons [3, 4]:

- cheap substrates based on sodium-calcium silicate glass can be used, which withstand a temperature of 500 °C;

- the amount of materials used in the fabrication is approximately 100 times less in comparison with that used in the fabrication of monocrystalline modules, so that it comprises a small fraction of the total cost;
- the production process can be completely automated; the next module can be obtained every 2 min [3], which allows the cost of the energy generated by a module to be reduced to 1 euro per peak watt.

Unlike the fabrication of silicon-based SCs, there is no common technological procedure for producing CdS/CdTe ones. Therefore, every company uses its own developments and equipment to fabricate SCs. The leading companies producing commercial modules on the basis of the CdS/CdTe structure include ANTEC GmbH (Germany) and First Solar (USA). In particular, the production capacity of First Solar exceeds 300 MW per year [5]. The both companies use the process of thermal sublimation for depositing the CdTe layer. Namely, this is the sublimation in a confined space, the closed-space sublimation (CSS) method, when the distance between the evaporated powder and the substrate amounts to only 3–5 mm [6].

Companies that apply other methods for the CdTe deposition include Golden Photon (spray pyrolysis), BP Solar (electrodeposition), and Matsushita (screen printing) [6, 7]. However, the mentioned companies faced a number of difficulties. In particular, SCs obtained by the spray pyrolysis had instable properties. The processes based on wet chemistry methods failed to be included into the common SC manufacturing line. Therefore, those companies stopped the SC production. However, it is the progress in the fabrication of CdS/CdTe-based SCs and their modules that is the fastest among the fabrication of thin-film SCs of other types. Initial investments in the production of modules on the basis of CdS/CdTe solar cells are estimated to be 0.8–2.0 million euros per megawatt [7].

Despite the achieved success, it is necessary to tackle problems aimed at reaching a value of 1 euro per peak watt, in order to become competitive with other energy sources [8,9]. For this purpose, substrates with a large area have to be used, which allows the cost of the production process to be reduced. Polycrystalline or amorphous films rather than epitaxial ones have to be grown. It is necessary to find a method to passivate grain boundaries in polycrystalline films. Without efficient passivation of grain boundaries, the "drain" of photo-generated charge carriers occurs along them, and the photocurrent yield is low [8, 9].

The typical structure of a CdS/CdTe solar cell includes four layers [10]. The first layer is a sheet of a transparent conducting oxide (TCO), which plays the role of a current-collecting contact. The second layer is a CdS film, which serves as a wide-bandgap window. The main absorbing layer is the third, CdTe, one, which is deposited onto the CdS layer. Finally, the fourth layer is deposited onto CdTe to provide a current-collecting contact. Each of the layers can be obtained, by using a variety of technological methods (magnetron sputtering, thermal evaporation, spray sputtering, wet chemistry methods, and so forth). When fabricating SCs, the main point consists in that the deposition methods should be combined into a common technological procedure.

The technology of layer deposition should also satisfy certain demands, which are made on each layer, in order to produce high-performance SCs. For example, the TCO layer should satisfy the following requirements [10]:

- a high transparency, not lower than 80–85%, in a wavelength interval of 400–600 nm;
- a low impedance of about $2 \times 10^{-4}\ \Omega \cdot \text{cm}$;
- a specific resistance of less than $10\ \Omega/\square$;
- a good stability at high temperatures that take place when the next layers are deposited and during the thermal annealing and chemical treatments; no diffusion of elements from the TCO layer into other ones is allowed.

A requirement to the CdS wide-bandgap window consists in a high concentration of free charge carriers of an order of $10^{17}\ \text{cm}^{-3}$ [10]. For this purpose, the stoichiometry, the growth morphology, the number of grain boundaries, and the types of generated defects have to be controlled. It is important to obtain a good quality of the heterojunction, namely, to minimize the number of adhesion and recombination centers between the layers. To improve the interface quality, additional technological techniques are applied, in particular, the chloride treatment. The diffusion processes between the CdS and CdTe layers, which affect the SC output parameters [7], have to be minimized.

Requirements to the CdTe absorption layer is also associated with the concentration of charge carriers and their mobility. The task of obtaining the layers with identical parameters under the same deposition conditions remains a challenging issue. Layers, which serve as current-collecting contacts, should not form barriers with CdS and CdTe. Tasks associated with the development of contacts have not been resolved at length [3]. This is a result of the fact that metals providing an ohmic contact with CdTe should possess a high work function, because it is difficult to dope CdTe with holes owing to the strong tendency of the latter to self-compensation [7]. Therefore, the issues dealing with the manufacturing technology for each layer are challenging.

In this work, a technology is developed for the fabrication of n-CdS/p-CdTe solar cells within the method of thermal evaporation in a quasiclosed space. This technology is cheap and, at the same time, provides a directional growth of polycrystalline films. The novelty of this work consists in the application of the degenerate p-$\mathrm{Cu}_x\mathrm{S}$ semiconductor as a current-collecting contact with CdTe, as well as thin conducting ZnO and ZnO : Al films obtained, by using the atomic layer deposition (ALD) method as a contact with CdS. The ALD method allows films that are dense, homogeneous by composition, and uniform by thickness to be deposited at low temperatures (100–200 °C) onto large areas (120×120 cm^2). It can be classified to nanotechnological methods [1, 11, 12]. The cost of the technological process with the application of the ALD method is reduced, because dozens of substrates with a large area can be simultaneously loaded into the working chamber.

Below, the influence of technological regimes on the crystalline structure of growing layers, their thickness, and electrical properties is studied. For this purpose, the methods of X-ray structural analysis, as well as optical and scanning electron microscopies, are used. The dependence of the optical band gap width on the thickness of CdS, $\mathrm{Cu}_x\mathrm{S}$, and CdTe films was determined from the optical reflection spectra. The film thickness was both measured on a profilometer and calculated on the basis of optical reflection spectra. The light and dark characteristics of SCs were measured, and their parameters were calculated.

2. Deposition Technology for ZnO and ZnO : Al Films and Their Properties

When fabricating a SC, the first stage consists in the deposition of a conducting material onto a substrate. In industry, a transparent conductive oxide is mainly deposited, by applying the sputtering (magnetron and so on) methods [3, 13]. However, those methods have some disadvantages: the rate of film deposition can be not high enough, and the resulting TCOs are hygroscopic [3]. Tin-doped indium oxide, $\mathrm{In_2O_3:Sn}$ (ITO), is the most commonly used TCO. The cost of this material rapidly increases every year. Moreover, it is toxic. At high temperatures, which are used at the CdS deposition, indium diffuses from ITO into the growing layer, which finally results in the formation of short circuits in the SC structure.

We studied materials, alternative to ITO, to be used for the lower current-collecting contact; namely, Mo, ZnO, and ZnO : Al, which is a novelty of this work. The material of the current-collecting contact has to form an ohmic contact with CdS. Theoretically, the molybdenum contact is ohmic, because its work function equals $\Phi = 4.8$ eV, which coincides with the corresponding value for CdS. For ZnO and ZnO : Al, the work function Φ equals 4.3 and 4.53 eV, respectively, which is also suitable for the creation of an ohmic contact [14]. Molybdenum was deposited onto pyroceramic substrates, by using the magnetron sputtering on an installation PVD 75 (Kurt J. Lesker).

ZnO and ZnO : Al films were grown, by using the ALD method. ZnO films were deposited in a TCO reactor Cambridge Nanotech Savannah-100 from vapor of deionized water and diethyl zinc ($\mathrm{Zn(C_2H_5)_2}$, DEZn). Trimetylaluminum vapor was additionally introduced into the reactor for doping the specimens with aluminum. It was found that, at an aluminum concentration of about 3 at.% in the ZnO:Al film, the resistivity of the latter was equal to 8×10^{-4} Ω cm. However, further researches showed that ZnO films with a required conductivity can be obtained even without their doping.

In particular, it was found that if the temperature of the substrate and the reactor equaled 200 °C, films could be obtained with a charge carrier concentration of about 10^{20} cm^{-3} and a conductivity of about 10^4 Ω^{-1} cm^{-1}, as in ITO films. The charge carrier mobility measured by the Hall method (equipment from PhysTech GmbH) amounted to 24.8 cm^2/(V s). This value is lower than the desired one, 65 cm^2/(V s) [12]. The thickness of the ZnO and ZnO : Al films was about 200 nm. Films with this thickness had a columnar polycrystalline structure and a transmittance of 80–85% in the visible spectral interval [1, 11]. The transmittance of ZnO : Al films was at the same level as for the ZnO films or slightly higher. The results of the ALD technology development for obtaining the transparent ZnO and ZnO : Al films, as well as the results of their researches, were reported in works [1, 15–20].

3. Technology for Obtaining CdS and CdTe Layers in Quasiclosed Space

The technology of film deposition in a quasiclosed space differs from the CSS method, first of all, by the distance between the powder and the substrate, and by the temperature. In our case, the corresponding distance amounted to 15 cm, and the deposition temperatures were lower than those in the CSS method. A feature of our technology is a successive deposition of the CdS and CdTe layers in vacuum in a common technological cycle without interruption, which distinguishes this process from analogous ones. As a result, when the CdS and CdTe films grow, a CdS_xTe_{1-x} variband layer is formed between them, which is also a novelty of this technology.

The constants of the CdS and CdTe crystalline lattices are known [3] to differ from each other by 9.7%. The formation of a variband layer diminishes the number of defects in the transient zone between the CdS and CdTe layers, which arise owing to the difference between both the crystal lattice parameters and the temperature expansion coefficients of the layers. The reduction in the number of defects should decrease the density of the inverse saturation current and, accordingly, increase the open-circuit voltage and the filling factor [8]. The process was carried out in a quasiclosed space of quartz glass with two branches. The latter contained annealed CdS and CdTe powders. Owing to the heating of the powders in a vacuum chamber (a vacuum of 10^{-3} Pa), they sublimated and condensed to form films on the substrate. The temperature of the latter was varied in an interval from 210 to 290 °C. The time evolution of both the film thickness and the grain size, and their dependence on the temperatures of the heaters and the substrate were studied. Some results of those studies and a detailed description of the used equipment were presented in work [21].

3.1. Researches of CdS Layers

CdS films were deposited at a heater temperature of 700–750 °C onto quartz glass covered with a thin ZnO or ZnO : Al film, as well as onto pyroceramic substrates metallized with molybdenum. On the basis of the results presented in work [21], the powder weight and the chamber (glass) and evaporator temperatures were selected to obtain films with required thicknesses. The sunlight losses in the CdS layer are known to decrease the short-circuit current. Therefore, the thickness of the CdS layer used in solar cells should be minimized.

However, CdS layers should not be made very thin (less than 50 nm), because they will be amorphous and, as a result, have a high resistance, which worsens the SC output parameters [22]. Moreover, if the film thickness is less than 200–300 nm, microscopic holes through the films are often observed [23]. In the case of narrow CdS films (≤100 nm), a parallel junction between CdTe and TCO can be formed, which provides a much higher recombination current than the CdS/CdTe junction [23].

A value of 200–300 nm for the CdS layer is indicated the most often in the literature [6]. In this case, light ($\lambda < 500$ nm) is almost completely absorbed in CdS. Therefore, in order to study the film properties, we should find deposition conditions to obtain polycrystalline films with a minimum thickness, a thickness of 200 nm (this value is recommended for producing SCs), and a thickness of 800 nm.

An analysis of the CdS film images obtained on an optical microscope Axioskop-2 MATmot "Carl Zeiss" showed that a time interval of half a minute is enough for a polycrystalline film to grow to a thickness of 0.444 μm (with an average grain size of about 0.5 μm and a maximum grain size of 1.0 μm). In this case, the substrate temperature was 278 °C, and the temperature of a powder heater equaled 750 °C.

The film parameters (the crystal lattice type, the phase composition, and the grain size) were studied on an X'Pert MPD diffractometer in an angular interval of 20°–100°. The spectrum of a CdS polycrystalline film deposited onto a pyroceramic substrate previously metallized with molybdenum is shown in Fig. 1. The phase composition of the material was determined by comparing the obtained peaks with a database. The spectral analysis showed that the applied technological process resulted in the growing of films with a predominantly hexagonal phase in the (002) plane. Peaks from the cubic phase were not detected. The growth of films with a dominating phase reduced the number of structural defects. The size D of coherent scattering regions (CSRs) was calculated

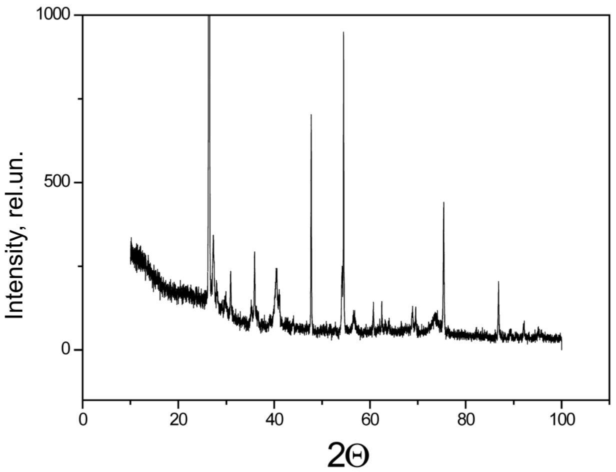

Fig. 1. X-ray diffraction spectrum of a CdS film

by the Scherrer formula

$$D_{hkl} = \frac{n\lambda}{\beta \cos\theta},$$

where $\lambda = 1.54$ Å is the radiation wavelength of a copper tube (the line CuK_α); θ the scattering angle; β the physical broadening of the diffractogram line in radians (on the 2θ-scale), this parameter is defined as the full line width at the half-height of the peak intensity; and n is a coefficient depending on the particle (CSR) shape, its value is close to unity. The CSR size was calculated, by using the peaks with the maximum intensity, namely, near the reflexes $2\Theta = 26.507°$ in the (002) plane. The corresponding size was found to equal 552–736 Å. The hexagonal film structure is considered to be better for producing SCs owing to a higher stability of this phase with respect to the stability of the cubic one [23].

The data for CdS films with the hexagonal structure obtained by us at a substrate temperature of 278 °C correlates with the data of work [23], where the influence of the substrate temperature on the structure and conductivity in CdS films was studied, by using the method of thermal evaporation in vacuum. The authors of work [23] made a conclusion that the film structure is sensitive to the substrate temperature. When depositing a film onto a substrate heated to below 100°, the structure was mainly cubic [23]. In a temperature interval of 100–200 °C, the film contained both the hexagonal and cubic phases. In the films deposited at 300 °C, only the hexagonal phase was observed in the (100) plane [23]. In our experiment, the substrate temperature was about 280 °C, which, according to the results of work [23], corresponded to the conditions of monophase film growth.

The obtained films were studied for the first time, by using optical methods and following the technique described in works [24, 25]. The optical gap width E_{opt} was determined from the spectral dependences of the optical constants n and k (the components of the complex dielectric permittivity index $N = n + ik$) for the films deposited on the satellite substrates: pyroceramic plates or quartz glass. Since the examined films were made from a direct-band material, their absorption coefficient

$$\alpha = 4\pi k/\lambda \sim \frac{1}{h\nu}\sqrt{h\nu - E_{\text{opt}}}$$

was proportional to the square root of the difference between the energy $h\nu$ of a light quantum incident on the film and the optical band gap width E_{opt} [24]. Hence, the dependence of the quantity $(\alpha h\nu)^2$ on the light quantum energy $h\nu$ (the so-called Tauc plot [24]), was a straight line in a vicinity of the band gap energy E_{opt}. The coordinate of its intersection point with the energy axis made it possible to determine the bandgap width E_{opt}.

The spectral dependences of the complex refractive index, in turn, were determined from the light transmittance and/or reflectance spectra and their fitting by the Fresnel formulas for multilayer thin films, as was done in work [25]. The calculations showed that the optical width of the forbidden gap E_{opt} slightly varies, depending on the film thickness. For instance, $E_{\text{opt}} = 2.46$ eV for films 0.44 μm in thickness and 2.454 eV for films 0.76 μm in thickness. The increase of the optical band gap width in comparison with a value of 2.42 eV for the bulk material is associated with the fact that the stoichiometry of a thin film is worse than that in the bulk. Furthermore, as was indicated in work [23], the optical band gap width depends on the film structure. In particular, films with a cubic phase have an optical band gap width of 2.4 eV, whereas hexagonal films 2.5 eV. On the basis of those data, the cubic phase may be available in our films.

Despite the almost monophase growth of the films and, as a result, their satisfactory structural perfection, the obtained CdS films did not possess a required charge carrier concentration of 10^{17} cm^{-3}. An electron concentration of about 10^{15} cm^{-3} was measured for thick films (5–7 μm) [26, 27]. Sulfur vacancies (Vs defect) and interstitial sulfur atoms (Is defects) are known [23] to be sources of free charge carriers in CdS. The defects of both types are donor sources. Due to the presence of the indicated defects, the concentration of charge carriers and, hence, the conductivity increase.

The number of defects can be controlled, in particular, by changing the substrate temperature [23]. For instance, if films were deposited onto a substrate with a temperature of 150–200 °C, a low conductivity of about 10^{-11} Ω^{-1} cm^{-1} was observed. This fact was explained by a reduction in the number of Is defects. In particular, if a film grows at relatively low substrate temperatures (below 150 °C), the atoms have a low mobility and practically remain at the same places, where they were deposited from the vapor phase. As a result, sulfur appears at the interstitial sites. When the substrate temperature increases to 150–200 °C, the mobility of the atoms at the growth surface increases, and they can reach more stable positions in the crystal lattice. As a result, the number of interstitial defects decreases. When the substrate temperature was increased to 300°C, the authors of work [23] observed a growth of conductivity to 10^{-6} Ω^{-1} cm^{-1}. The cited authors drew a conclusion that, when the temperature increases from 200 to 300 °C, sulfur atoms, due to their volatility, escape from the film, which gives rise to the formation of sulfur vacancies and, as a result, to the conductivity growth.

A similar result was reported in work [8]. In order to increase the charge carrier concentration up to 10^{15}–10^{16} cm^{-3} in a CdS layer obtained by the sputtering in vacuum, the cited authors recommended to use a hot substrate ($\geq$300 °C). The low conductivity value observed in our experiment at a substrate temperature of 280 °C (this is a temperature regime that should hypothetically provide a high conductivity) is most likely associated with the fact that the measurements were carried out, by using rather thick films (more than 4 μm). At the same time, it is known [28] that the concentration of charge carriers thermally generated in CdS films increases, if the film thickness decreases.

3.2. Researches of CdTe Layers

In the CSS technology, which is used, for example, by First Solar, CdTe is deposited at temperatures of 500–600 °C. It is known that if the substrate temperature exceeds 449 °C, a stoichiometric condensation of CdTe into a stable phase takes place [7]. The resulting films are of the p-type with the charge carrier concentration $p < 10^{15}$ cm^{-3} due to a small deficiency of cadmium atoms. A low concentration of charge carriers in an interval of 10^{14}–10^{15} cm^{-3} instead of the desirable 10^{16}–10^{17} cm^{-3} is one of the reasons why the SC efficiency has not been elevated above 16.5% within more than a decade [29]. Really, at such low concentration, the barrier height at the heterojunction decreases, and there arise difficulties with the formation of ohmic contacts. The both effects lead to a decrease of the $V_{\rm oc}$ and, accordingly, efficiency values.

In work [30], it was shown by mathematical calculations that the additional doping of CdTe can only be successful under the conditions of quasiequilibrium or non-equilibrium film growth. The introduction of additional dopants into the vapor phase will also be ineffective. It was shown that it is in the CdTe case that the methods of additional doping can neither increase the solubility of desired dopants nor change the position of the shallow acceptor level. The authors of work [30] recommended to suppress the formation of secondary phases that contain acceptors during the growth process.

Therefore, impurities were not used in order to increase the charge carrier concentration during the proposed technological process. We expected to find a technological window, in which, due to the self-doping, the concentration of charge carriers would be about 10^{16}–10^{17} cm^{-3}. In particular, after the heaters for the CdS evaporation had been switched-on, the process of CdTe powder evaporation began at a heater temperature of 480–550 °C. The substrate temperature was 130–245 °C at that, which was well below the stoichiometric growth temperature (449 °C). In the experiment, we also varied the powder weight and the sputtering time (from 90 s to 10 min). The corresponding thickness of the obtained CdTe layer was 0.414–3 μm. We did not try to grow CdTe films more than 3 μm in thickness, because a theoretical calculation carried out in work [10] showed that the optimum thickness of CdTe layer for SCs equals 2–4 μm. The parameters of grown CdTe mainly depend on its crystalline structure [3]. The grain boundaries are known to be able to accumulate all elementary metal impurities that are responsible

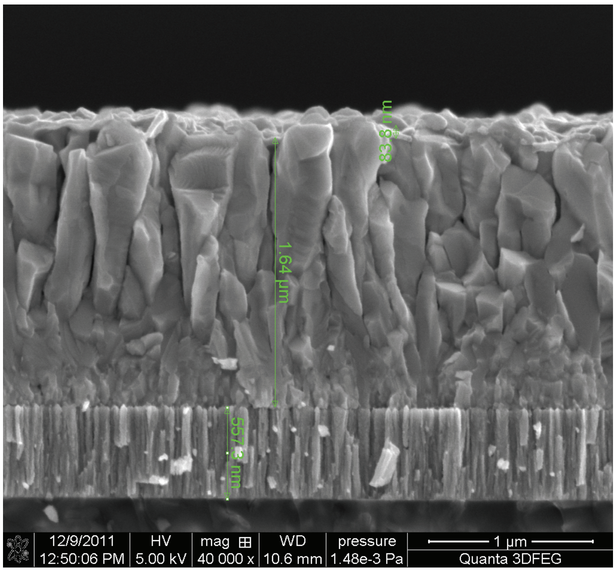

Fig. 2. Microscopic image of a cleaved facet of the CdS/CdTe/Cu_xS structure

for the doping of the p- or n-type, so that their concentration at those boundaries can be several orders of magnitude higher than in the material bulk.

Our research of the CdTe films obtained by the thermal-emf method showed that they had a weak conductivity of the p-type. In order to study the electrical properties of CdTe films, a batch of Mo/CdTe/p-Cu_xS specimens was fabricated with the thickness of a CdTe layer varying from 270 to 2100 nm. The corresponding current-voltage characteristics (CVCs) of the specimens were linear. No current rectification was observed in the CVCs. Therefore, a conclusion was drawn that the Schottky barrier between molybdenum and CdTe had not been formed. It is most probable that the Fermi level in the obtained CdTe layers was located near the level of intrinsic conductivity, which reduced the work function for the charge carriers and made it possible to obtain an ohmic contact.

The measured CVCs were used to calculate the concentrations of charge carriers, which turned out to equal $(6.154 \div 6.91) \times 10^{15}$ cm^{-3} for the thicknesses $d = 1.540 \div 2.100$ μm. However, a value of 3.5×10^{17} cm^{-3} was obtained for the thin film with $d = 270$ nm. This fact testifies that the number of defects in the thick film significantly reduced the number of free charge carriers. The obtained concentrations of charge carriers in thick CdTe films of the p-type (10^{14}–10^{15} cm^{-3}) were typical [29] and lower than a desired value of 10^{15}–10^{17} cm^{-3}. The electrical characteristics of heterojunctions with the CdTe film depend on the microstructure at the interface between the CdTe and partner films, and on the grain boundaries in the CdTe film itself [8]. A structural imperfection of the interface and the shunting effect due to the charge flow along the grain boundaries reduce the open-circuit voltage and the filling factor [8].

The crystal structure of the films was studied on a scanning electron microscope. Figure 2 illustrates a cleavage cross-section of the CdS/CdTe/Cu_xS structure deposited onto a pyroceramic substrate metallized with molybdenum. The thicknesses of the layers are also indicated: d(CdS) = 557.3 nm, d(CdTe) = = 1.64 μm (including the thickness of the variband layer), and d(Cu_xS) = 83.8 nm. The CdTe film had a columnar structure, with the growth direction being perpendicular to the substrate. The image also demonstrates that an interlayer between the fine-grained columnar CdS film and the coarse-grained CdTe film is dense and free of pores. This fact is advantageous, because, as is known from the literature, the CSS technology produces grains with large sizes (about 5 μm) [3]. Therefore, pores are formed between the grains, and, in order to reduce the microscopic holes, films with a thickness of 8–10 μm have to be grown. Such films have a high resistance, which worsens the SC efficiency [3].

As a rule, when manufacturing SCs, after the CdTe layer has been deposited, the chloride and temperature treatments are applied [3, 4, 6, 8, 10]. Without the former, the SC efficiency is low. During the chloride treatment, a $CdCl_2$ film 300–400 nm in thickness is deposited onto the CdTe layer. The obtained structure is annealed at a temperature of 400 °C for 15–20 min in air or an inert gas (e.g., Ar) environment. In the course of annealing, small CdTe grains sublimate and then crystallize again. The recrystallization results in larger grains, but the voids between the large grains become considerably smaller. Owing to the recrystallization, the number of defects in the film decreases. The presence of Cl_2 provides a local transport of CdTe vapor in the polycrystalline film. As a result of the chloride treatment, the CdS/CdTe interface becomes reorganized, and small grains disappear [10].

Furthermore, the chloride treatment stimulates a reaction between CdS and CdTe [8]. As a result, a thin CdS_xTe_{1-x} film is formed at their interface. Relevant researches [6] showed that Cl dopes CdS and increases the number of electrons both in CdS and at the CdS/CdTe interface. The SC effectiveness after this treatment increases from 1 to 9% [8] or from 10 to 25% [4].

However, the chloride treatment faces a number of serious difficulties [3]. In particular, $CdCl_2$ is a hygroscopic and toxic material. Therefore, the process of chloride treatment should not be performed in the open air. For this purpose, a special vacuum equipment has to be used. Therefore, in this work, no chloride treatment was carried out at this stage.

4. Ohmic Contact Preparation

Since p-CdTe has a high electron affinity, it forms a Schottky barrier with the majority of metals. This barrier restricts the motion of holes into p-CdTe [29]. Copper is a metal that is used most often to form a non-rectifying contact with p-CdTe.

Before copper is deposited, the p-CdTe surface is usually subjected to the chemical etching in order to enrich it with tellurium. The latter, by reacting with Cu, forms a Cu_xTe compound with $1 \leq x \leq 2$ [31]. This compound also serves as a buffer layer that prevents copper from diffusing along the grain boundaries into the CdTe matrix and, further, to the heterojunction. The copper diffusion creates shunting paths, which reduces the SC operating time [3]. On the other hand, the copper diffusion in the CdTe layer itself reduces its resistance and, hence, increases the SC efficiency [31]. Most researchers make contacts with p-CdTe, by using Cu-containing compounds such as Cu–Au layers, Cu_2Te, ZnTe : Cu, and Cu_2S [3]. There are also other technical procedures for creating the ohmic contacts. For example, this the formation of a strongly doped p^+-layer at the contact followed by the gold sputtering [5], the deposition of the Sb_2Te_3 contact [3], and others [31].

Films of Cu_xS were used in CdS/Cu_2S solar cells that were developed as long ago as in 1954 [8]. This type of SCs was not developed further because of the electrochemical decomposition of Cu_2S at voltages above 0.33 V and the subsequent diffusion of copper through the heterojunction [8]. However, it is known [30] that copper and sulfur can compose a number of crystallographic and stoichiometric forms: chalcocite (Cu_2S with an orthorhombic crystalline lattice), djurleite ($Cu_{1.96}S$, an orthorhombic structure), digenite ($Cu_{1.8}S$, an orthorhombic structure), anilite ($Cu_{1.75}S$, an orthorhombic structure), covelline (CuS, a hexagonal structure), and others. Their optical and electrical properties depend on the Cu content x in the Cu_xS compound, which depends, in turn, on the growth conditions.

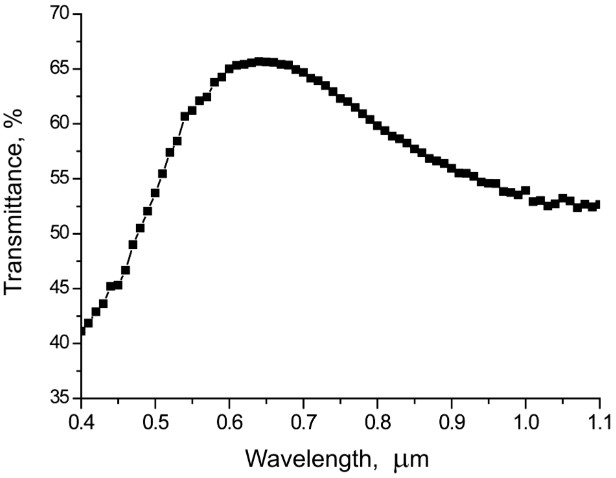

Fig. 3. Spectrum of light transmission through a glass substrate covered with a Cu_xS layer at the normal light incidence

In our experiment aimed at producing a contact, sulfur and copper powders were thermally evaporated in a vacuum chamber. Preliminary sputtered sulfur created a buffer layer that prevented the diffusion of copper into the structure. The thickness of the Cu_xS layer amounted to 30–80 nm. This choice was dictated by the following factors. The layer could not be narrower than 30 nm, because very thin films have insufficient conductivity to play the role of current-collecting contacts. Very thin films are not continuous. At the same time, thick films absorb light, do not transmit it to the CdTe layer, and thereby worsen the SC parameters. Figure 3 demonstrates the optical transmittance spectrum obtained for a Cu_xS film about 50 nm in thickness deposited onto a glass substrate. One can see that already at 50 nm, Cu_xS absorbs significantly (35–50%), which will worsen the SC characteristics.

The results of the X-ray diffraction at the obtained Cu_xS film showed the presence of peaks inherent to the tetragonal structure of $Cu_{1.81}S$, the hexagonal structure of β-Cu_2S, and the rhombohedral structure of $Cu_{1.8}S$. No dominating growth orientation was observed. The measurements of the specific re-

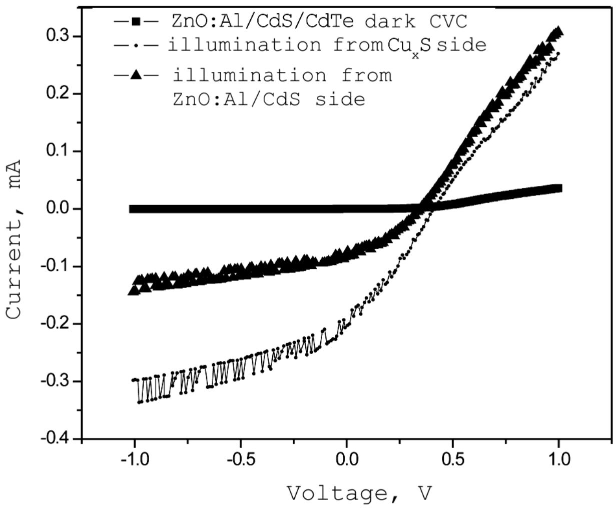

Fig. 4. CVCs of the ZnO : Al/CdS/CdTe solar cell at frontwall and backwall illumination

sistance by the four-electrode method gave a value of 4.9×10^3 Ω cm. The electrical properties of the $Cu_{1.8}S$ film were considered in works [26, 27, 33]. In particular, these are the hole concentration $p = 5\times10^{21}$ cm^{-3} and a work function of 5.5 eV.

5. Researches of CVCs

Hence, the following solar cells were fabricated. Pyroceramic substrates metallized with molybdenum were used to sequentially grow CdS and CdTe layers on them in a quasiclosed space. Afterward, in the next technological stage, a degenerate semiconductor p-Cu$_x$S was deposited onto them. Similar structures were obtained on glass substrates covered with thin ZnO and ZnO : Al films. The work area of each fabricated SC amounted to 0.196 cm^2.

It is known that, depending on the SC side which is illuminated, the configurations are classed as frontwall (or substrate), when the light falls from the side of the contact deposited on CdTe, and backwall (or superstrate), when light falls from the side of the substrate (glass) with a transparent conducting oxide and CdS [3].

We measured the dark and light CVCs of the obtained structures at their illumination from both the front and rear contacts. A tungsten incandescent lamp was used as a light source. The illumination power was 0.013 and 0.136 W/cm^2. The influence of the substrate type (Mo, ZnO, or ZnO:Al) and the thicknesses of the CdS (67 nm, 200 nm, 800 nm), CdTe (1 μm, 1,5 μm, 2 μm, and 3 μm), and Cu$_x$S (30 nm and 80 nm) layers on the SC parameters was studied. The SC parameters were calculated in accordance with the method described in work [34]. The results of CVC measurements showed that, when the SC is illuminated from the Cu$_x$S side (the frontwall configuration), a higher filling factor is observed in comparison with the illumination from the transparent-substrate side (Fig. 4).

The result obtained testify that, despite that the ZnO and ZnO:Al films had a high light transparency and a small thickness (200 nm), and the CdS layer was thin (200 nm), the optical and electrical losses in them were higher as compared with the Cu$_x$S layer. Therefore, after a number of experiments that confirmed the advantage of the frontwall configuration, all further experiments were performed only under the condition of SC illumination from the Cu$_x$S side. The influence of the Cu$_x$S layer thickness (30 and 80 nm) on the SC characteristics was studied. Larger thicknesses led to a decrease of the filling factor, which correlated with our results on the optical transmittance (Fig. 3); namely, a considerable light absorption in films about 50 nm in thickness. Further experiments were carried out with a Cu$_x$S layer thickness of about 30 nm.

The increase of the CdTe layer thickness from 1 to 3 μm resulted in the efficiency growth from 1.23% to 1.71%. This improvement mainly took place owing to the increase of the filling factor in the case of a thicker CdTe layer. However, in further experiments, a similar efficiency value (1.75–1.77%) was obtained for a thickness of about 1.0 μm as well.

The influence of the CdS layer thickness on the CVCs did not reveal clear regularities. Nevertheless, the maximum number of conditionally good specimens was obtained for the smallest thickness (67 nm). This result coincides with the conclusion of work [28] that, in the case of thin CdS films, the number of charge carriers is larger as compared with the thicker ones.

The study of the influence of the substrate type showed that, statistically, the larger fraction of specimens fabricated on glass substrates covered with ZnO films had an efficiency of 1.75–1.89%. A some smaller fraction of conditionally good specimens was obtained on the ZnO : Al films, and even smaller on the Mo ones. The best characteristics for SCs on quartz glass with ZnO films were as follows: the short-circuit current $J_{\mathrm{sc}} = 2.49$ mA/cm^2, the open-circuit voltage $V_{\mathrm{oc}} = 0.3695$ V, the filling factor $FF = 26.7\%$, and an efficiency of 1.89% under an illumination of 0.013 W/cm^2. The value $V_{\mathrm{oc}} = 0.3695$ V is close to a value of 0.38 V, which was obtained in work [35], where the technology of thermal evaporation was also used for the fabrication of CdS/CdTe structures. The best specimens had an efficiency of 1.75–1.89% at the thicknesses $d = 67$ nm for the CdS layer, $d \approx 1{,}0$ μm for the CdTe layer, and $d \approx 30$ nm for the Cu$_x$S layer. The magnitudes of the series, R_{ser}, and shunt, R_{shunt}, resistances were calculated from the light CVCs. The calculations showed that R_{ser} is equal to hundreds of ohms – e.g., 550 Ω – which is too large in comparison with a required value of tens of ohms. The value of R_{shunt}, on the contrary, turned out too small – e.g., 912 Ω – in comparison with the required hundreds of kΩ's. A small value of R_{shunt} results in that the generated photocurrent “drains” along the structure surface and does not contribute to the photocurrent. The low value of V_{oc} is associated, first of all, with the low conductivity of the CdTe layer. Despite that we used layers with the minimum possible thickness in order to reduce the recombination currents, the value of J_{sc} was also small, which testifies to the presence of a significant number of defects in the bulk of the layers and at the interfaces between the layers. The low filling factor may also be connected with a high resistance of current-collecting contacts [35].

Having analyzed the fact that a much larger number of good specimens were fabricated on the substrates with ZnO films than with Mo ones, provided a simultaneous deposition of structures on those substrates, a conclusion can be drawn that the polycrystalline columnar structure of the applied ZnO films [36, 37] stimulates the growth of a more oriented and, hence, less defective CdS layer. The number of recombination centers is therefore reduced. The energy band diagram of the obtained structures was discussed in work [11], where a conclusion was made that a barrier formed between the ZnO and CdS layers gives an additional contribution to the increase of the built-in electric field, thereby increasing the photocurrent.

Thus, we may formulate a number of problems to be solved for the fabrication of SCs using the quasiclosed space method. Since CdTe and CdS are self-doped semiconductors, whose conductivity strongly depends on the growth conditions, the study of how the deposition conditions affect the electrical properties of those materials has to be continued. In order to increase the value of R_{shunt}, a method to passivate the surface is required.

6. Conclusions

To summarize, it is shown that the quasiclosed space method makes it possible to deposit polycrystalline oriented n-CdS and p-CdTe films with a charge carrier concentration of about 6×10^{15} cm^{-3} in thick films. A charge carrier concentration of about 10^{17} cm^{-3} was obtained only in the case of a thin (270 nm) CdTe film. The determined temperature regimes make it possible to obtain n-CdS films with a dominating hexagonal structure, which satisfies the requirements for CdS to be used in SCs. The CdTe layer has an oriented columnar growth of grains with the absence of visible pores between them. The application of degenerate semiconductor p-Cu$_x$S as a front contact allowed an ohmic contact with CdTe to be formed. The results of CVC measurements showed that the CdS/CdTe structure behaves as a solar cell with an efficiency of 1.75–1.89%, with the frontwall configuration having better characteristics than the backwall one. The thicknesses of the CdS ($d = 67$ nm), CdTe ($d \approx 1.0$ μm), and Cu$_x$S ($d \approx 30$ nm) layers were determined, at which the SC characteristics are the best.

A comparison between the parameters of SCs that were formed on the Mo and ZnO substrates allows the ZnO films obtained by the atomic layer deposition method to be recommended for the fabrication of SCs.

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1. T.V. Semikina, S.V. Mamykin, G.I. Sheremet, L.N. Shmyreva. ZnO thin films obtained by atomic layer deposition as a material for photovoltaics. *Ukr. J. Phys.* **61**, 732 (2016).
2. M.A. Green, K. Emery, Y. Hishikawa, W. Warta, E.D. Dunlop, D.H. Levi, A.W.Y. Ho-Baillie. Solar cell efficiency tables (version 49). *Prog. Photovolt. Res. Appl.* **25**, 3 (2017).
3. A. Bosio, N. Romeo, S. Mazzamuto, V. Canevari. Polycrystalline CdTe thin films for photovoltaic applications. *Prog. Cryst. Growth Ch.* **52**, 247 (2006).
4. L.L. Kazmerski. Solar photovoltaics R&D at the tipping point: A 2005 technology overview. *J. Elect. Spectrosc. Rel. Phenom.* **150**, 105 (2006).
5. A.G. Aberle. Thin-film solar cells. *Thin Solid Films* **517**, 4706 (2009).
6. R.W. Miles, K.M. Hynes, I. Forbes. Photovoltaic solar cells: An overview of state-of-the-art cell development and environmental issues. *Prog. Cryst. Growth Ch.* **51**, 1 (2005).
7. A. Jager-Waldau. Status of thin film solar cells in research, production and the market. *Sol. Energy* **77**, 667 (2004).
8. T.L. Chu, S.S. Chu. Thin film II–VI photovoltaics. *Sol. St. Electron.* **38**, 533 (1995).
9. A.D. Compaan. Photovoltaics: Clean power for the 21st century. *Sol. Energy Mat. Sol. Cells* **90**, 2170 (2006).
10. A. Morales-Acevedo. Can we improve the record efficiency of CdS/CdTe solar cells? *Sol. Energy Mat. Sol. Cells* **90**, 2213 (2006).
11. T.V. Semikina, S.V. Mamykin, M. Godlewski, G. Luka, R. Pietruszka, K. Kopalko, T.A. Krajewski, S.S. Gieraltowska, J. Wachnicki, L.N. Shmyryeva. ZnO as a conductive layer prepared by ALD for solar cells based on n-CdS/n-CdTe/p-Cu$_{1.8}$S heterostructure. *J. Semicond. Phys. Quant. Electron. Optoelectron.* **16**, 111 (2013).
12. T.V. Semikina. Atomic layer deposition as a nanotechnological method for producing functional materials: A review. *Uch. Zapis. Tavrich. Nat. Univ. Ser. Fiz.* **22**, No. 1, 116 (2009) (in Russian).
13. C.G. Granqvist. Transparent conductors as solar energy materials: A panoramic review. *Sol. Energy Mat. Sol. Cells* **91**, 1529 (2007).
14. X. Jiang, F.L. Wong, M.K. Fung, S.T. Lee. Aluminum-doped zinc oxide films as transparent conductive electrode for organic light-emitting devices. *Appl. Phys. Lett.* **83**, 1875 (2003).
15. M. Godlewski, E. Guziewicz, K. Kopalko, G. Łuka, M.I. Lukasiewicz, T. Krajewski, B.S. Witkowski, S. Gieraltowska. Zinc oxide for electronic, photovoltaic and optoelectronic applications. *Low Temp. Phys.* **37**, 235 (2011).
16. N. Huby, S. Ferrari, E. Guziewicz, M. Godlewski, V. Osinniy. Electrical behavior of zinc oxide layers grown by low temperature atomic layer deposition. *Appl. Phys. Lett.* **92**, 023502 (2008).
17. S. Gieraltowska, L. Wachnicki, B.S. Witkowski, M. Godlewski, E. Guziewicz. Atomic layer deposition grown composite dielectric oxides and ZnO for transparent electronic applications. *Thin Solid Films* **520**, 4694 (2012).
18. T.A. Krajewski, G. Łuka, L. Wachnicki, A.J. Zakrewski, B.S. Witkowski, M.I. Lukasiewicz, P. Kruszewski, E. Lusakowska, R. Jakiela, M. Godlewski, E. Guziewicz. Electrical parameters of ZnO films and ZnO-based junctions obtained by atomic layer deposition. *Semicond. Sci. Technol.* **26**, 085013 (2011).
19. T. Krajewski, E. Guziewicz, M. Godlewski, L. Wachnicki, I.A. Kowalik, A. Wojcik-Glodowska, M. Lukasiewicz, K. Koplako, V. Osinniy, M. Guziewicz. The influence of growth temperature and precursors' doses on electrical parameters of ZnO thin films grown by atomic layer deposition technique. *Microelectr. J.* **40**, 293 (2009).
20. G. Łuka, M. Godlewski, E. Guziewicz, P. Stahira, V. Cherpak, D. Volonyuk. ZnO films grown by atomic layer deposition for organic electronics. *Semicond. Sci. Technol.* **27**, 074006 (2012).
21. N.V. Yaroshenko, T.V. Semikina, Yu.N. Bobrenko, W. Pashkovich, R. Minikaev, L.N. Shmyreva, V.N. Komashchenko. Preparation of thin-film heterostructures by the hot-wall method and the study of current transfer mechanisms. *Elektron. Svyaz* **2**, 28 (2011) (in Russian).
22. L.A. Kosyachenko, E.V. Grushko. Prospects for the use of thin-film cadmium telluride in solar energetics. *Ukr. Fiz. Zh. Ogl.* **7**, 3 (2012) (in Ukrainian).
23. A.Y. Jaber, S.N. Alamri, M.S. Aida, M. Benghanem, A.A. Abdelaziz. Influence of substrate temperature on thermally evaporated CdS thin films properties. *J. Alloy. Compd.* **529**, 63 (2012).
24. H. Fujiwara. *Spectroscopic Ellipsometry: Principles and Applications* (Wiley, 2007) [ISBN: 9780470016084].
25. N. Dmitruk, L. Dózsa, S. Mamykin, O. Kondratenko, G. Molnár. Effect of annealing on optical properties of thin films with β-FeSi 2 quantum dots. *Vacuum* **84**, 238 (2009).
26. S.Yu. Pavelets, Yu.M. Bobrenko, A.M. Pavelets, M.M. Kretulis. High effective surface-barrier sensors with low resistive surface layers. *Optoelektron. Poluprovodn. Tekhn.* **37**, 112 (2002) (in Russian).
27. Yu.N. Bobrenko, A.M. Pavelets, S.Yu. Pavelets, V.M. Tkachenko. Short-wave photosensitivity of surface-barrier structures based on degenerate semiconductor-semiconductor junctions. *Pis'ma Zh. Tekhn. Fiz.* **20,** No. 12, 9 (1994) (in Russian).
28. S.A. Mahmoud, A.A. Ibrahim, A.S. Riad. Physical properties of thermal coating CdS thin films using a modified evaporation source. *Thin Solid Films* **372**, 144 (2000).
29. K.K. Chin. p-Doping limit and donor compensation in CdTe polycrystalline thin film solar cells. *Sol. Energy Mat. Sol. Cells* **94**, 1627 (2010).
30. S.B. Zhang, S.-H. Wei, Y. Yan. The thermodynamics of codoping: How does it work? *Physica B* **302–303**, 135 (2001).
31. N. Romeo, A. Bosio, A. Romeo. An innovative process suitable to produce high-efficiency CdTe/CdS thin-film modules. *Sol. Energy Mat. Sol. Cells* **94**, 2 (2010).

32. M. Ramaya, S. Ganesan. Study of thickness dependent charactericties of Cu_2S thin film for various applications. *Iranian J. Mater. Sci. Eng.* **8**, No. 2, 34 (2011).
33. Yu.N. Bobrenko, S.Yu. Pavelets, T.V. Semikina, O.A. Stadnyk, G.I. Sheremetova, M.V. Yaroshenko. Thin-film solar converters based on the p-$Cu_{1.8}S/n$-CdTe surface-barrier structure. *Semicond. Phys. Quant. Electr. Optoelectr.* **18**, 101 (2015).
34. G.S. Khrypunov, G.I. Kopach, R.V. Zaitsev, A.P. Dobrozhan, M.M. Kharchenko. Flexible solar cells based on underlying CdTe layers obtained by magnetron sputtering. *J. Nano Electr. Phys.* **9**, 02008 (2017) (in Russian).
35. S.S. Babkair. Charge transport mechanisms and device parameters of CdS/CdTe solar cells fabricated by thermal evaporation. *JKAU: Sci.* **22**, 21 (2010).
36. A. Wojcik, M. Godlewski, E. Guzievicz, R. Minikaev, W. Paszkovicz. Controlling of preferential growth mode of ZnO thin films by atomic layer deposition. *J. Cryst. Growth* **310**, 284 (2008).
37. E. Przeździecka, Ł. Wachnicki, W. Paszkowicz, E. Łusakowska, T. Krajewski, G. Łuka, E. Guziewicz, M. Godlewski. Photoluminescence, electrical and structural properties of ZnO films, grown by ALD at low temperature. *Semicond. Sci. Technol.* **24**, 105014 (2009).

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ТЕХНОЛОГІЯ ОТРИМАННЯ ТА ВЛАСТИВОСТІ CdS/CdTe СОНЯЧНИХ ЕЛЕМЕНТІВ З ВИКОРИСТАННЯМ МЕТОДА КВАЗІЗАМКНЕНОГО ПРОСТОРУ

Резюме

Розроблена технологія квазізамкненого простору для осадження шарів CdS та CdTe з подальшим виготовленням сонячних елементів (СЕ). Досліджуються та аналізуються технологічні чинники, від яких залежить структура кристалічної ґратки, ширина оптичної забороненої зони та провідність CdS та CdTe. Запропонована технологія виготовлення омічного контакту до p-CdTe на основі виродженого напівпровідника Cu_xS. Аналізуються характеристики СЕ виготовлених на підкладках з різними провідними плівками (Mo, ZnO, ZnO : Al). Результати обробки світлових та темнових вольт-амперних характеристик показують перевагу ZnO та ZnO : Al плівок, отриманих методом атомного пошарового осадження, для застосування в СЕ. Визначено товщини шарів CdS (d = 67 нм), CdTe (∼1 мкм) та Cu_xS (30 нм), при яких була отримана кра-ща ефективність (η = 1,75–1,89%) та показано, що використання тонких плівок в структурі СЕ покращує їх характеристики.