Thin film solar cells based on CdTe and Cu(In,Ga)Se$_2$ (CIGS) compounds

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Abstract. We are publishing recent results in chalcogenide photoelectric convertors fabrication, which are efforts of many scientific teams from Russia, Belarus, Ukraine, and Kazakhstan. Competitively high efficiency of photoelectric convertors (11.4% for CdTe and 11% for CIGS) was achieved in the process of our work. Furthermore, luminescent filters for improvement of spectral response of such chalcogenide solar cells in a short wavelengths region were also developed and investigated here.

1. Introduction

A market of thin film chalcogenide photoelectric convertors (PhEC) on the base of CdTe and Cu(In,Ga)Se$_2$ (CIGS) are growing extensively due to their lower cost per watt of installed capacity in comparison of silicon solar cells [1]. An efficiency of thin film solar cells is 12-14%, which allows to obtain about 100 watts of electric power from one square meter of photovoltaic surface. Unlike silicon, chalcogenide materials have an optimal band gap, better light absorption and good radiation resistance. Moreover, current efficiency of such solar cells does not reach a half of theoretical limit (24-29%). Thus, they have large potential for efficiency growth in the future. Another advantage of chalcogenide systems is the ability of manufacture of thin, light and flexible cells on the base of polymer [2-3] and metal foil [4] substrates.

In this paper we represent different scientific centers, which joined their efforts in solar energy conversion area for research and developing of PhEC.

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Active layer formation for CdTe and CIGS solar cells (see fig.1) is usually realized by variety of vacuum techniques. At this moment such methods are well known and applied for layer sputtering widely.

Also, there are so-called “wet-methods” for the layer deposition. Wet methods are usually based on deposition from different solutions of appropriate chemicals or on the modern printing technologies (such as ink jet, etc.) Moreover, we have to note that wet methods can give some advantage over standard vacuum sputtering such as lower price and higher speed of layer deposition. Obviously, that is very important in the case of mass manufacture.

2. Experimental

Well known that different schemes for CdTe and CIGS PhEC fabrication can be applied. The difference between them is mostly in the order of layer deposition and nature of some working layers. Assembling of CdTe PhEC usually starts from glass or polymer substrate with transparent conductor layers (such as ITO, etc.). This approach has been called “substrate method”. Opposite scheme of assembling is called “superstrate method” and it is usually applied in the case of CIGS (see fig. 1).

2.1. Vacuum technologies for thin film structures formation

2.1.1. Thermal vacuum technologies and close space sublimation. Thermal vacuum technologies were used for thin film solar cells ITO/CdS/CdTe/Cu/Au formation on the base of flexible polyimide films [2].

2.1.2. Ion-beam sputtering. Ion-beam sputtering was used for transparent electroconductive SnO$_2$ layer forming on glass substrate.

2.1.3. Magnetron sputtering. Magnetron was used for sputtering of ITO, CdS and CdTe layers, as well as for metal layer of back contact in CdTe PhEC.

2.1.4. Ion-plasma sputtering. Ion-plasma method was used for metal precursors (Cu-In-Ga) sputtering with 10 nm/min rate.
2.1.5. Metal precursor selenization. Metal precursor selenization is very important stage of CIGS PhEC production. The selenization was carried out in two stages. First stage is the reaction between metals and selenium at reasonably low temperature (250 °C). Second stage is slow recrystallization of semiconductor layer at the temperature region from 250 to 540 °C.

2.2. Wet technologies of thin film structure formation

2.2.1. Chemical deposition methods. Chemical bath deposition is used for buffer CdS layer deposition in different PhEC constructions [6]. This process is based on thiourea decomposition reaction in presence of cadmium salt water solution (see equations 1-3).

\[
4\text{NH}_3 + \text{Cd}^{2+} \leftrightarrow [\text{Cd(NH}_3)_4]^{2+} \quad (1)
\]

\[
\text{SC(NH}_2)_2 + 2\text{OH}^- \rightarrow \text{S}^2^- + \text{CH}_2\text{N}_2 + 2\text{H}_2\text{O} \quad (2)
\]

\[
[\text{Cd(NH}_3)_4]^{2+} + \text{S}^2^- \rightarrow \text{CdS} + 4\text{NH}_3 \quad (3)
\]

2.2.2. Pulverization method. Pulverization method was used for TCO and CdTe layers formation. For this aim we had synthesized special colloidal CdTe dispersion that can be applied for such process.

2.2.3. Electric deposition. The advantage of electric deposition process is in ability of preparation of high homogenous films for large areas, which is important for mass production. Electrochemical behavior of Se (IV), Cu(II), In(III), Ga(III) ions is studied in different electrolytes on the base of sulfuric, sulfanic, citric and sulfosalicylic acids at pH (0,5÷3) on glass-carbonic and molybdenum electrodes [7]. Process can be described with following reactions:

\[
\text{Cu}^{2+} + \text{In}^{3+} + 2\text{H}_2\text{SeO}_3^- + 8\text{H}^+ + 13\text{e}^- \rightarrow \text{CuInSe}_2 + 6\text{H}_2\text{O} \quad (4)
\]

\[
\text{Cu}^{x^2+} + x\text{H}_2\text{SeO}_3^- + 4x\text{H}^+ + (2+4x)\text{e}^- \rightarrow \text{CuSe}_x + 3x\text{H}_2\text{O} \quad (5)
\]

\[
2\text{CuSe}_x + 2x\text{H}^+ + 2x\text{e}^- \rightarrow \text{Cu}_x\text{Se} + x\text{H}_2\text{Se} \quad (6)
\]

\[
\text{Se}^{x^2} + \text{In}^{x^3} = \text{In}_x\text{Se}_3 \quad (7)
\]

3. Results

3.1. Development of CIGS PhEC

For production of CIGS PhEC with Mo/Cu(In,Ga)Se2/CdS/ZnO/(Al-Ni) structure on glass substrate there were tested various combinations of wet and vacuum technologies. In the basic technology films were sputtered onto glass substrates with proportions 7.0 x 2.5 cm². Metal precursors (Cu-In-Ga) were sputtered with ion-plasma sputtering with the speed of 10 nm/min. After that heat treatment of the initial Cu-In-Ga layers in an inert atmosphere in the presence of Se and S vapors to self-organized synthesis of homogeneous films Cu(In,Ga)(S,Se)₂ solid solutions was held. At the first stage selenium including into precursor and binary phase formation was held under temperature of 250 °C. It supports slow reaction of Se with binary phase, which leads to better quality of crystal film. It also allows to include Se into precursors before recrystallization process, which supports better p-type conductivity. Second stage of CIGS films formation is held with 250-540°C. Further temperature rising did not lead to structure properties enhancement. Ratio of Cu:In:Ga:Se elements in film was 25,24:20,47:5,17:49,12, respectively. Best laboratory CIGS samples achieved efficiency 11%. Optimization of Ga concentration in Cu(In,Ga)Se₂ is expected to improve PhEC parameters and develop stable technologies of production of solar cells with efficiency higher than 15% at glass substrate and 10-12% at metal substrate.
Comparative analysis of In$_2$S$_3$ layer usage instead of toxic CdS was also held. An analysis of the charge-transport mechanism showed that replacement of the CdS barrier layer by In$_2$S$_3$ in the obtained thin-film heterostructures (TFHSs) does not result in significant changes in the electrical properties. Observed broadband photoconversion and induced photopleochroism are indicative of interference antireflection of TFHSs. Thus, it was established that In$_2$S$_3$ films can be introduced into TFHSs as barriers. This technology can be used for the fabrication of ecologically safe cadmium-free next generation of TFHSs, while the use of polarization photoelectric spectroscopy can ensure the monitoring of the widerange antireflection of these photoconverters.

The electrochemical behavior of Se (IV), Cu(II), In(III), Ga(III) ions in different electrolytes (Sulfuric, sulfomat, citric, sulfosalicylic acid-based electrolytes for pH (0,5÷3) on glass carbon and molybdenum electrodes is studied. The cyclic sweep method is used to research the characteristics of reduction these ions in details. The new electrolyte on the base of sulfosalicylic acid allows to electrodeposite the thin films of compounds CuInSe$_2$ and CuInGaSe$_2$ [7].

3.2. Development of CdTe PhEC

Various combinations of vacuum and wet technologies were used for CdTe PhEC producing. CdTe contact with metal forms Schottky barrier. So there was formed an intermediate system of layers between CdTe and metal electrode. Best efficiency for CdTe PhEC was achieved for thin film solar cells ITO/CdS/CdTe/Cu/Au. They were formed at polyimide films by vacuum methods [2]. Technological conditions, output parameters and light diode characteristics of this thin film solar cells were investigated.

Experimental research demonstrated that optimal thickness of CdS in flexible ITO/CdS/CdTe/Cu/Au solar cells (fig. 2) comes to 0.5 μ. It depends on two competitive physical processes. First is diode saturation current density and the second is photocurrent density.

It was revealed that polyimide films with TCO layers preliminary annealing with 400 °C temperature allows to improve solar cell efficiency up to 11.4%. It improves because of open circuit voltage growth from 733 mV to 765 mV, fill factor growth from 0.59 to 0.71 and short circuit current growth from 19.3 to 20.9 mA/cm$^2$. Light diode characteristics analysis demonstrates that efficiency improvement occurs because of serial resistance decrease to $R_s = 2.1 \, \Omega/cm^2$, diode current saturation decrease to $J_0 = 1.0 \cdot 10^{-9} A/cm^2$, photocurrent increase up to $J_F = 21 mA/cm^2$, and shunting resistance increase up to $R_{sh} = 6400 \, \Omega \cdot cm^2$.

![Figure 2. Flexible CdS/CdTe based solar module sample.](image-url)
with 4.5%, composed of four parallel elements. Analysis shows that cause of micromodule lower efficiency is in decreasing of all output parameters (fig.3). It is connected with active area enlarging, which causes higher probability of macrodefects formation.

Methods of thin film CdTe PhEC producing with ion-beam deposition of SnO$_2$ at glass substrate, chemical deposition of CdS and electrochemical CdTe deposition were also developed. Speed of electrochemical deposition is limited by tellurium diffusion to electrode. Optimal electrochemical deposition potential satisfies requirements of tellurium (IV) reduction-limit current, but does not reach redox of cadmium potential.

The morphology of surface had been investigated by AFM microscope. It showed the column structure. The sizes of the particles as-deposited CdTe film on CdS were 50-100nm and width of the forbidden zone of CdTe layers was 1,5 eV. It is more than 1,44 eV for CdTe monocrystal. Such methods result in high fill factor 71-75%. It allows to predict 10% efficiency. [7].

![Figure 3. J-V curves of flexible micromodule (a) and full module (b).](image)

Also methods of formation thin film CdTe PhEC based on magnetron and “wet” technologies are developed. They show encouraging results. In particular PhEC with 3.5% efficiency was obtained at balanced magnetron with using cold glass substrate and 6.5% at balanced magnetron with hot glass substrate. Thicknesses of layers were optimized. Optimal materials and technique of back contact deposition were selected. Also active layers are supposed to be deposited by unbalanced magnetron at polyimide films as substrate. Modules would be produced by laser scribing.

3.3. Luminescent filters (LF) for PhEC efficiency increasing
Common disadvantage of chalcogenide PhEC is low efficiency of photoelectrical conversion in spectral region below 500 nm. The problem of loses in short wavelengths region is connected with
presence of CdS buffer layer, which is good absorber of sunlight in blue spectral area. Furthermore, these losses increase under polyimide film usage as a substrate instead of glass. One of the ways of this problem overcoming is down-conversion of solar radiation by LF. Such filters contain organic luminophores (OL) or colloidal quantum dots (CQD) [9,10] (see fig. 4). Undoubted advantage of CQD relatively to OL is in high radiation resistance and stable optical properties during long operation under solar radiation treatment. State-of-the-art synthetic capabilities allow to modify full width half maximum and wavelength of CQD fluorescence in wide spectral area. That is good for optimal spectral response of solar cells.

![Figure 4. Concept to improving of efficiency of CdTe and CIGS solar cells with luminescent filter.](image)

Figure 5 shows spectral characteristics of CdTe solar cells without LF and with LF. It demonstrates efficiency increasing due to down conversion of some amount of sun power from blue region to the reddish (useful) one. OL which have been used in our work are depicted in table 1. Comparative investigation showed that both CQD and OL can be used in fabrication of LF.

Photopolymerization of polymethylmethacrylate (PMMA) and other acrylic monomers was mostly used for LF production in our work. Acrylic copolymers are sufficient transparent polymeric matrix for OL, as well as for CQD. The set of experimental investigations helped us to reveal an optimal concentration of OL and thickness of LF. As an example, we found that OL MNBI-4 has limited solubility in acrylic monomers. The maximum concentration of MNBI-4 luminophore can be only about 0.5 g/L. Definitely, this fact influences on down conversion efficiency of LF. Coumarin-6 is good soluble, so its concentration varied from 1 to 2 g/L. The higher concentration of luminophore leads to the higher efficiency of down conversion. Also, to get the best results we played with thickness of LF, so it was varied from 0.08 to 0.94 mm.
In the set of experiments we used LF with different thicknesses and different concentration of luminophores. Under increasing of thickness with the same concentration of luminophores short circuit photocurrent saturates and even tends to go down as you can see from figure 6. It allows to find an optimal thickness of LF and concentration of OL for the best sun light conversion.

Table 1. OL used in our work.

| Luminophor                              | Thickness (mg cm$^{-2}$) | Fluorescence quantum yield, % |
|-----------------------------------------|--------------------------|-------------------------------|
| 4-MNBI                                  |                          | 40 – 50                       |
| 4-morpholine-1,8-naphteline-1',2'-benzoimidazole |                         |                               |
| Coumarin 6                              |                          | 78 (in ethanol)               |
| 3-(2-benzothiazolyn)-7-(diethylamino) coumarin |                     |                               |
Application of LF gave the relative increasing of efficiency for CdTe (10%) and for CIGS (9%). Thus, summary efficiency of CdTe and CIGS PhECs can be lift up to 11%.

4. Conclusion
Various methods of production of chalcogenide PhECs were investigated. Maximal efficiencies 11.4% for CdTe PhEC and 10.7% for CIGS PhEC are achieved. Application of LF allows to increase efficiency of chalcogenide PhECs up to 10% additionally to the maximal efficiency. Joint efforts of scientific teams from Russia, Belarus, Ukraine, and Kazakhstan allow to solve problems of production of thin film chalcogenide solar cells with competitive technical and economical properties.

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