

# Atomic Force Microscopy Study of Cross-Sections of Perovskite Layers

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## Abstract

Improvement of methods for imaging of the volume structure of photoactive layers is one of the important directions towards development of highly efficient solar cells. In particular, volume structure of photoactive layer has critical influence on perovskite solar cell performance and life time. In this study, a perovskite photoactive layer cross-section was prepared by using Focused Ion Beam (FIB) and imaged by Atomic Force Microscopy (AFM) methods. The proposed approach allows using advances of AFM for imaging structure of perovskites in volume. Two different types of perovskite layers was investigated: FAPbBr<sub>3</sub> and MAPbBr<sub>3</sub>. The heterogeneous structure inside film, which consist of large crystals penetrating the film as well as small particles with sizes of several tens nanometers, is typical for FAPbBr<sub>3</sub>. The ordered nanocrystalline structure with nanocrystals oriented at 45 degree to film surface is observed in MAPbBr<sub>3</sub>. An optimized sample preparation route, which includes FIB surface polishing by low energy Ga ions at the angles around 10 degree to surface plane, is described and optimal parameters of surface treatment are discussed. Use of AFM phase contrast method provides high contrast imaging of perovskite structure due to strong dependence of phase shift of oscillating probe on materials properties. The described method of imaging can be used for controllable tuning of perovskite structure by changes of the sample preparation routes.

## 1. Introduction

Number of papers related to development of organic-inorganic perovskite solar cells (PSC) has been increasing in geometric progression since 2009 [1]. Recently, metal halide perovskite solar cells (PSC) with general formula ABX<sub>3</sub> achieve power conversion efficiency (PCE) of 22% [2], which exceed efficiency of an average silicon solar cell. Methylammonium (MA) and formadinium (FA) are most widely used cations utilized in light absorbing layers of PSC, which demonstrate strong absorption in visible and near IR spectral regions up to 780 nm [3] and very large diffusion length of charge carriers in microcrystalline films (0.4–1 microns). Iodide and bromide are most efficient anions, which utilized for tuning band gap in the range 1.4–2.2 eV in different stoichio-

metric compositions. MAPbBr<sub>3</sub> (CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>) – methylammonium lead bromide with band gap E<sub>g</sub>~2.2 eV is the basic material for synthesis organo-inorganic hybrid perovskites used in field emission transistors, green LED etc.

Despite high efficiency, the modern PSCs have large problems with high sensitivity to humidity level, low thermo- and photostability [4–6]. Instability of PSC in humid atmosphere can be reduced by encapsulation, however thermo- and photostability are completely determined by materials of PSC, in which photons and heat promote degradation of perovskite layer. The highest thermal instability is observed in most promising cation MA. Perovskites with this cation are crystallized at temperature 100 °C and under working conditions of PSC are decomposed into initial precursors MAI – PbI<sub>2</sub> at temperatures 60–80 °C. For solving this problem the hybrid composition FA-MA or single cationic FA are used, since FA has higher

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transition temperature to photoactive “black”  $\alpha$ -phase at 170 °C and enable long annealing at 100 °C, which is enough for PSC operational conditions [7]. Formamidinium bromide (FABr ( $\text{CH}_3(\text{NH})_2\text{Br}$ )) is utilized mainly as basic material for mixed perovskites ( $\text{FAPbIyBr}_{3-y}$ ). Material  $\text{FAPbBr}_3$  with its band gap of 2.23 eV is a promising candidate for using it in tandem solar cells.

One of important directions of investigation of PSCs is establishing structure-property relationships in these samples, which helps for better understanding processes of phase transition and degradation as well as finding methods for stabilization of PSC [8, 9]. The quality and type of information obtained from imaging the perovskite layer cross-section depends strongly on methods of sample cross-section preparation and imaging. The most widespread method used for imaging PSC cross-section is mechanical cleavage and following SEM imaging of obtained cross-section [9–10]. Disadvantage of this method is not controlled damage of the sample and not sufficient regular resolution of SEM as well as limited number of available methods. The use of focused ion beam (FIB) milling for cross-section preparation allows for more reliable and reproducible SEM data [11]. Here we describe and apply another combination of methods for imaging of perovskite cross-section, which is based on the use of FIB milling for cross-section preparation and following AFM measurements of it. Previously, this method was used for investigations of polymer solar cells [12]. Combination of FIB and AFM enable to observe structure in volume, allowing high-resolution mapping of different properties visualized by AFM methods, including different local electrical properties [12]. Despite its obvious advantages, FIB-AFM approach for study of sample structure is not widely used. In this article the sample preparation route is described and two different perovskite samples  $\text{FAPbBr}_3\text{B}$  and  $\text{MAPbBr}_3$  were imaged by the proposed method.

## 2. Experimental section

### 2.1. Material synthesis

The samples of perovskites  $\text{FAPbBr}_3$  and  $\text{MAPbBr}_3$  were prepared in several stages: preparation of basic solution (concentration of 1 M in dimethylformamide), spin-coating with crystallization in antisolvent (toluene), annealing at 100–120 °C during 10–20 min [8]. The substrate was silicon wafer with size of 10×10 mm.

### 2.2. Characterization

The dual beam system Quanta 3D FEG (FEI) with Schottky cathode, combining focused Ga ion beam and SEM was used for sample milling and preparation of perovskite film cross-section. The device also equipped by gas injection system for Pt deposition by decomposition of gas precursor under electron or ion beam. Everhard-Tornley detector was utilized for secondary electron imaging. The atomic force microscope SMART1000 (AIST-NT) was used for imaging obtained cross-section in tapping mode.

## 3. Results and discussion

The most important is volume structure of PSC and perovskite layer between electrodes. Direct visualization of perovskite structure between electrodes requires cleavage of the PSC sample in order to get device cross-section. Another, more advanced approach is the use FIB milling. There are different methods of imaging structure of cross-section of perovskite layer. The most widespread one is SEM. The atomic force microscopy is another technique to study sample surface and its local properties by large variety of methods. The advantage of AFM is better regular resolution (~1 nm) and high contrast imaging (e.g. phase contrast) caused by high sensitivity to mechanical, electrical and magnetic properties of the samples. However, the use of AFM requires relatively flat surfaces due to limited z-scanning range and influence of topography on measured signal through different contact area. In order to use advantages of AFM for imaging the structure of perovskite in volume the careful FIB milling is required.

The scheme of the proposed measurements is shown in Fig. 1. A dual beam device used in experiments allows for FIB milling of samples and SEM imaging of cross-sections. After milling, the sample should be transferred to AFM and place of interest should be found in optical microscope. A general procedure of sample preparation is similar to one suited for lamella preparation for transmission electron microscopy measurements.

The first step of surface preparation for AFM measurements is deposition of electron beam deposited (EBD) Pt layer to protect perovskite surface from ion beam during etching. The thickness of the EBD Pt layer should be enough to protect perovskite layer from FIB damage. It also serves as support when AFM measurements on the cross-section are performed, moving edge of the sample far

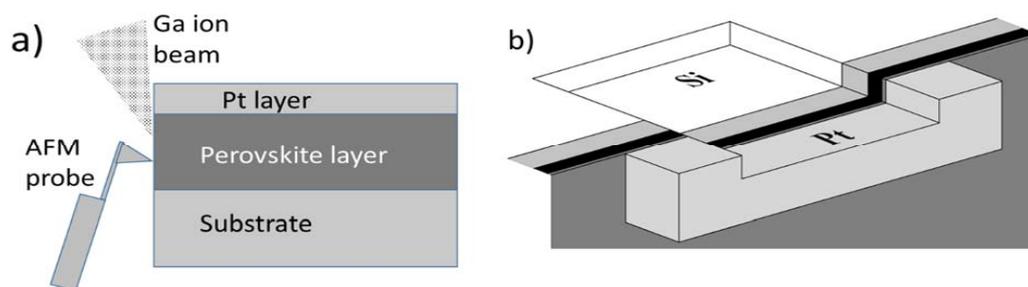


Fig. 1. (a) – Scheme of measurements; (b) – cross-section of layered sample after polishing.

from cross-section. In order to make initial EBD Pt layer thicker, the FIB assisted Pt deposition was performed after EBD. We have deposited Pt layer with thickness of approximately 1 micrometer and lateral size  $(10\div 30)\times 2$  micrometers. During preliminary etching of surface by Ga ions with the energy of 30 kV modification of the etched surface by ions takes place. In order to avoid such unwanted destruction the additional surface treatment is required. It was found that treatment of the surface by low energy Ga ions (2 kV) at low angle (less than  $10^\circ$  to the etched surface) improves quality of obtained surface, making it suitable for AFM imaging. In case of polycrystalline structure, the selective etching of the surface takes place, which additionally improves contrast of AFM topography image. The optimal time of this additional treatment (denoted below as “polishing”) is around 10 sec, longer time leads to worse quality of the surface. Figure 2 shows AFM topography images of the two surfaces with cross-sections of FAPbBr<sub>3</sub>

layer before and after polishing. A significantly better quality of the image after polishing with clear and reproducible structure is observed in Fig. 2b. From comparison of Fig. 2a, c and 2b d, the reduced surface bump near the left side of photoactive layer in polished sample is seen. At the same time, color bars and cross-sections in these images indicate up to two times deeper placement of the polished perovskite surface under sample surface. This fact means that thin layer of material was removed from both perovskite layer and background surface. Thus, polishing by low energy Ga ions at small angles ( $\sim 10^\circ$ ) to the surface plane makes sample surface smoother and removes amorphized layer destroyed by initial Ga beam, which hides original perovskite structure. Appearance of particles on surface of perovskite layer in Fig. 2b, d is, most probably, a result of selective etching of heterogeneous surface by Ga ions, after initially amorphized layer (Fig. 2a, c) was removed by polishing.

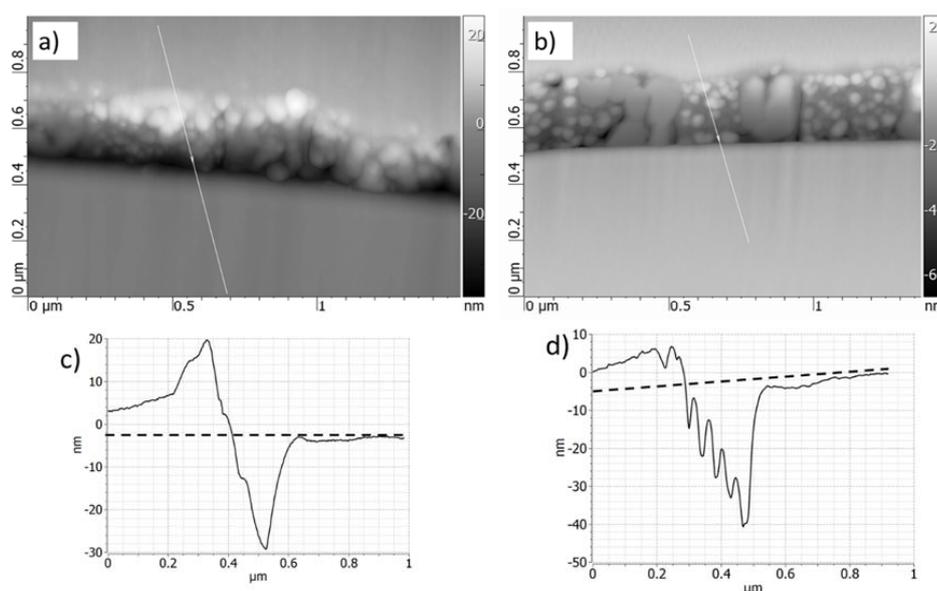


Fig. 2. AFM topography images of FAPbBr<sub>3</sub>: before (a, c) and after (b, d) polishing by Ga ions at 10 degrees. Topography (a, b) and corresponding cross-sections of topography images (c, d). Dashed lines approximately correspond to the surface plane.

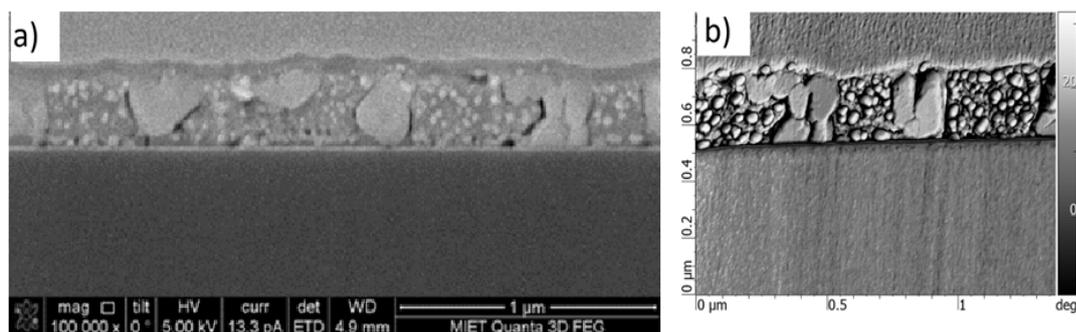


Fig. 3. Cross-section of FAPbBr<sub>3</sub> film: (a) – SEM image; (b) – AFM phase image.

Figure 3 demonstrates cross-section of FAPbBr<sub>3</sub> layer on silicon imaged by SEM and AFM. A porous FA film consist of PbBr<sub>2</sub> and PbBr<sub>3</sub> crystallites of different sizes. Some of them penetrate film completely. The smaller domains are placed between large crystallites. Such a not uniform structure is explained by fast non controlled crystallization of FA at room temperature. Significant improvement of resolution and contrast obtained by AFM in comparison with SEM is clearly visible. At the same time, a convolution effects due to finite size of the AFM tip are also seen, which lead to increased sizes of small features. AFM phase images obtained in tapping mode in repulsive regime are influenced by both topography features due to feed-back error and material properties via dissipation processes, which provides high contrast visualization. The regular resolution of AFM in tapping mode is about 1 nm. The large crystallites in film appear most probably

due to sample preparation (solvent evaporation after spin-coating and/or annealing) as well as following degradation, since no encapsulation was used for these samples. The voids around these crystallites, which are visible in Fig. 3, are cracks growing inside film.

Second sample imaged by same way was cross-section of MAPbBr<sub>3</sub> (Fig. 4). The structure of this sample is completely different and consist of crystallites with similar size of ~100–200 nm, which are ordered at the angle close to 45°. Such a uniform crystalline structure of MAPbBr<sub>3</sub> is responsible for improved electrical properties of this material. The possible reason of drastic difference between MAPbBr<sub>3</sub> and FAPbBr<sub>3</sub> is different influence of annealing.

Better resolution provided by AFM phase image in comparison with SEM is explained by small tip-sample interaction area in tapping mode.

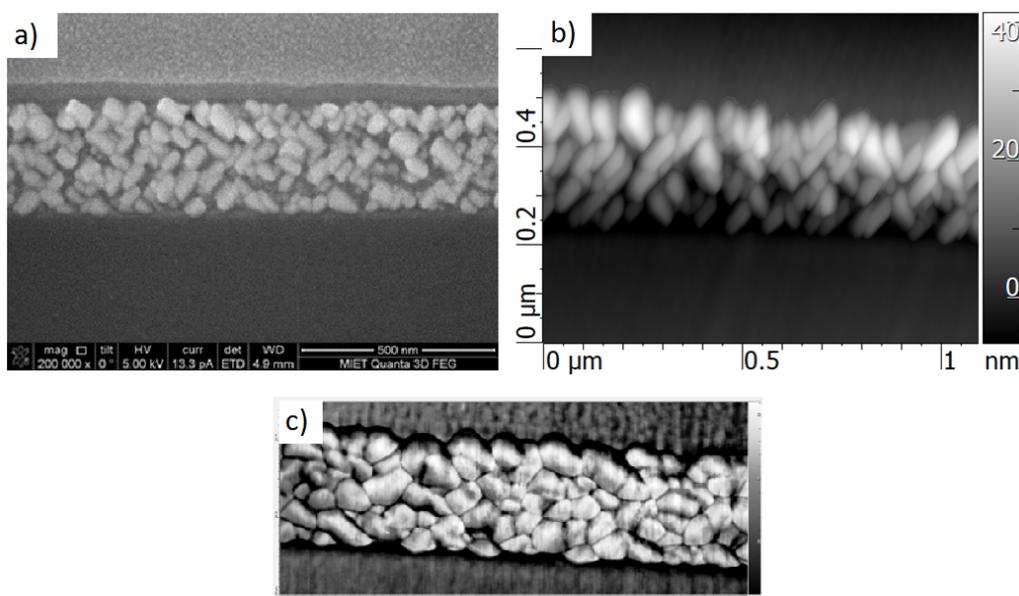


Fig. 4. Cross-section of MAPbBr<sub>3</sub> film: (a) SEM image, (b) AFM topography, (c) AFM phase image. (b) and (c) have same x range.

Sensitivity of oscillating cantilever phase shift to sample properties additionally provides high contrast images revealing variations of properties inside crystallites (Fig. 4c). The next step in investigations of perovskite materials in volume by proposed method should be the use of different electrical methods of AFM (surface potential, current distribution and electrostatic forces etc.) as well as high-resolution optical methods (scanning near-field optical microscopy, nano infrared microscopy, tip enhanced Raman spectroscopy).

#### 4. Conclusions

In this article, the procedure of perovskite film preparation by FIB for AFM investigation of perovskite structure was described. It was found that additional treatment of surface with cross-section of perovskite layer by low energy Ga ions (2 kV) at angles around or less than 10 degree is necessary to obtain not modified structure. Volume structures of two different perovskite materials MAPbBr<sub>3</sub> and FAPbBr<sub>3</sub> were imaged by proposed method. AFM imaging of perovskite layer cross-section reveals not uniform structure inside FAPbBr<sub>3</sub> and highly ordered crystallites in MAPbBr<sub>3</sub> film. Better resolution of FIB-AFM approach was demonstrated in comparison with SEM imaging. Variations of properties inside crystallites of MAPbBr<sub>3</sub> were discovered by AFM phase imaging. The main disadvantage of AFM imaging of perovskite layer cross-section in comparison with SEM is convolution effect.

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