International Conference on Renewable Energies and Power Quality (ICREPQ'18)
Salamanca (Spain), 21th to 23th March, 2018
Renewable Energy and Power Quality Journal (RE&PQJ)
ISSN 2172-038 X, No.16 April 2018

Technology adjustment for manufacturing of flexible thin-film CdTe/CdS photovoltaic structures

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Abstract. The paper presents the results of the investigation on flexible photovoltaic structures based on CdTe/CdS semiconductor compounds. The aim of conducted research was focused on adjusting of manufacturing technology used for rigid CdTe/CdS solar cells for flexible substrates requirements. The production technology of cadmium telluride based photovoltaic cells, used by authors previously for rigid cells, requires high temperatures which are not acceptable for standard flexible substrates. Thus, the technology process parameters must have been changed in order to match the temperature resistance of the substrate. Additionally, this technology change must include the conservation of obtained layers' parameters. After a lot of experiments, such a compromise has been finally achieved.

Key words

flexible photovoltaic structures, thin-film solar cells, cadmium telluride, cadmium sulfide

1. Introduction

The subject of these research is focused on photovoltaic cells with active layers based on cadmium semiconductor compounds, such as CdTe and CdS, and their realization as flexible structures.

The construction of CdTe/CdS solar cell is heterojunction structure, where p-n junction is created by the connection of two materials with different values of band gaps. This enables broadening of the absorption range of solar irradiation photons.

In heterojunction photovoltaic structures, the important element is relatively suitable matching of their crystalline lattices. In this case, cadmium sulfide usually has a hexagonal wurtzite structure, with the direction of polycrystalline grains growth following along the vertical axis. Whereas cadmium telluride usually found in the form of a regular structure, which contributes to the formation of grains of relatively large dimensions, so that the average value of carrier diffusion path and consequently the efficiency of photovoltaic conversion are also high. The mismatch of crystalline lattices between these materials is estimated at 9.7% [1].

Heterojunction CdTe/CdS makes relatively well-matched structure. Apart from reasonably low level of crystalline lattice mismatch, both these materials are characterized by very similar thermal expansion coefficients and thermal processing temperatures. In order to the lack of significant stresses on the boundary of the CdTe base and the CdS emitter layers, it is possible to conduct efficient recrystallization processes through the heating of the structure.

Apart from semiconductor active layers of CdTe base and CdS emitter, very important elements of thin film flexible solar cell are electrical contacts. As ohmic base contacts for CdTe layer, such materials as: Mo, Au, Ag, HgTe, ZnTe:Cu or Cu_2Te, are used [2-6]. Emitter contacts are usually made as transparent conductive layers, predominantly metal oxides such as ITO, SnO_2, Zn_2SnO_4, Cd_2SnO_4 or ZnO:Al (AZO), as well as CdO, ZnO and $RuSiO_4$ [7-9].

In this work however, authors are focused on deposition methods of cadmium telluride and cadmium sulfide as solar cell base and emitter layer respectively. Conducted research are focused on the application of these structures in flexible device constructions.

2. Manufacturing technology of CdTe/CdS photovoltaic structures

As manufacturing technology for flexible CdTe/CdS structures, physical vapor deposition (PVD) method have been chosen. The selection this technique out of many others was motivated as the most optimal in such solutions. Using PVD technology it is possible to achieve very thin layers of significantly well quality, which enables potential applications in flexible constructions.

Additionally, this method provides high purity, uniformity and material quality of the structure. Moreover, in high quality equipment with the possibility of placing several vapor sources in one chamber, it enables continues deposition of active layers without breaking the vacuum. The advantage of such procedure is the efficiency increase of the obtained photovoltaic structures.

The results of first experiments on CdTe layers deposition on flexible substrates are presented in Fig. 1. Fig. 1a) shows the photograph of layers manufactured in PVD technology on flexible Upilex polyimide foil, with previously PVD deposited copper layer (as ohmic contact layer). Fig. 1b) presents the other variant where after Cu contact, graphene layer was screen-printed on the surface for better CdTe layer absorption. In both cases, during the PVD process of CdTe layer deposition, the pressure inside the chamber was $4\cdot10^{-6}$ mbar and the substrate was heated up to the temperature of 350°C. In both experiments, good surface adhesion and structure homogeneity was observed.

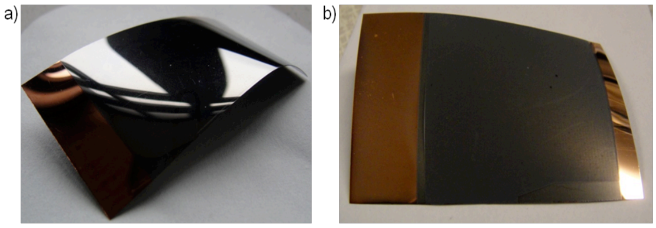

Fig. 1. Layers of CdTe deposited in PVD technology: a) on Upilex flexible substrate with previously deposited Cu layer, b) on Upilex substrate with previously deposited Cu and printed graphene layers.

The deposition of the CdTe/CdS semiconductor active layers of solar cells by this technique requires additionally a recrystallization process in order to make the layers functional.

The recrystallization, also called the activation process, consists in transforming the deposited amorphous layer into a polycrystalline structure. This process takes place at relatively high temperature, through connecting and increasing the crystallites of the material. For cadmium telluride and cadmium sulfide layers deposited on rigid substrates, recrystallization process is conducted in accordance with the temperature profile, assuming a temperature in the range of 550÷600°C in about 30 min in an inert gas environment [10].

In the recrystallization process of CdS and CdTe layers an auxiliary catalyzer component of $CdCl_2$ is used. The application of cadmium dichloride provokes the dissolution of CdS and CdTe compounds, which allows to increase the columnar grain sizes and the improvement of their arrangement and packing. Consequently, it leads to the additional improvement of the polycrystalline structures' quality. Cadmium dichloride can be deposited on CdS or CdTe layers, for example using one the fallowing methods:
-) physical vapor deposition (PVD) using $CdCl_2$ powder target;
-) chemical deposition of $CdCl_2$ in saturated solution of methanol.

The residues of $CdCl_2$ should be removed from the semiconductor surface in order to avoid the material dissolution during the further technological steps. The process of removing cadmium dichloride is realized either by its evaporation during the heating of the structures or by chemical etching in the bromine and methanol solution. The influence of recrystallization process with the adhibition of $CdCl_2$ is shown in Fig. 2. Fig. 3 shows the SEM images after the recrystallization process without (a) and with (b) the application of the $CdCl_2$ catalyst. Both CdS and CdTe, as well as $CdCl_2$ were deposited using PVD technology process in high vacuum.

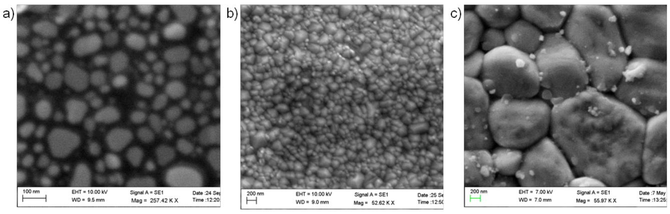

Fig. 2. Microstructures of the CdS layers: a) directly after the deposition, b) after the deposition and standard recrystallization without $CdCl_2$ application, c) after the deposition and recrystallization with $CdCl_2$ application.

Considering CdS layer and its crystallite's diameters size, directly after the deposition process their diametrs are approximately 100 nm and they are characterized with the high level of dispersion. In the recrystallization process according to the standard procedure however, with no catalyst usage of $CdCl_2$, the diameters of the grains are exciding the value of 200 nm and additionally they are highly arranged considering the crystalline structure. The recrystallization process including $CdCl_2$ catalyst allows achieving more expected results through the formation of the compact crystallites with the diameters up to 3 μm, with the average size of 1.5-2 μm.

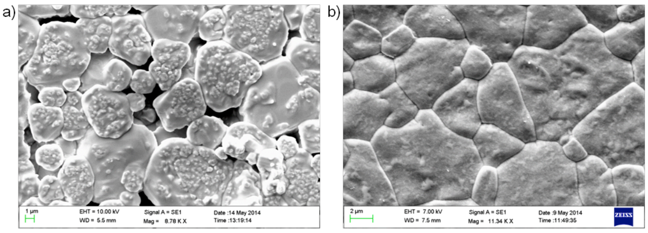

Fig. 3. Microstructure of CdTe layer: a) after recrystallization process **without** the application of $CdCl_2$, b) after recrystallization process **with** the application of $CdCl_2$

The SEM images shown in Fig. 2 and Fig. 3 show the real picture of the influence of catalyst on CdS and CdTe layers used in the process. Applied catalyst allows to increase the grain size, improve their quality and decrease the level of the layer porosity.

Irregular composition of crystallites and wide distances between grains (Fig. 3 a) influences the charges flow and causes the increase of the parallel resistance decrease, which leads to the significant increase of the voltage obtained in the photovoltaic conversion.

The utilization of cadmium dichloride can additionally influence the reduction of the diffusion between CdS and CdTE semiconductor compounds, which is favorable in terms of p-n semiconductor junction.

3. Technology adjustment for flexible substrates

The high temperature process, which is necessary for obtaining good quality polycrystalline layers, is critical for most flexible substrates that are not thermally resistant in such range. Thus, the adaptation of this technology to flexible CdTe/CdS solar cells structures requires finding the compromise between temperature resistance of the substrate and the lowest possible temperature of the recrystallization process with preserving the significant structure's quality level.
In order to solve the stated problem, some studies have been undertaken to evaluate the possibility of decreasing the temperature of the recrystallization of the CdS and CdTe semiconductor layers while retaining the functionality of the process, resulting in satisfactory and high quality polycrystalline structures.

A series of experiments have been conducted, involving the deposition of CdS and CdTe layers and their recrystallization with $CdCl_2$ catalyst, at temperatures below 600°C in accordance with the time profile of 30 minutes at a given temperature followed by gradual cooling. In the next step, the recrystallization time was extended to 60 minutes. The obtained cadmium sulfide and cadmium tellurium layers were then examined by SEM microscope to evaluate the polycrystalline quality of the structures. Samples for these experiments were prepared on glass substrates, due to the necessity of conducting part of the tests at critical temperatures (higher than the flexible substrates resistance) and in order to have a reliable comparison. Both CdTe and CdS layers were deposited using PVD method. The pressure in the vacuum chamber during the deposition process was about $4 \cdot 10^{-6}$ mbar. In order to improve the adhesion of the deposited material to the substrate, a specially designed temperature-controlled base for sample placement was used. The substrates during the deposition process of CdS layer were heated up to a temperature of 150 to 165°C, while for the cadmium telluride deposition was conducted at the substrate temperature of 330 to 350°C. These temperatures have been determined as the optimal for depositing of these materials on the basis of previous studies [11-14]. In further step, on CdS and CdTe semiconductor layers, the catalyst layer of $CdCl_2$ was deposited using the same technique and process parameters. The deposition of cadmium chloride proceeded without heating the substrate material.

As a result of conducted experiments, it was shown that high quality polycrystalline structures of both cadmium sulfide and cadmium telluride can be obtained, while the temperature of the recrystallization process is reduced to 420°C. In this case, however, it is necessary to increase the process time up to about 60 minutes. Below this temperature, despite the increased process time, no effective recrystallization of the investigated structures was observed. Fig. 4 shows the effect of the recrystallization time (in the temperature reduced to 420°C), on the quality of the polycrystalline structure, on the example of the CdS layer.

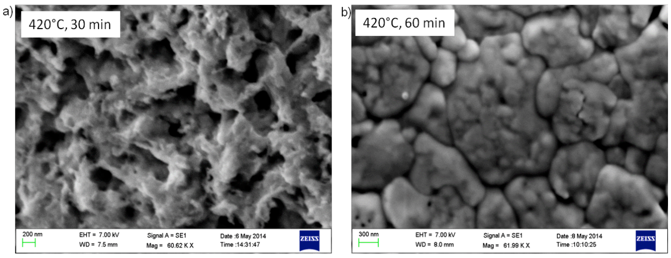

Fig. 4. Microstructure of CdS layer: a) after recrystallization process in temperature of 420°C and time of 30 minutes, b) after recrystallization process in 420°C and 60 minutes

The microscope SEM image of CdS layer microstructure, recrystallized at 420°C within the time of 60 minutes, indicates the correct and compact packing of the crystallites in the layer structure. Their surface area is very irregular, and the grain diameters vary from 400 nm to 2.2 µm. As shown in Fig. 2, CdS layer recrystallized at 420°C within 30 minutes is still covered with $CdCl_2$ catalyst material, which makes it impossible to assess its quality accurately. Extending the process to 60 minutes causes the cadmium dichloride layer to evaporate, exposing the crystalline structure of CdS. SEM studies show similar dependence of partial retention of $CdCl_2$ compound also for CdS and CdTe layers recrystallized at higher temperatures. Microstructure SEM images for various temperatures and process times for CdS layers are shown in Fig. 5.

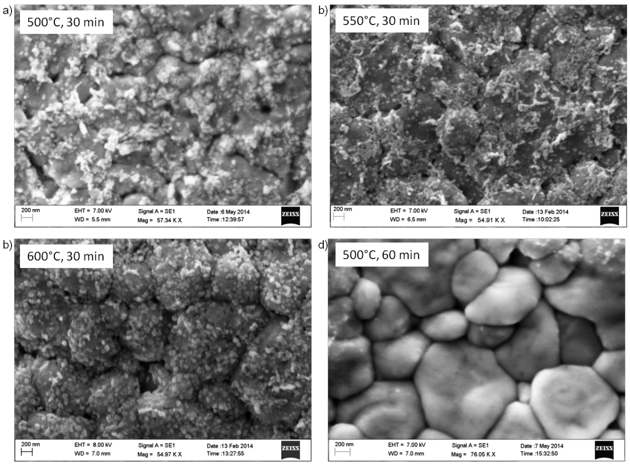

Fig. 5. Microstructure of CdS layer after the recrystallization process in various temperatures and process duration times: a) 500°C, 30 min, b) 550°C, 30 min, c) 600°C, 30 min, d) 500°C, 60 min.

The above SEM images of investigated microstructures show that the increasing of the recrystallization time has a positive effect on the quality of the CdS layer. Additionally, the increase in the recrystallization time of a thin layer of cadmium sulfide may not only result in complete removal of the $CdCl_2$ catalyst compound, but also partial evaporation of the CdS structure. This results in a reduction in the thickness of the active layer, which should be taken into account when designing the target photovoltaic structure dimentions. Placing the overly thin CdS layer and attempting to recrystallize it over an extended period of time may result in complete evaporation of the desired structure from the substrate. Fig. 6 shows the cross section of the CdS layer deposited directly on the glass substrate in two variants: after deposition before heat treatment and after 60 minutes of recrystallization. In the second case, the thickness of the layer decreased almost three times from the value of about 1.56 µm, measured immediately after deposition, to about 0.59 µm after recrystallization. Ultimately, the thickness of the CdS emitter layer in the photovoltaic cell should be in the range of 100 to 600 nm, thus in this case, the adopted technological process was achieved.

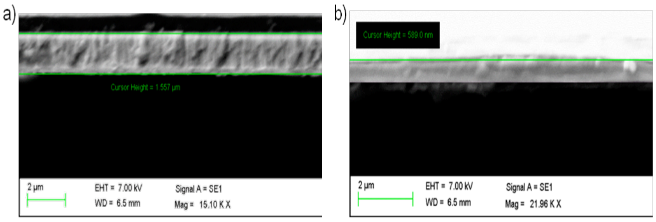

Fig. 6. Cross section of CdS structure: a) directly after deposition (1.56 µm thickness), b) after recrystallization process in increased time (0.59 µm thickness),

Analogous observations concerning the reduction of the temperature of the recrystallization process and the need to increase the time to obtain good quality polycrystalline layers, were also reported for CdTe structures. Fig. 5 shows a comparison of microstructure CdTe layers recrystallized at 420°C for 60 minutes and 600°C for 30 minutes. Measurements of grain diameters, conducted using SEM microscope software, have not shown any significant differences in their sizes for samples of both variants. Correspondingly as for the polycrystalline CdS structures, the grain surfaces in a given structure are irregular and in this case they diameters vary in the range of about 2 to 10 µm.

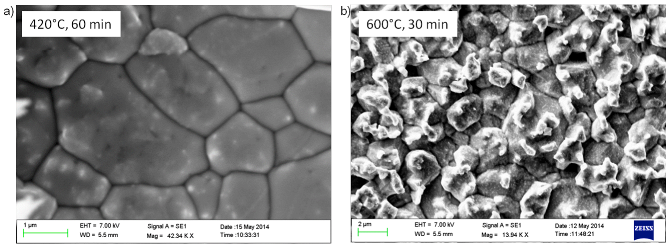

Fig. 7. Microstructure of CdTe layer after recrystallization process: a) in temperature of 420°C and 60 minutes time, b) in temperature of 600°C and 30 minutes time

The SEM images, as shown in Fig. 7, confirm the expediency of the recrystallization time increase, taking into account both modified (420°C) and standard (550÷600°C) temperature profiles. Although the structure recrystallized at 600°C for 30 minutes is characterized by visible features of the polycrystalline material, it is fully covered with catalytic residues of the $CdCl_2$ compound, which may impair its final parameters. It is also possible to remove the residue of cadmium dichloride by chemical etching, but the choice of such solution raises the complexity of the whole PV production process by introducing an additional procedure. Moreover, this type of additional process may contribute to the introduction of undesired surface contaminations resulting from the transport of the sample between the technological devices. Therefore, due to the desire of simplifying the process as much as possible and minimizing the number of treatments leading to the final quality structure, the choice to increase the recrystallization time, also to evaporate the $CdCl_2$ auxiliary seems to be more optimal in this case.

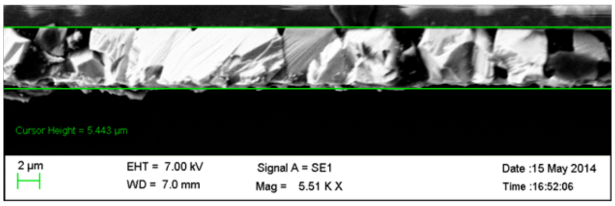

Fig. 8. Cross section of CdTe structure (5.4 µm thickness),

The cadmium telluride layer, as a base of phtovoltaic cell, is roughly thicker than the CdS emitter layer. In standard solar cells of this type, cadmium thickness are in the range between 2 and 8 µm. Scanning microscope characteristics of investigated samples showed values in the range of 5.2 and 6 µm. Fig. 8 shows an exemplary cross section of CdTe structure with indicated thickness measurement.

4. Conclusions

Conducted research showed the possibility of technology adjustment for active CdTe/CdS solar cells' layers deposition on flexible substrates. For this application PVD vacuum deposition technique was chosen with adjusted temperature and time of the final recrystallization procedure. Although the critical temperature has been reduced from 600°C to 420°C, the use of substrates resistant to high temperatures is still necessary. This is however a significant difference reducing the condition of the substrate's temperature resistance, which significantly increases the research area of suitable elastic materials fulfilling this criterion.

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