

T.V. SEMIKINA,<sup>1</sup> S.V. MAMYKIN,<sup>1</sup> G.I. SHEREMET,<sup>1</sup> L.N. SHMYREVA<sup>2</sup><sup>1</sup> V.E. Lashkaryov Institute of Semiconductor Physics, Nat. Acad. of Sci. of Ukraine  
(41, Prosp. Nauky, Kyiv 03028, Ukraine; e-mail: tanyasemikina@gmail.com)<sup>2</sup> National Technical University of Ukraine "Kyiv Polytechnic Institute"  
(33, Peremogy Ave., Kyiv 03056, Ukraine)UDC 537.311.322; 539.232;  
621.315.529.9; 621.383.51**ZnO THIN FILMS OBTAINED BY ATOMIC LAYER DEPOSITION AS A MATERIAL FOR PHOTOVOLTAICS**

*The tasks to be solved while developing solar cells have been reviewed. The analysis of technological methods used for the fabrication of thin transparent conducting ZnO films from the viewpoint of their application in organic and thin-film solar cells demonstrates the advantage of the atomic layer deposition method. It is shown that this method provides a low-temperature (100–200 °C) growth of films with a required resistivity of about  $10^{-3} \Omega \cdot \text{cm}$  and a transparency of 85–90%. The application of ZnO films in organic photovoltaic structures improves the time stability of their rectification characteristics. The investigation of organic structures with ZnO as a cathode or an anode showed the potential of the usage of ZnO as a cathode. The study of ZnO as a transparent conductive electrode in a CdTe-based inorganic photovoltaic structure shows an increase in the photocurrent and a decrease in the recombination in comparison with a Mo electrode.*

*Keywords:* atomic layer deposition method, transparent conducting ZnO films, organic solar cells, CdS/CdTe solar cells.

**1. Introduction**

Every year, the developments in photovoltaics become more and more required, in view of the economic and political tendencies associated with the energy consumption from conventional sources. Despite the major production volume of solar cells (SCs) includes elements and modules fabricated on the basis of crystalline and polycrystalline silicon, we will intend to demonstrate the expediency of the designing of thin-film silicon-free SCs as a possible variant for the development of photovoltaics in Ukraine.

In the recent years, the interest of SC developers has been concentrated on the so-called architectural application of SCs as constructional elements of buildings, e.g., the coverage of roofs with silicon solar modules and the coverage of glasses with thin-film transparent SCs. Nevertheless, the considerable attention still remains to be focused on the application of solar modules with small dimensions to various household appliances. A number of requirements are specific for the products on this market [1]. In

particular, the solar cells must be cheap, flexible, light, transparent in some cases, ecologically safe, and portable (for charging batteries). Proceeding from those requirements, the solar cells on the basis of cadmium telluride, Cu(InGa)Se<sub>2</sub>(S) compounds, dyes, and organic compounds have good prospects, because the cost of their manufacture is lower in comparison with that of silicon, organic, and dye-based SCs. Moreover, they can be fabricated on a flexible basis and be transparent. Solar cells of the mentioned types are manufactured on the basis of film technologies and, therefore, have a low weight.

The main criteria for the SC estimation are the efficiency and the cost of energy per watt. The averaged efficiency of the mentioned SC types ranges from 5% to 20%. In work [1], the data concerning the cost and the efficiency of commercially accessible SCs are quoted. For instance, the efficiency of CdTe solar cells amounts to 9–11% at a cost of 2.3–2.5 \$/W, although a cost reduction to 0.52–0.62 \$/W is expected in the near future. For CIGS solar cells, the efficiency of modules equals 14–16%, and the cost is 2 \$/W with a forecast of 1–1.3 \$/W. For polymer solar cells, the efficiency equals 5–8% and, for the modules, 3% at a cost of 11–12 \$/W.

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Table 1. Solar cell parameters measured under spectrum AM1.5 (1000 W/m<sup>2</sup>) and at a temperature of 25 °C [2]

Classification	Efficiency, %	Area, cm <sup>2</sup>	U <sub>oc</sub> , B	J <sub>sc</sub> , mA/cm <sup>2</sup>	FF, %	Test center and date	Firm manufacturer
CIGS SCs	20.5 ± 0.6	0.9882	0.752	35.3	77.2	NREL, March 2014	Solibro, on glass
CdTe SCs	21.0 ± 0.4	1.0623	0.8759	30.25	79.4	Newport, October 2014	First solar, on glass
SCs on dyes	11.9 ± 0.4	1.005	0.744	22.47	71.2	AIST, September 2012	Sharp
Organic thin-film SCs	11.0 ± 0.3	0.993	0.793	19.40	71.4	AIST, September 2014	Toshiba

Table 2. Current and predicted volumes of the polymer SC market [1]

Estimation	2010	2014	2018
Market volume, \$ mln	0.2	87.9	462.3
Polymer SC price, \$/W	11.5	1–2	1–0.5
Currently produced volumes of power, GW	1.005	1.005	1.005
Approximate usage of produced power, MW	5	44–88	462–924

Table 1 contains the data as of 2015 taken from work [2]. In particular, they demonstrate the best results for various types of silicon-free solar cells. High values of such parameters as the efficiency, short circuit current  $J_{sc}$ , open-circuit voltage  $U_{oc}$ , and filling factor  $FF$  confirm a promising characteristic of works in this direction. In Table 2, as an example, the data taken from work [1] on the market of polymer solar cells are quoted. The development of SCs of this type traditionally invokes the largest skepticism. The market of polymer SCs is evaluated in \$462.3 mln in 2018 (in 2009–2017, the market is estimated in \$1026.5 mln). From Table 2, one can see that the current cost of energy per watt amounts to 1–2 \$, and the energy production is estimated to equal 462–924 MW at the beginning of 2018.

Therefore, the developments in thin-film photovoltaics have both scientific and commercial expediency. The results of patent analysis testify that a considerable number of researches are aimed at the search for materials and technologies for reducing the SC manufacture cost. This work is devoted to a discussion of this issue from the viewpoint of substituting tin-doped indium oxide (ITO) by such an alternative material as transparent conducting zinc oxide films obtained by the method of atomic layer deposition.

## 2. Oxide Thin-Film Materials for Photovoltaics

All designs of thin-film solar cells contain layers of conducting oxide materials (Fig. 1). Layers of transparent conducting oxides (ZnO, SnO<sub>2</sub>, ITO, TiO<sub>2</sub>) are deposited to improve the current collection and to modify the optical properties (e.g., to match the refractive indices), as well as to create a diffusion barrier [3]. It is necessary to mention that, at present, the development of transparent conducting oxides (TCOs) with definite electric and optical properties and optimal surface texture is a challenging problem for all types of solar cells [3]. In Table 3, one can see requirements that the transparent conducting oxides have to satisfy if they are intended to be used as rear and front contacts or reflecting layers in the case of configurations of the *p-i-n* and *n-i-p* types [3].

In addition to the requirement that TCOs should be characterized by a high transparency and a low specific surface resistance, they have to be wide-band-gap semiconductors, irrespective of whether they are used as electrodes or SC windows.

Tin-doped indium oxide is the most widely used oxide material. In solar cells, it is applied as a transparent electrode. ITO films have very good optical and electric properties: the average optical transmittance amounts to about 80% in the visible spectral range, and the electrical resistivity equals  $1 \times 10^{-4} \Omega \text{ cm}$ . At the same time, ITO films have substantial shortcomings. First of all, this is a high price of the material, because the demand for indium in the world market exceeds its supply. The ITO price grows every year. Therefore, in order to reduce the cost of the solar cell manufacture, ITO should be substituted by another material. The second shortcoming consists in the toxicity of indium. The corresponding results confirm the adverse effect of ITO on human health

Table 3. Requirements to transparent conducting oxides used in solar cells [3]

SC configuration	Front TCO	Rear TCO
<i>p-i-n</i> type	<ul style="list-style-type: none"> <li>– low specific surface resistance (<math>&lt; 10 \Omega/\square</math>);</li> <li>– high optical transmittance in an interval of 350–1100 nm;</li> <li>– surface roughness (5–200 nm)</li> </ul>	<ul style="list-style-type: none"> <li>– low specific surface resistance if the reflector is not conducting;</li> <li>– the specific surface resistance has no restrictions, if the reflector is conducting;</li> <li>– high optical transmittance (<math>&gt; 80\%</math>) in an interval of 650–1100 nm</li> </ul>
<i>n-i-p</i> type	<ul style="list-style-type: none"> <li>– low specific surface resistance (<math>&lt; 10 \Omega/\square</math>);</li> <li>– high optical transmittance (<math>&gt; 80\%</math>) in an interval of 350–1100 nm;</li> <li>– surface roughness: has no restrictions (roughness is partially set by a polycrystalline layer of Si)</li> </ul>	<ul style="list-style-type: none"> <li>– low specific surface resistance, if the reflector is not conducting;</li> <li>– the specific surface resistance has no restrictions, if the reflector is conducting;</li> <li>– high optical transmittance (<math>&gt; 80\%</math>) in an interval of 650–1100 nm</li> <li>– surface roughness has no restrictions: it is set by the texture of a rear reflector or a substrate</li> </ul>

[4]. Therefore, the problem of substituting ITO by another material, which would possess similar optical and electric properties, but be non-toxic, still remains challenging.

ZnO is a material that is the most widely studied as a transparent conducting oxide, including its consideration as an alternative to ITO. This is a direct-band-gap semiconductor with an energy gap width of 3.37 eV at room temperature. ZnO films are transparent in the visible and near infra-red spectral ranges, even if heavily doped [5]. ZnO can be heavily doped, with aluminum and gallium being used the more often for this purpose. The lowest resistivity obtained for aluminum-doped ZnO films amounts to  $2 \times 10^{-4} \Omega \text{ cm}$  [4]. The electron concentration in ZnO films can be changed from  $10^{15}$  to  $10^{20} \text{ cm}^{-3}$  by varying technological regimes, and the maximum electron mobility can reach  $50\text{--}60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in polycrystalline films [4]. Zinc oxide is also a chemically stable non-toxic material.

### 3. Technologies of ZnO Film Fabrication. Method of Atomic Layer Deposition

Thin ZnO films can be obtained, by using various technological methods: magnetron sputtering, molecular beam epitaxy, pulsed laser deposition, chemical vapor deposition, pyrolysis, and methods of colloid chemistry, e.g., the sol-gel method. A detailed description of those methods of ZnO deposition can be

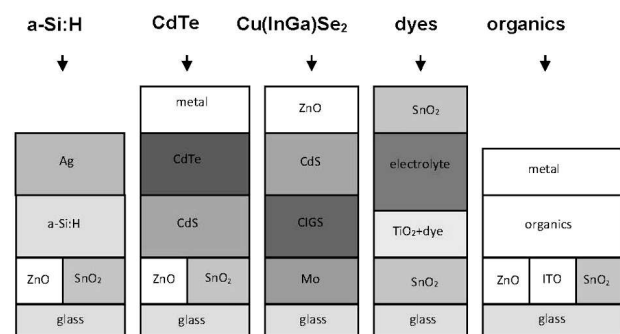


Fig. 1. Schematic structures of solar cells with transparent oxide materials

found in work [6]. Let us consider them from the viewpoint of obtaining a transparent conducting film for thin-film photovoltaics. This application puts forward at once a number of requirements to films; namely, the low cost and simplicity of the technology; a capability of depositing the films that are uniform in thickness and have a homogeneous crystalline structure onto large surfaces ( $100 \times 100 \text{ cm}^2$ ); and the application of glasses and polymer materials as substrates, which demands that the technological processes should be carried out at low temperatures (below  $300 \text{ }^\circ\text{C}$ ). In the case of polymer solar cells on Dacron, the requirements become even more severe: conducting coverages has to be sputtered onto polymer substrates at temperatures that do not exceed the softening temperature of the material (for

Dacron, it amounts to 110 °C). The problem of obtaining the coverages with a high conductivity at low substrate temperatures (lower than 100–110 °C) and without their subsequent annealing is urgent, e.g., at the manufacture of multilayered coverages for solar batteries, because the processes of interlayer diffusion are slowed down at low temperatures. It is known that the undesirable diffusion reduces the SC functioning efficiency.

In the method of magnetron sputtering, which is the most widely applied in industry [6], heated substrates are used. In order to obtain TCOs on the basis of ZnO with a low specific resistance, substrates with temperatures above 200 °C should be used, which makes this method inapplicable at once in our case. Fluxes of charged particles with a high energy are narrowly directed [7] and act on the substrate, destroying it, if the substrate is a polymer or organic material. Moreover, this method does not allow a uniform film to be grown up on a large area.

Molecular beam epitaxy is a complicated expensive method. Therefore, it will not be considered for the solution of our tasks.

The method of pulsed laser deposition requires that the substrate should be heated up to temperatures of 300–750 °C [6]. In addition, this method is not suitable for industrial applications. The pyrolytic method and the method of chemical vapor deposition are also realized at high substrate temperatures: 450–650 °C for pyrolysis, 500–700 °C for chemical vapor deposition, and 350–600 °C for metal-organic chemical vapor deposition [6].

The most attractive from the viewpoint of thin-film photovoltaics are the methods of colloid chemistry. They are simple and cheap. They are well adapted for industrial applications and make it possible to create coverages on large areas. The significant shortcoming of the sol-gel method consists in the necessity to carry out a high-temperature annealing for 30 min and even longer after the deposition [8]. The annealing provides a carrier mobility of  $5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  [7]. Without this operation, the films possess a low conductivity.

A good alternative to the described methods is the method of atomic layer deposition (ALD). This method was implemented in industry at the beginning of the 1970s for manufacturing the thin-film electroluminescent displays [9]. This scope of its application was major for ALD till the time, when

the semiconductor industry (namely, the Intel company) started to use ALD for the deposition of layers that were oxides with a high value of dielectric constant (high- $\kappa$  oxides) as gate insulators at manufacturing field-effect (MOSFET) transistors. This method makes it possible not only to monitor the layer thickness and uniformly cover the surfaces of various types, morphologies, and shapes, including three-dimensional configurations, but also—which is very important for thin-film photovoltaics—to perform the processes at low temperatures and deposit layers on large areas ( $100 \times 100 \text{ cm}^2$  and more) on industrial installations. When depositing the films on the latter, dozens of substrates with a large surface area are arranged simultaneously in the reaction chamber, which allows cheap TCOs to be obtained. In more details, the ALD method was described in work [10].

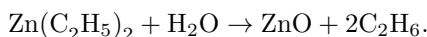
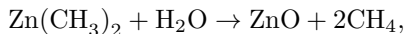
#### **4. Fabrication Technology and Properties of ZnO Films Obtained on Installations Savannah-100 and F-120**

One of the leaders in obtaining and researching the films of transparent conducting metal oxides using the ALD method were the Polish physicists M. Godlewsky, E. Guzewicz, and others [4, 5, 9]. Most of their works were carried out on installations Cambridge NanoTech Savannah-100 and F-120 (ASM-Microchemistry Ltd). The further analysis of the fabrication technology and the properties of ZnO films will be made on the basis of the results obtained by the Polish authors and our own results obtained during the work at the Institute of Physics of the Polish Academy of Sciences in Warsaw.

ZnO films can be grown up, by using various reactors. The latter differ from one another not only by their design, area, and shape of substrates, but also by the technological regimes and the types of precursors, i.e. chemical reagents, whose vapor is used at the chemical vapor deposition of films. In the ALD process, the vapors of precursors are sequentially introduced into the growth chamber, where they reach the surface of a growing film. After the introduction of the precursor vapor, which lasts for a few seconds, the chamber is cleaned by inletting a neutral gas, e.g., nitrogen, and pumping it out. Then, within ten milliseconds, water vapor is introduced, and the cleaning of the chamber by a neutral gas is

repeated. This sequence of operations comprises a cycle, during which one monoatomic layer of the film is formed. The film thickness is almost proportional to the number of cycles.

ZnO films grown in a satellite reactor F-120 were deposited from the vapors of DMZn precursor and water, whereas, in the case of a Savannah-100 reactor, the DEZn precursor was used [9]:



An advantage of the application of organic reagents containing zinc consists in a high pressure of vapor ( $>10$  Torr at 300 K), which allows the film growth temperature to be reduced below 100 °C. Various materials were used as substrates: silicon, glass, quartz, glass covered with an ITO layer, polymer films, organic materials, and others. The film growth was studied in a temperature interval of 80–250 °C. The film thickness amounted to 100–200 nm, and it was varied by changing the number of deposition cycles (500–1000 cycles).

To check the electron concentration in ZnO, the influence of technological parameters on the crystal structure and the stoichiometry (the ratio Zn:O) in the obtained films was analyzed. The necessity of this analysis is associated with the fact that natural defects, such as zinc inclusions ( $\text{Zn}_i$ ) and oxygen vacancies ( $\text{V}_\text{O}$ ), are donors in the ZnO crystal lattice. They increase the electron concentration  $n$  to a level of  $10^{18}$ – $10^{20}$   $\text{cm}^{-3}$ . While considering the electron mobility, such limiting factors as the electron scattering by ionized impurities and grain boundaries [11] have to be taken into account. The results of X-ray diffraction (XRD) studies [11] showed that the obtained films have a polycrystalline structure, even if they are deposited at low temperatures (100, 130, and 180 °C) onto substrates with an amorphous surface, such as glass. It was demonstrated that the growth temperature is a major factor affecting the formation of a prevailing orientation of the growing crystal lattice.

The increase of the growth temperature from 120 to 140 °C results in a drastic increase of the electron concentration in the growing film. Already at the indicated temperatures, the magnitude of  $n$  reaches  $10^{19}$   $\text{cm}^{-3}$ , and the film conductivity becomes metallic [4]. Besides the electron concentration growth, an

increase of the mobility is also observed above 120 °C, which is different from the results obtained for ZnO films deposited using other technological methods [4]. This discrepancy can be explained by the fact that the temperature growth improves the quality of the crystal lattice owing to a reduction in the number of formed defects, which is confirmed by the results of photoluminescence researches.

Simultaneously with this process, a relative growth of zinc inclusions in the crystal lattice is observed, which leads to an increase of the charge carrier concentration. At growth temperatures of about 200 °C, the minimum resistivity of the undoped film (of an order of  $10^{-3}$   $\Omega$  cm) was registered. The same minimum resistivity was also observed for undoped ZnO films in works devoted to the fabrication of zinc oxide films by other technological methods [4]. If the films are used in inorganic solar cells, such value of resistivity is considered to be too high. Therefore, the additional doping of films with aluminum or other elements of group III is applied. As a result, the resistivity diminishes to a value of  $(2\div 3) \times 10^{-4}$   $\Omega$  cm, which is comparable with the corresponding parameter for ITO films ( $1 \times 10^{-4}$   $\Omega$  cm). However, for the purposes of organic optoelectronics and photovoltaics, a resistivity of  $10^{-4}$   $\Omega$  cm is not mandatory [4]. In a number of publications [4], an effective work of organic devices with transparent conducting ZnO films with a resistivity of about  $10^{-3}$   $\Omega$  cm was demonstrated. Nevertheless, the ALD method makes it possible to obtain a resistivity of  $(7\div 8) \times 10^{-4}$   $\Omega$  cm for undoped ZnO films in the case where the film is sufficiently thick (of about 1  $\mu\text{m}$ ) [4], which is an order of magnitude better than the resistivity of ZnO films obtained using the sputtering and pulsed laser deposition.

Besides the deposition temperature, the charge carrier concentration can also be affected by the period of the chamber cleaning with the use of a neutral gas [12]; this stage is the next one in the cycle after inletting water vapor. In particular, the prolongation of the chamber cleaning time resulted in a reduction of the electron concentration. This phenomenon can be explained by the fact that this prolongation allows more hydroxyl groups containing hydrogen atoms to be removed. Hydrogen, when being built into the film, gives rise to the formation of vacancies that increase the charge carrier concentration.

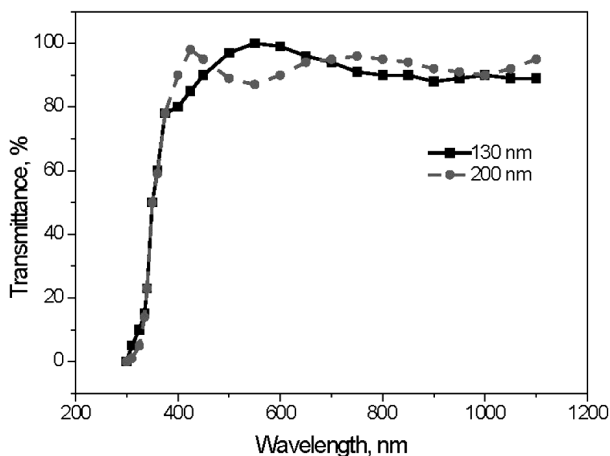


Fig. 2. Optical transmittance spectra of ZnO films 130 and 200 nm in thickness

The mobility of electrons usually falls within an interval of  $10\text{--}50\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , although, in the case of ZnO films deposited onto a crystalline substrate, this quantity can reach  $100\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  [12].

An important parameter for the application of ZnO as an upper transparent electrode in the solar cell structure is the transparency. For various technological parameters, the transparency of ZnO films can change from 80% to 90%. The growth of the film thickness gives rise to an increase in the charge carrier concentration, but the transparency decreases at that. In Fig. 2, the optical transmittance spectra for films 200 and 130 nm in thickness deposited on glass substrates and having a resistivity of about  $10^{-3}\ \Omega\text{ cm}$  are depicted. Films with those thicknesses were later used by us to fabricate solar cells on the basis of CdTe. The optical spectra were measured in the wavelength interval of 300–1100 nm on an optical spectrometer Solar CM2203. The figure testifies that the films were transparent. The average optical transmittance amounted to approximately 90%.

Hence, in this section, we have formulated technological conditions of film deposition, which make it possible to obtain films with a high transparency and a high conductivity for their further application in solar cells.

## 5. Organic Solar Cells with ZnO Films

Low-temperature regimes are obligatory, when ZnO layers are deposited onto organic materials or flex-

ible polymer substrates. The melting temperatures of those substances lie within an interval of 80–400 °C [4]. Besides low sublimation temperatures, organic materials dictate additional technological requirements. The properties of organic semiconductors are unstable in time and gradually worsen. This circumstance is associated with the presence of oxygen and water vapor in the atmosphere, which enter into a reaction with the organic material. Therefore, the passivation of the organic material surface and its protection against the atmospheric influence are very important. Both those issues can be successfully decided by depositing the ZnO films, by using the ALD method.

As the organic semiconductor, the authors of work [4] used nickel phthalocyanine (NiPc). NiPc is an organic semiconductor with the *p*-type conductivity and a charge carrier mobility of an order of  $10^{-1}\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ . This value is an order of magnitude lower in comparison with that in pentacene or amorphous silicon; however, it is relatively high, if compared with other phthalocyanines. NiPc is photosensitive and, therefore, is used in organic photovoltaics. The photosensitivity of NiPc can be enhanced by doping this material with oxygen. However, on the other hand, the presence of a considerable amount of oxygen can result in the deterioration of the time stability of NiPc properties.

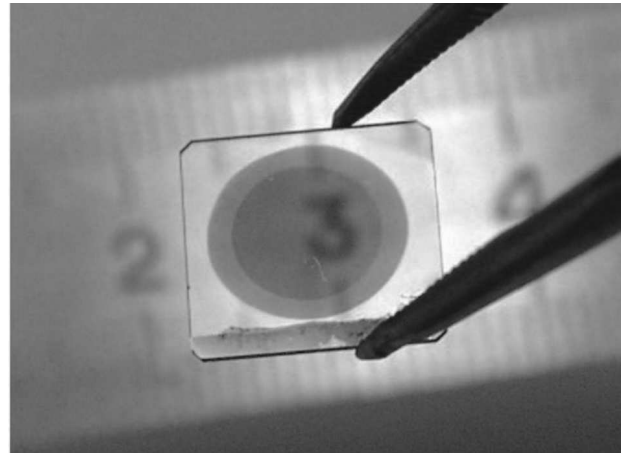
While fabricating the structure with NiPc [4], the problems of passivating the NiPc layer and its protection against the atmosphere, as well as against the diffusion of metal atoms moving from the metal electrode, were solved simultaneously. The following structure was made. A NiPc layer 400 nm in thickness was deposited using the thermal evaporation method on a glass substrate covered with an ITO layer. Then, by applying the low-temperature (100 °C) ALD method and using DEZ and  $\text{H}_2\text{O}$ , a thin ZnO film 30 nm in thickness was deposited above. Finally, an upper aluminum electrode was deposited above the whole structure using the thermal evaporation method. The active region of this ITO/NiPc/ZnO/Al device was equal to  $1\text{ cm}^2$ . A similar structure, but without a ZnO film, was also fabricated for comparison. Dark current-voltage (*I*–*V*) characteristics measured for both structures revealed their rectifying diode properties: the rectification factor at the voltage  $U = \pm 1\text{ V}$  was equal to 41 for the structures with a ZnO layer and to 2 for the struc-

tures without it. The structures with a ZnO layer had a higher photocurrent. The presence of a ZnO layer improved the time stability of the examined devices. In particular, the  $I-V$  characteristics measured once more in 30 days showed the disappearance of a rectification for the structures without ZnO and some deterioration of the rectification factor to a value of 32 for the structures with a ZnO layer, which demonstrated the advantage of the application of a zinc oxide film.

The work of Finnish authors H. Saarenpaa *et al.* [13] was devoted to the study of ZnO films obtained on an F-120 reactor, doped with aluminum, and used as transparent electrodes in the organic photovoltaic structure. The organic material poly(3-hexylthiophene-2,5-diyl) (PHT) was used as a donor of electrons, 3,4,9,10 perylene-tetracarboxylic diimide (PTCDI) as an acceptor material, and tris(8-hydroxyquinoline) (Alq3) as a buffer layer. The cited authors fabricated structures containing a ZnO:Al layer in two different configurations: this film served as a cathode in one of them, and as an anode in the other. The examined structures were compared with similar specimens, in which an ITO layer was used instead of the ZnO:Al one. As a result of researches, it was found that the structures with the ITO layer as an anode and the structures with the ZnO:Al layer as a cathode revealed similar photovoltaic characteristics. A conclusion was drawn that the ZnO:Al layer should be better used as a cathode than as an anode. The application of ZnO:Al instead of ITO also resulted in a better stability of the photo-electric characteristics of analyzed structures. For instance, a repeated measurement in 40 days testified to the absence of degradation in the parameters for the structures with ZnO:Al, whereas the conversion efficiency became considerably worse for the structures with ITO. The basic cause of the degradation is the diffusion of indium from the ITO layer, which demands that an additional buffer layer should be deposited between the ITO layer and the organic material.

## 6. Photovoltaic Structure $n\text{-CdS}/n\text{-CdTe}/p\text{-Cu}_{1.8}\text{S}$ with ZnO Films

We fabricated SCs on the basis of materials of groups II-VI. The CdS/CdTe structures were deposited us-

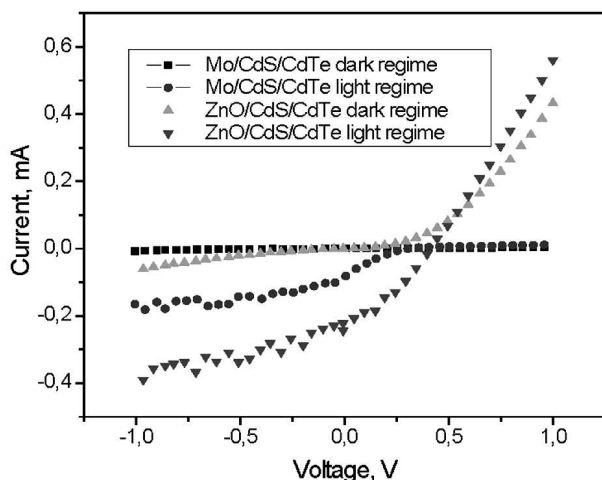


**Fig. 3.** CdS/CdTe/Cu<sub>x</sub>S structure on quartz glass covered a ZnO layer

ing the sublimation method in a quasiclosed volume on substrates of two types: glassceramic covered with molybdenum and quartz glasses covered with ZnO films obtained by the ALD method. The temperature in a reaction chamber was equal to 550 °C. CdS and CdTe layers were deposited alternately in the same technological cycle at temperatures of 750 and 500 °C, respectively. The  $n\text{-CdS}$  layer provided an ohmic contact with the upper electrode (Mo or ZnO). Accordingly, the CdTe layer was absorbing with a thickness from 1 to 3  $\mu\text{m}$ . The annealing and chlorination operations, which are required to obtain effective (with an efficiency of about 10%) CdTe SCs, were not used. In order to form a  $p\text{-}n$  junction with  $n\text{-CdTe}$ , we used a thin (of about 30 nm)  $p\text{-Cu}_{1.8}\text{S}$  layer, which also served as an upper current-collecting electrode. Figure 3 demonstrates the image of the obtained SC. The working area amounted to 0.196  $\text{cm}^2$ .

Light and dark current-voltage characteristics of SCs were measured at two illumination intensities: 0.013 and 0.136  $\text{W}/\text{cm}^2$  (a tungsten lamp). For comparison, the SCs were illuminated from the upper and lower electrode sides. The results showed that the efficiency of a SC was higher in the case where the SC was illuminated from the  $\text{Cu}_{1.8}\text{S}$  side.

The measured dark and light  $I-V$  characteristics of SCs are depicted in Fig. 4. One can see that the structures deposited on ZnO films have better parameters in comparison with the structures on Mo. For instance, the best specimens on ZnO had an efficiency of



**Fig. 4.** Dark and light  $I$ - $V$  characteristics of CdS/CdTe/ $\text{Cu}_x\text{S}$  structures on ZnO and Mo

1.89%, the short circuit current  $j_{sc} = 2.49 \text{ mA/cm}^2$ , the open-circuit voltage  $U_{oc} = 0.3695 \text{ V}$ , and the filling factor  $FF = 26.7\%$ . The experimental results were described in more details in work [14]. The better parameters of SCs deposited on ZnO can be explained by the influence of several factors. Rather a good polycrystalline structure of ZnO stimulated the oriented growth of CdS, which reduced the number of recombination processes in the CdS layer and at the ZnO/CdS interface. As a result, the short circuit current in those structures was higher in comparison with that in SCs on Mo. The analysis of the band diagram showed the formation of a higher barrier for holes and, hence, the strengthening of the built-in electric field in the case where ZnO was used. Therefore, an increase of the photocurrent was observed.

## 7. Conclusions

The method of atomic layer deposition makes it possible to deposit ZnO films that satisfy the requirements of thin-film photovoltaics. By varying technological regimes, the structural, optical, and electric properties of films can be modified in wide intervals. The determination of low-temperature technological parameters allows us to grow the ZnO film with a transparency of about 90% in the visible spectral range and a resistivity of about  $10^{-3} \Omega \text{ cm}$ . The application of low-temperature growth regimes allowed the obtained ZnO films to be used as a pro-

TECTIVE passivating layer in organic solar cells, and as an upper transparent electrode. The application of ZnO films in the inorganic photovoltaic structure on the basis of CdTe made it possible to obtain SCs with better parameters in comparison with the structures on molybdenum, which is widely applied as an electrode. The ALD method is recommended for the development of photovoltaic structures in Ukraine.

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1. T.D. Nielsen, C. Cruickshank, S. Foged, J. Thorsen, and F.C. Krebs, *Sol. Ener. Mater. Sol. Cells* **94**, 1553 (2010).
2. M.A. Green, K. Emery, Y. Hishikawa, W. Warta, and D. Dunlop, *Prog. Photovolt.: Res. Appl.* **23**, 1 (2015).
3. *Thin Film Solar Cells: Fabrication, Characterization, and Application*, edited by J. Poortmans and V. Archipov (Wiley, New York, 2007).
4. G. Luka, M. Godlewski, E. Guziewicz, P. Stahira, V. Cherpak, and D. Volonyuk, *Semicond. Sci. Technol.* **27**, 074006 (2012).
5. M. Godlewski, *Low Temp. Phys.* **37**, 235 (2010).
6. A.I. Yevtushenko, G.V. Lashkaryov, V.Y. Lazorenko, V.A. Karpyna, and V.D. Khranovskyi, *Fiz. Khim. Tverd. Tila* **9**, 869 (2008).
7. N. Huby, S. Ferrari, E. Guziewicz, M. Godlewski, and V. Osinniy, *Appl. Phys. Lett.* **92**, 023502 (2008).
8. T. Kawahara, T. Ishida, H. Tada, and N.S. Tohge Ito, *J. Mater. Sci. Lett.* **21**, 1423 (2002).
9. S. Gieraltowska, L. Wachnicki, B.S. Witkowski, M. Godlewski, and E. Guziewicz, *Thin Solid Films* **520**, 4694 (2012).
10. T.V. Semikina, *Uchen. Zapisk. Tavrich. Nats. Univ. Ser. Fiz.* **22**, No. 1, 116 (2009).
11. TA. Krajewski, G. Luka, L. Wachnicki, AJ. Zakrewski, BS. Witkowski, MI. Lukasiewicz, P. Kruszewski, E. Lusakowska, R. Jakiela, M. Godlewski, and E. Guziewicz, *Semicond. Sci. Technol.*, **26**, 085013 (2011).
12. T. Krajewski, E. Guziewicz, M. Godlewski, L. Wachnicki, I.A. Kowalik, A. Wojcik-Glodowska, M. Lukasiewicz, K. Koplako, V. Osinniy, and M. Guziewicz, *Microelectr. J.* **40**, 293 (2009).
13. H. Saarenpaa, T. Niemi, A. Tukiainen, H. Lemetyinen, and N. Tkachenko, *Sol. Ener. Mater. Sol. Cells* **94**, 1379 (2010).



14. T.V. Semikina, S.V. Mamykin, M. Godlewski, G. Luka, R. Pietruszka, K. Kopalko, T.A. Krajewski, S. Gieraitowska, J. Wachnicki, and L.N. Shmyryeva, *J. Semicond. Phys. Quant. Electr. Optoelectr.* **16**, 111 (2013).

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*Т.В. Семікіна, С.В. Мамікін,  
Г.І. Шеремет, Л.Н. Шмирева*

ТОНКІ ПЛІВКИ ZnO,  
ОТРИМАНІ МЕТОДОМ АПО,  
ЯК МАТЕРІАЛ ДЛЯ ФОТОВОЛЬТАЇКИ

Резюме

У роботі представлений огляд задач, що вирішуються при розробці сонячних елементів. Аналіз технологічних методів

отримання тонких провідних прозорих плівок оксиду цинку ZnO з точки зору застосування в органічних і тонкоплівкових сонячних елементах показує переваги технології атомного шарового осадження (АПО). Показано, що метод АПО забезпечує низькотемпературний (100–200 °C) ріст плівок, які мають необхідні значення опору  $\sim 10^{-3}$  Ом·см і пропускання світла  $\sim 85$ –90%. Використання ZnO плівок в органічних фотовольтаїчних структурах показало поліпшення стабільності у часі випрямляючих характеристик даних структур. Дослідження органічних структур з ZnO як катода і анода показало перспективність використання ZnO в ролі катода. Вивчення ZnO в ролі прозорого провідного електрода в неорганічній фотовольтаїчній структурі на основі CdTe показало збільшення фотоструму і зменшення рекомбінації в порівнянні з молібденовим електродом.