ORGANIC–INORGANIC HYBRID SOLAR CELLS

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Abstract: The purpose of the presented work is to find an optimal way for the preparation of the organic-inorganic hybrid solar cells based on perovskite structure $CH_3NH_3PbI_{3-2}Cl_2$ /$PC_{61}BM$. The main idea of the work is to create an eight solar cell samples with the highest possible conversion efficiency and stable structure. Conversion efficiency of created samples reached approximately η_{MAX} = 2, 5 %. Samples were futher analyzed and based on that were implemented other techniques for their improvement.

Keywords: Organic – inorganic hybrid solar cells, perovskite solar cells, conversion efficiency.

1. INTRODUCTION

Predicted reduction of the fossil energy sources and increasing environmental needs, leads to an intensive research of the new renewable energy sources - especially the methods of conversion the solar energy via alternative photovoltaic cells. The attention was focused on the development of solar cells based on perovskite in the recent years. Well-known scientist Michael Grätzel called perovskite as "unusually cheap" material that could operate successfully in solar cells and combine the seemingly incompatible - low acquisition cost and high efficiency of energy conversion of sunlight into electricity [1]. Advantages of perovskite solar cells lies in their potential use in a broad application such as windowpanes, facade systems and much lower production costs (also availability of materials) in comparison to a traditional silicon solar cells with a relatively easier methods of its preparation. Perovskite solar cells can be considered as promising power source worthy attention.

2. ORGANIC-ANORGANIC HYBRID SOLAR CELLS

2.1. PEROVSKITE SOLAR CELL

Perovskite in general is a name for a group of substances with the same crystal structure as $CaTiO_3$. In photovoltaic cells, modified compounds of $CaTiO_3$ are used for absorbing of sunlight. A semiconductor is created as an organic-inorganic hybrid composition as $CH_3NH_3PbX_3$ (X = Cl, I, Br). Solar cells based on perovskite have been continuously developed in the last five years. The first time of publication of this material in the solar cells was in 2009 - energy conversion efficiency of photovoltaic solar cells with liquid electrolyte was 3.13% and 3.81% ($CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$) [2]. In the following years, due to optimizations of various parameters of the photovoltaic cells there has been a rapid increase in energy conversion efficiency in a relatively short time [2].

Presented work deals with a hybrid peroskvit solar cell structure of $CH_3NH_3PbI_{3-2}Cl_2/PC_{61}BM$. Fig. 1 shows the general device structure of the perovskite solar cells.

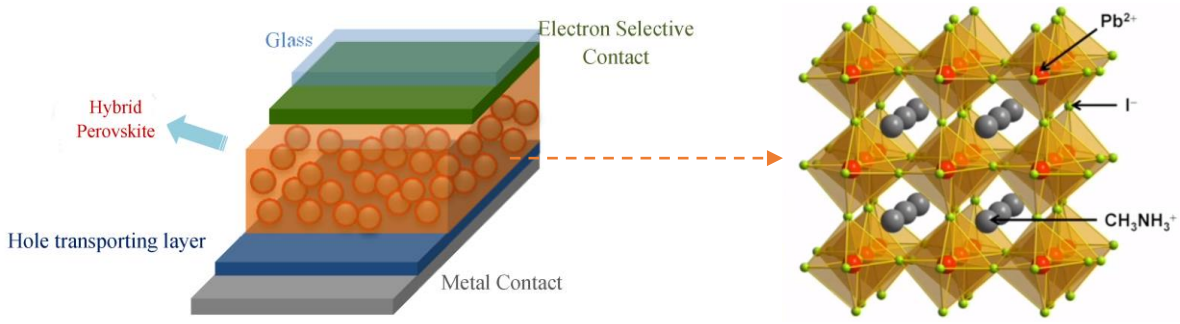


Figure 1: a) General structure of perovskite solar cells [1]

2.2. MANUFACTURING OF PEROVSKITE SOLAR CELL

An important step of work was to choose an appropriate process of manufacturing of examined peroskvite solar cell. Solar cells were fabricated on PEDOT coated indium tin oxide glass (ITO) with emphasis on the optimal way of heat treatment. The ITO substrates were before this process cleaned in an ultrasonic bath. $CH_3NH_3PbI_{3-2}Cl_2$ film was formed through a spincoating of a mixture of CH_3NH_3PbI, PbI_2 and $PbCl_2$. After verifying that the precursor solutions were successfully synthesized, the organic semiconductor $PC_{61}BM$ was deposited. To prevent the creation of interdiffusion between CH_3NH_3I and $PC_{61}BM$, high temperature wasn´t applied. Finally, aluminum cathode was deposited through a mask on the active layer. A detailed description of the preparation is given in the following text.

Preparation of the carrier substrates with an ITO layer was proceeded according to the following steps: the substrates were firstly put into the beaker with a 5-10% of NaOH solution. Subsequently, after a period of 3-5 minutes, were left in the ultrasonic bath, then rinsed with MilliQ water and finally cleaned with an isopropylalcohol.

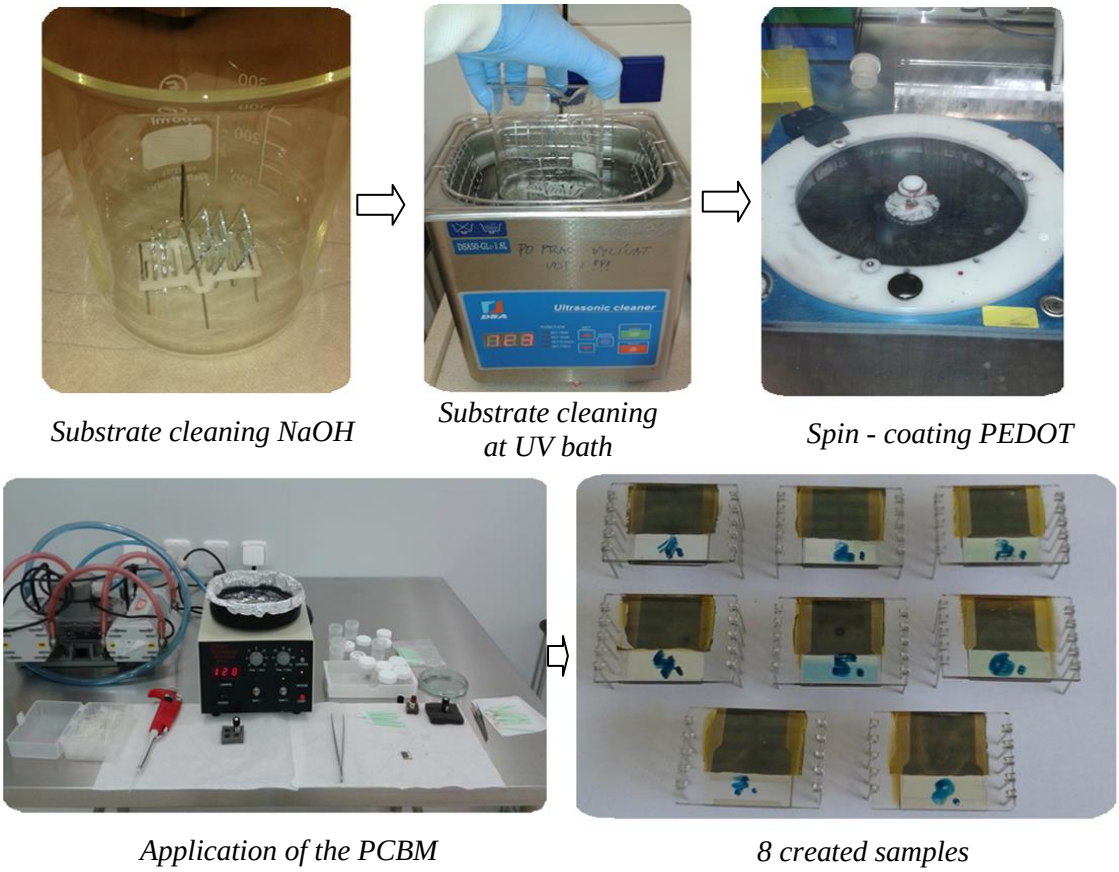
PEDOT: PSS was before applying filtered through a 45 μm PVDF filter. A 55 ml of solution was used. Spin-coating was adjusted to a rotational speed of 3000 rpm (with the acceleration speed of 500 rpm) for 30 seconds. The cathode strip was after this process purified by MilliQ water. The final layer thickness after annealing (120 ° C for 30 sec.) was 30 - 40nm.

Perovskite layer was prepared from molar solution of the mass fraction of 1:1:4 with a total concentration of 9 percentage by weight. In numbers it means: of CH_3NH_3PbI (0.19561g), PbI_2 (0.141822g) and $PbCl_2$ (0.08555g). The solution was prepared within the laboratory conditions for 12 hours at the temperature of 60 °C with the stirring speed of 650 rpm. The solution was then filtered with a 45μm filter and applied to a preheated glass slides (125 °C for a 30 sec) by spin-coating in an amount of 35μl with the rotational speed of 3000 rpm with a speed acceleration of 500 rpm. After deposition was on the slides cleaned anode strip. After this step were slides transferred to a hot plate with an 100 °C temperature for a period of 120 minutes. This process wasn´t unfortunately successful - created samples has shown a low efficiency in the light spectrum of 280 - 350 nm. It could be due to burn-through of layers which was indicated by the higher amount of carbon contained in the samples (see chapter Microscopic Analysis of Defective Sample). The procedure was therefore adjusted to heating for only 30 seconds and preheating of the glass was reduced from 100 ° C to 70 ° C. After this steps did not occur burn-through of layers anymore.

The layer of $PC_{61}BM$ was applied similarly. The solution was prepared from 10 mg / ml of $PC_{61}BM$ in a mixture of anhydrous solvents of chloroform-chlorobenzene (1: 1). Deposition was performed through a spin-coating at 1200 rpm for 60 sec. in an amount of 50 ml, but this time without a subsequent annealing. Cathode strip was refined with a chloroform.

In the end an aluminum electrodes were vapor-deposited with a thickness of 100 nm followed by encapsulation of the samples with the epoxy resin. Cover glass with contacts were also attached.

The result of the manufacturing process were 8 created samples. Samples no. 7 was damaged due to incorrect technological procedure. This sample was used for an microscopic inspection. Shortened process of realization of samples is for demostration purposes shown in Fig. 2.



Substrate cleaning NaOH *Substrate cleaning at UV bath* *Spin - coating PEDOT*

Application of the PCBM *8 created samples*

Figure 2: Manufacturing Process of the Perovskite Solar Cell

3. MEASURED DATA

In the structure of the peroskvite solar cells was necessary to monitor various parameters that influenced the resulting device functionality. One of the parameters investigated in the work was the preparation of optimized layer $CH_3NH_3PbI_{3-2}Cl_2$ / $PC_{61}BM$, which was used to form functional and stable reference solar cell with the best electrochemical and physical properties. The structure of these films were scanned by several methods using environmental scanning electron microscope and an atomic force microscope. The chemical composition of the layers was then examined via X-ray diffraction spectroscopy for a suitable setup of deposition processes.

3.1. MICROSKOPIC ANALYSIS OF DEFECTIVE SAMPLE

Microscopic scanning of the cross section of sample number 7 has shown that the solar cell did not have required structure. This can be caused by burn-through of layers during the manufacturing process which could be indicated by a very high amount of carbon contained in the sample. This assumption was also confirmed by images from the SEM microscope Vega3 Tescan and X ray spectroscopy analysis measured at Brno University of Technology. Based on this observation were the manufacturing process of other samples changed - a temperature of preheating during application perovskite material was reduced from 100°C to 70°C, as was mentioned before.

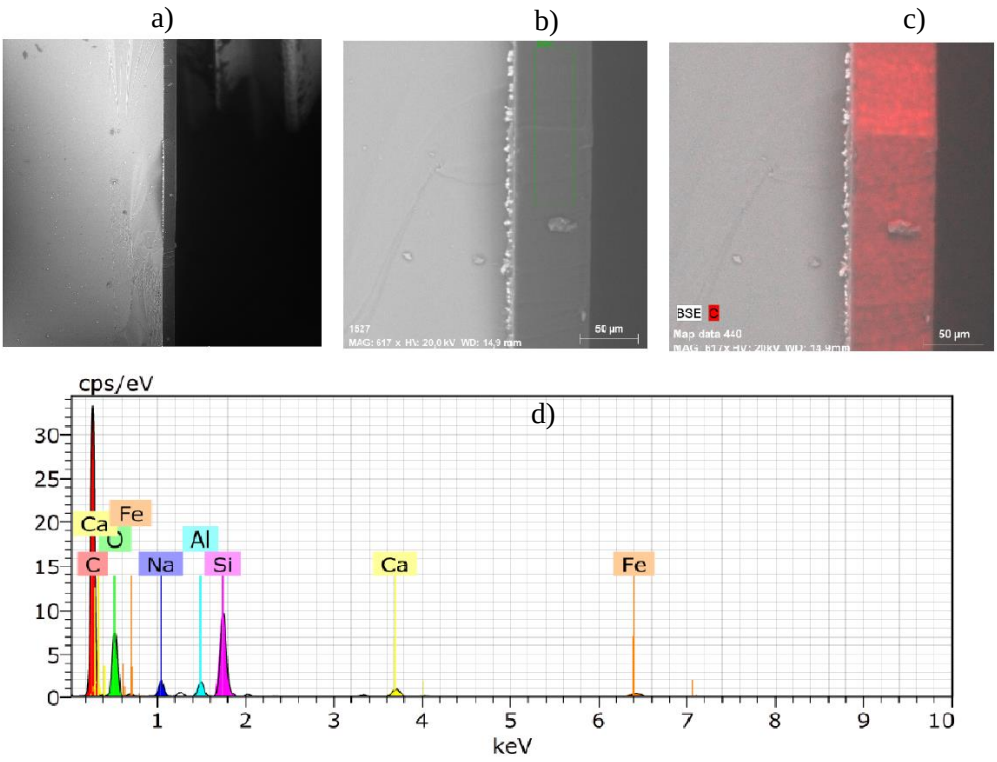


Figure 3: a) Microskopic analysis of the deffected sample 7 by SEM Vega3 Tescan -magnitude 150x, HV 20kV; b) X ray spectroscopy analysis - magnitude 617x, HV 20kV, c) X ray spectroscopy analysis- BSE C magnitude 617x, HV 20kV d) increased incidence of carbon cauesed probably by burn-through of applied layers

3.2. REACHED CONVERSION EFFICIENCY AND CURRENT-VOLTAGE CHARACTERISTIC

Initial measurement has shown efficiency of the created perovskite solar cells around 2 percent. The highest conversion efficiency was achieved in sample no. 1 (η_{MAX} = 2.46%); no.2 (η_{MAX} = 2.85%) and no.4 (η_{MAX} = 2.56%). Measurements were done through a solar simulator with source of light energy of 1000 W/m^2. Investigated solar cells generated values in average shown in Table I.

Parameters	I_{SC} [mA]	U_{OC} [mV]	I_{MAX} [mA	U_{MAX} [mV]	P_{MAX} [mW]	*FF* [%]	η [%]
Average value	0.439	570.228	0.289	366.565	0.109	41.749	1.817

Table 1: Averague value of parameterers of measured samples

For an example are in fig. 4 shown current-voltage characteristic of samples no.4, no.5 and no.6.

With a measurement during illumination the efficiency has increased to a certain value, then again has dropped. The reason is probably in the temperature of the sample during measurements (samples were rapidly heating). Samples were also measured consecutively in short intervals. The gradual degradation of the material, well-known phenomenon of perovskite solar cells, has occurred later. The conversion efficiency of the cells has decreased significantly one week after the measurements. Degradation of the perovskite solar cells is currently one of the biggest problem of these materials [3]. Subsequent research will focus mainly on preventing of the degradation by applying the appropriate interlayers between perovskite and its metal contacts. The Cr_2O_3 interlayers will be studied in the context of resistance of the perovskite material against environmental influences [3]. The Cr_2O_3 layer will be applied through magnetron sputtering equipment in the Department of Electrical and Electronic Technology of Brno University of Technology.

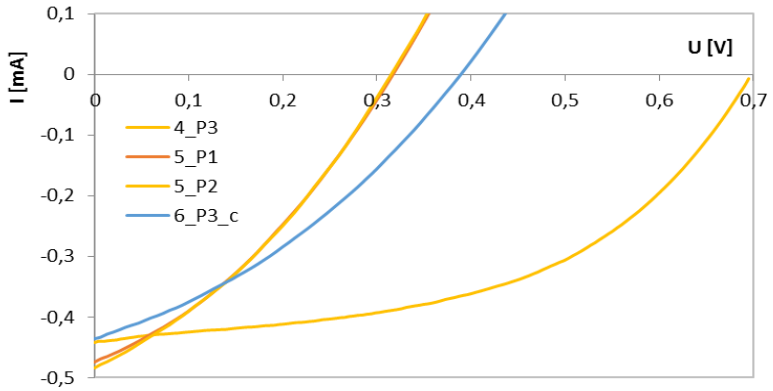


Figure 4: Current-voltage characteristic of solar cells

4. CONCLUSION

This work is aimed at optimizing the perovskite solar cells with synthehis of $CH_3NH_3PbI_{3-2}Cl_2$ through a mixture of CH_3NH_3PbI, PbI_2 and $PbCl_2$. In the perovskite solar cell was examined the influence of reactant ratio, time and annealing temperature during its preparation with an emphasis on the absorbation and stability of the used layers.

The first measurements of realized samples according to chosen procedure has shown an efficiency of peroskvite solar cells in the units of percent. The highest conversion efficiency was achieved in sample no. 1 (η_{MAX} = 2.46%); no.2 (η_{MAX} = 2.85%) and no.4 (η_{MAX} = 2.56%). Microscopic scanning of the sample number 7 has shown burn-through of layers during the manufacturing process (indicated by a very high amount of carbon contained in the sample).

Originally, there were perovskite solar cells prepared in combination with a liquid electrolyte, but there occurred rapid degradation due to dissolution of crystals of perovskite. Presented work aims to find the optimal method for the synthesis and preparation of peroskvit solar cell based on $CH_3NH_3PbI_{3-2}Cl_2$ /$PC_{61}BM$. The main idea of the following work is to achieve the highest quality and most stable structures of synthesized materials and to build the long-term stable solar cells with high efficiency of photovoltaic conversion.

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