DEVELOPMENT OF STABLE PEROVSKITE CELLS

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Abstract: The main purpose of the work is to find an optimal way for the preparation of stable perovskite photovoltaic cell. Ten solar cells have been created with the active area consisting of $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_{3-2}Cl_2$ solutions. It was concluded that the $CH_3NH_3PbI_{3-2}Cl_2$ structure is more stable against environmental influences because of chlorine addition. Supplementary experiments were done to confirm the moisture influence. During the research has been found that films formed in humidity with 15 % RH have a different structure than perovskite manufactured in dry glove boxes filled with nitrogen atmosphere. We are concluding that perovskite grains have unified and their volume has increased. These processes have had a positive impact on the efficiency and stability of the cells.

Keywords: Perovskite photovoltaic cells, stability of perovskite solar cells, impact of moisture on perovskite, incorporation of chlorine atoms into perovskite structure.

1 INTRODUCTION

Perovskite photovoltaic cells can be classified as hybrid organic - inorganic materials. Their general structure is shown in Figure 1. Perovskite structure can be understood as a positively charged atom **A** located in the center of the cube with the cations **B** at the corners of cube. The cube walls are then surrounded by the anions **X**.

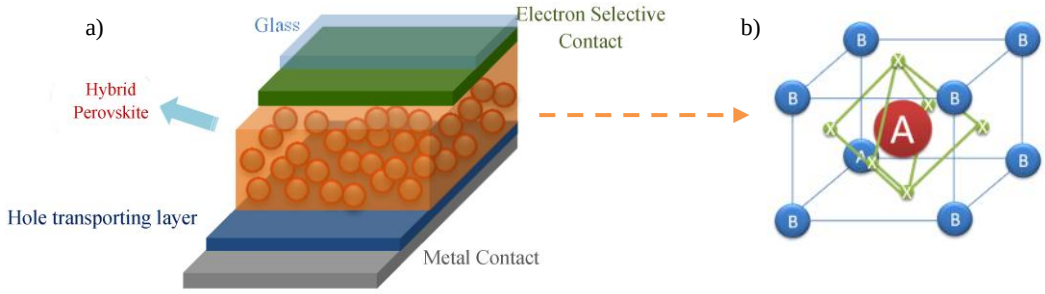

Figure 1: a) General perovskite solar cells structure[1]; b) Crystal arrangements of perovskites

The main problem of perovskite photovoltaic cells is their stability. The lifetime of silicon solar cells is almost 30 years. The lifetime of the perovskite solar cells is about a couple of months. Degradation of perovskite photovoltaic cells is not fully understood. Their main causes are known as the effects of humidity and impact of irradiance, but the physical and interlayer processes influencing the stability are not sufficiently explained [2].

The degradation of perovskite solar cell can be generally divided into an *extrinsic* degradation – external influences of oxygen, incident radiation, humidity, temperature and *intrinsic* degradation – influence of temperature and electric field inside the structure. Perovskite materials (eg. $CH_3NH_3PbI_3$) are very susceptible to the presence of oxygen and water and can degraded within the minutes, at most hours during the atmospheric influences [2]. One of the main reasons for reducing cell performance is the effect of moisture [3]. There are several theories that H_2O mole-

cules disturb perovskite causing its fading (due to the presence of NH_3 and PbI_2 formation after H_2O intrusion) [3]. Single molecule of water can cause material degradation. Moisture can decompose the hybrid organic-inorganic perovskite completely and release hydroiodic acid HI and methylammonium CH_3NH_2 [3].

2 PEROVSKITE SOLAR CELL MANUFACTURING WITH CHLORINE ADDITION

In total it was prepared 10 samples with composition:

- Cathode: vapor-deposited - Al
- Electron selective contact: $PC_{61}BM$ methyl-ester [6,6]-fenyl C_{61} butyric acid
- Perovskite layer: 5x $CH_3NH_3PbI_3$ and 5x $CH_3NH_3PbI_{3-2}Cl_2$
- Hole transporting layer: PEDOT:PSS (Poly3,4etylenedioxythiofen): poly(styrensulfonate)
- Glass: ITO (Indium Tin Oxide) In_2O_3-SnO_2

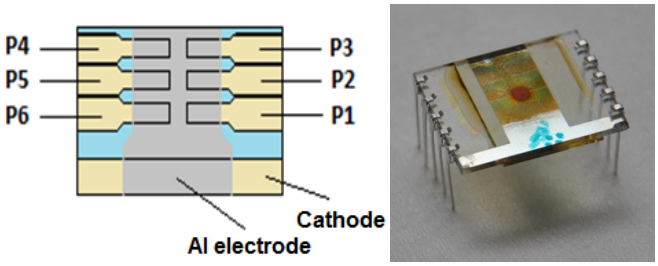

Figure 2: a) Pattern of the perovskite solar cell [4]; b) Perovskite solar cell sample 1

Interesting results have been achieved by chlorine addition to the active layer of perovskite. Comparing the structure $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_{3-2}Cl_2$, it was concluded that the $CH_3NH_3PbI_{3-2}Cl_2$ structure was after two weeks of an ambient environment exposure up to 25% more resistant. For the first-mentioned structure, the power output drop was approximately 75 % after 2 weeks, whereas the second structure has fallen only half of its original power output value.

This confirms the assumption about "reorganization" of the perovskite crystal structure. Smaller chlorine anions have created more compact structure more resistant to degradation. Chlorine anions also reduce the lattice constant, which is similar with the substitution of iodide using bromide [5]. Compact structure would decrease the sensitivity of the $CH_3NH_3PbI_{3-2}Cl_2$ material to moisture, light and temperature due to its higher binding constant compared to the $CH_3NH_3PbI_3$ structure.

Therefore, a deeper analysis including microstructural and crystallographic studies must be performed to confirm the origin of this observation. The rest of the article will focus on the influence of moisture on the perovskite structure.

3 INFLUENCE OF MOISTURE ON MANUFACTURED PEROVSKITE SOLAR CELL

In order to analyze the effects causing degradation of perovskite photovoltaic cells, it was necessary to create appropriate reference samples. Three samples of perovskite solar cells were manufactured with the structure ITO/PEDOT:PSS/$CH_3NH_3PbI_{3-2}Cl_2$/$PC_{61}BM$/Al electrode in 15 % RH (relative humidity) environment and three of them in dry box with minimal humidity (less than 1 ppm of H_2O). Perovskite sample 1 and its preparation can be seen in Figure 2.

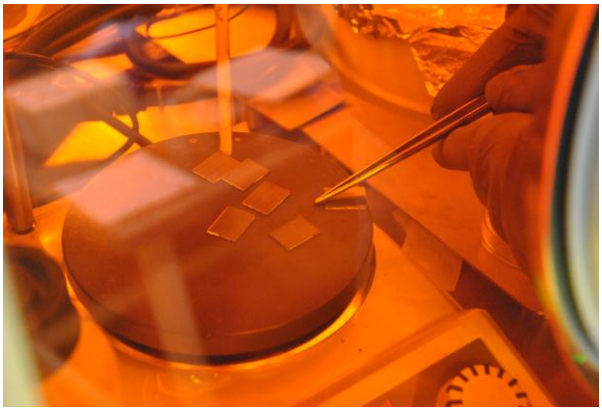

Figure 2: Preparation of perovskite solar cells in glove box

Moisture has significant impact on $CH_3NH_3PbI_{3-2}Cl_2$ perovskite layer. Because of hygroscopic nature of the methylammonium it has a crucial influence during perovskite crystal formation. Films formed in humidity with 15 % RH have different structure than perovskite manufactured in dry glove boxes with nitrogen atmosphere. Perovskite layer has a less continuous morphology and film formation was faster. The perovskite grains have unified leading to the enlargement of its volume. This may reduce the number of grain boundaries which forms a barrier to the current. The open – circuit voltage was also improved. For an observation of ongoing processes was done AFM microscope analysis, see Figure 3.

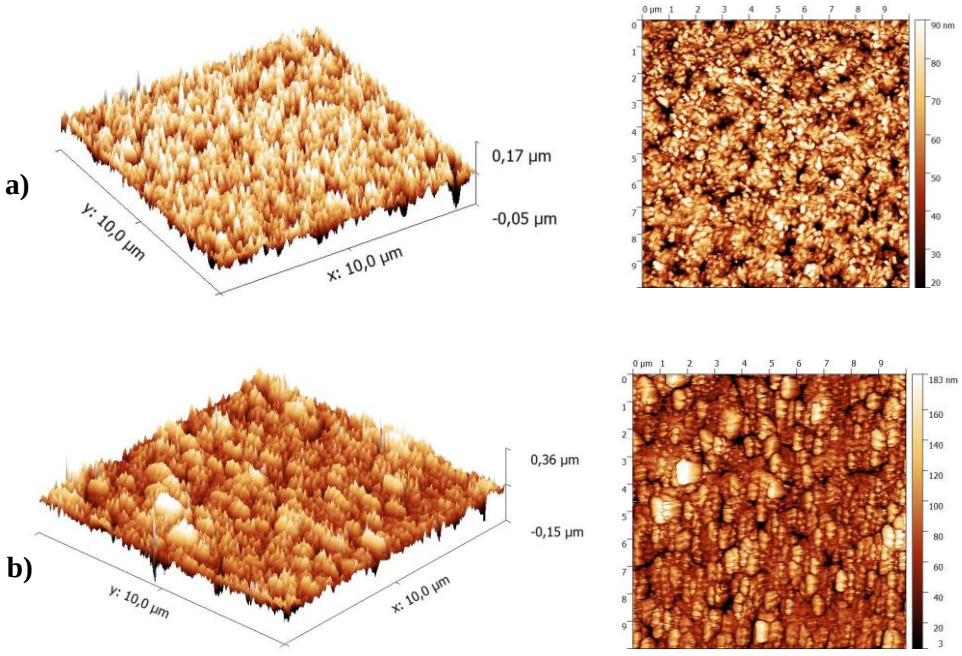

Figure 3: a) AFM microscopy analysis of active layer of perovskite solar cell where the moisture was not used during manufacturing process, **b)** AFM microscopy analysis of active layer of perovskite solar cell with perovskite applied at 15 % RH humidity

Other experiments were done to confirm the influence of moisture. An active perovskite layer of first cell was exposed to an inert atmosphere and the second one to the external influences of moisture and irradiation. The sample exposed to external influences significantly bleached, see Figure 4. Applied films has changed color more quickly in a moist atmosphere, in which they form faster.

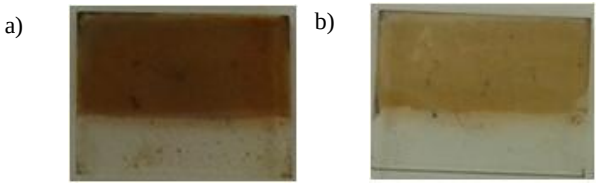

Figure 4: a) Sample with active layer formed under inert atmosphere, b) sample with an active layer exposed to a moisture and UV rays.

In the current-voltage characteristics, see Figure 5, can be seen that the impact of moisture is significant in the open-circuit voltage and also in the short-circuit current. Perovskite cell manufactured without moisture influences has open-circuit voltage of approximately 0.891 V (1_P2) and 0.919 V (1_P3). On the other hand, perovskites annealed in a humid environment have open – circuit voltage approximately 0.946 V (1_P4) and even higher 0.933 V (1_P5). Perovskites created in a moisture atmosphere have significantly higher short circuit current J_{SC}. This corresponds with higher power conversion efficiency of the cells 1_P2 and 1_P3, see Table 1.

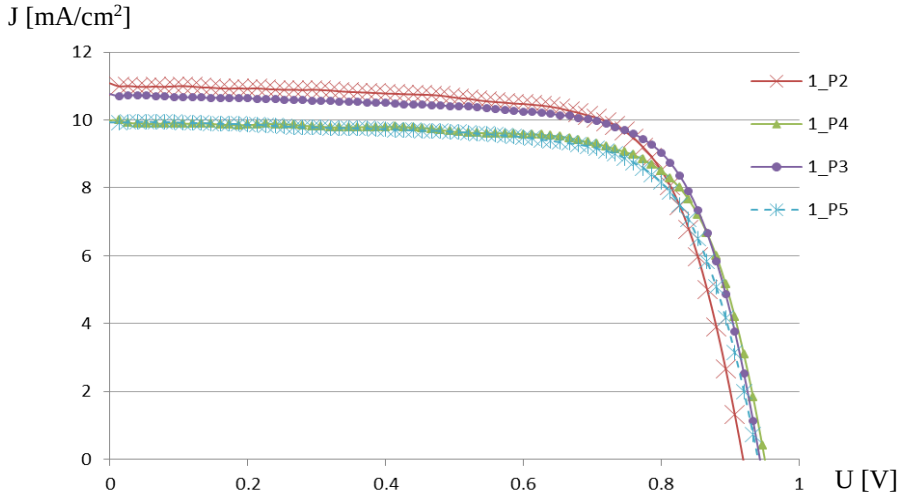

Figure 5: a) Perovskite solar cells manufactured in 15 % RH 1_P2; 1_P3 and perovskite solar cells manufactured with humidity less than 1ppm 1_P4; 1_P5

Device	J_{sc} [mA/cm^2]	V_{oc} [mV]	P_{mpp} [W]	*FF* [%]	η [%]
1_P2	11.08	891.67	0.33	70.92	7.12
1_P3	10.77	919.98	0.33	71.34	7.22
1_P4	9.99	946.73	0.27	64.72	5.95
1_P5	9.93	933.34	0.22	55.62	5.42

Table 1: Average parameters of manufactured perovskite solar cells

It is important to distinguish between manufacturing process and degradation of the perovskite film during moisture exposure. The presence of humidity changes the formation of the perovskite during the crystallization but also has a harmful effect on a crystallized film. Exposure to moisture after manufacturing process will decomposed methylammonium lead iodide. The unanswered question is whether a change of perovskite crystal formation is due to moisture atmosphere permanent or just a short-term affair. Further research will focus on this.

CONCLUSION

In total has been created ten solar cells. Five of them with $CH_3NH_3PbI_3$ perovskite structure and the rest with $CH_3NH_3PbI_{3-2}Cl_2$ structure. Photovoltaic cells with chlorine were more resistant against degradation. It was probably caused by more compact structure. Conversion efficiency of created cells were approximately 6 %. The best sample no.1 has reached promising 7.22 % value. To observe the influence of moisture were three samples manufactured in 15 % RH and three samples in an N_2 environment with minimal humidity environment.

An interesting phenomenon has occurred when were samples 1_P2; 1_P3 exposed to the moisture during manufacturing process. Conversion efficiency has increased to $\eta = 7.22$ % and 7.12 % value. The grains have unified which led to the enlargement of its volume, see Figure 3. The impact of UV rays and moisture was also observed in bleaching of an active perovskite layer, see Figure 4.

Moisture influence on the perovskite material and especially the effect of humidity during the perovskite fabrication is an important factor which should continue to be investigated. Moisture can be critical in the formation of high-quality perovskite films with the highest possible conversion efficiency. There is a wide variation of manufacturing conditions between the laboratories which are often not reported.

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