공학석사 학위논문

하이브리드 금속-유기 페로브스카이트 열화 현상에서 나타나는 표면 전하 재분배와 군집현상

Anomalous charge redistribution and appearance of polarization domain on the surface of degrading hybrid metal and organic halide perovskite

2018 년 8 월

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지도교수 최 만 수

이 논문을 공학석사 학위논문으로 제출함

2018년 4월

서울대학교 대학원

기계항공공학부

방 기 준

방기준의 공학석사 학위논문을 인준함

2018년 6월

위 원 장 이 정 훈

부위원장 최 만 수

위　　원 전 누 리

Anomalous charge redistribution and appearance of polarization domain on the surface of degrading hybrid metal and organic halide perovskite

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Mechanical engineering
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Abstract

Although metal and organic halide perovskite solar cell has efficiency comparable to record high silicon solar cell, its stability under illumination is critical problem in commercializing the photovoltaic device. Recently, charges along grain boundary was reported to be the cause of degradation of perovskite film. This article explains how perovskite lattice structure and fabrication process. It is followed by the notion that a large degree of freedom when generated arises from its defect tolerance structure property. To study how defects are dispersed on surface, electrical Force Microscopy (EFM) which is embed in atomic force microscopy was employed. EFM can effectively extract electrical signal from topography signal which enables study of charge and polarization on the surface of hybrid metal and organic halide perovskite (HHP). Polarization domain was observed under external bias and charges redistributed along polarization domain when bias was changed properly. In addition, surface potential was in-situ scanned continuously so that we can unravel degradation mechanism. In particular, polarization domain was spotted either under bias or light and gave pictures of degrading $MaPbI_3$.

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keywords : perovskite, EFM. polarization, charge, surface potential

Student Number : 2016-28866

Contents

Chapter 1

Introduction

1.1. Research objective

1.1. Research objective

Hybrid metal and organic halide Perovskite soared as new candidate for light harvesting material in solar cell device. Efficiency of this novel material has been reported to exceed twenty percent which is comparable to the highest record. However, light induced degradation of Perovskite film stacked in photovoltaic device is a catastrophic problem on the way of stabilizing the device. Below picture was taken every 8hours while the photovoltaic device was maintained under light in ambient air.

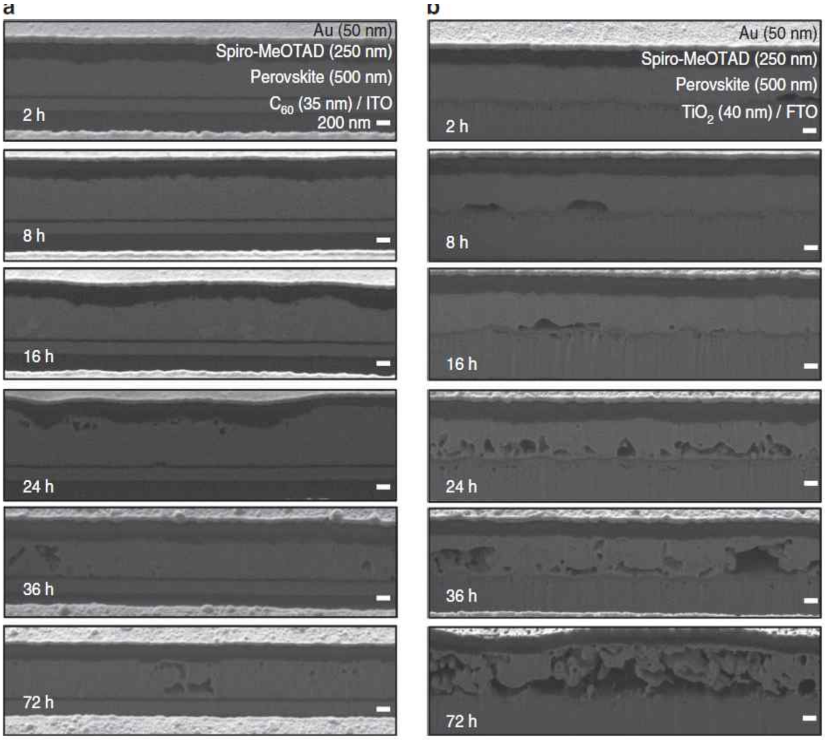


Figure 1 Degradation of perovskite film in solar cell device. Cross section image taken by Scanning electron microscopy, ref[1]

Compositions of air was also proved to be critical in degrading process of perovskite film. Nitrogen state air(99%) did not give rise to considerable change in optical band gap of the material. Whereas in high humid air, rate of degradation propelled and was completely within 2 days. Following graph compares the rate either in dark or under illumination with respect to humidity.

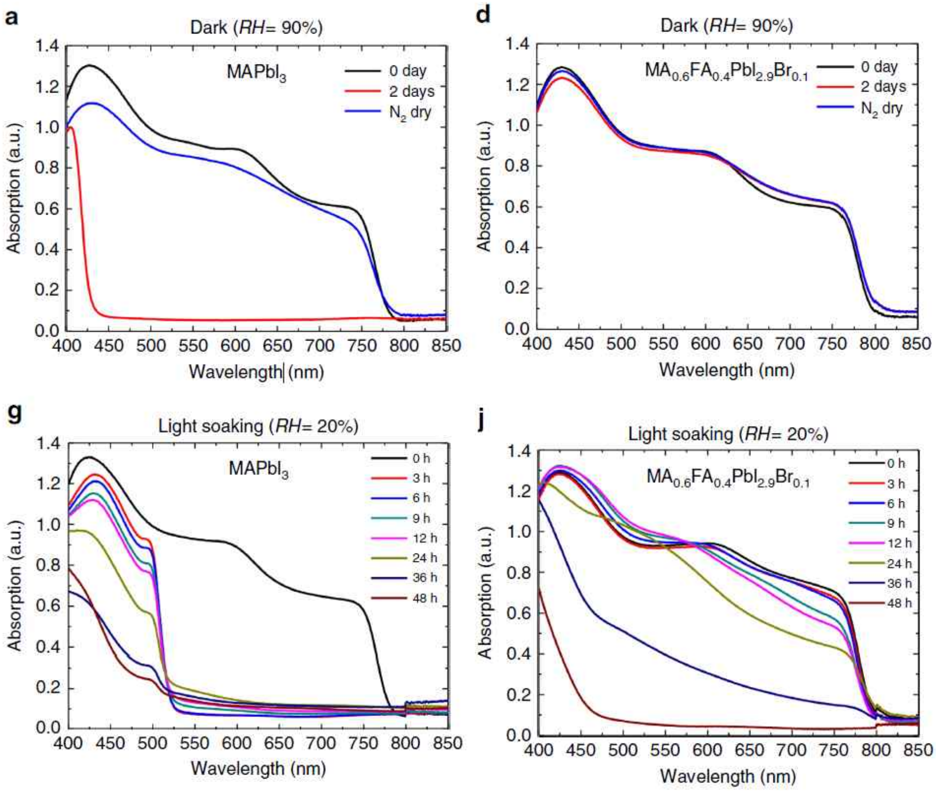


Figure 2 Change in light absorbance of Perovskite film in dark (a), (d) and under light (g) and (j), ref[1]

Having observed the surface of degrading Perovskite film with Scanning electron microscopy, boundaries of grain was seen to where topography initially tear down. In order to elucidate particulars along grain boundary, atomic force microscopy was employed for mapping surface potential.

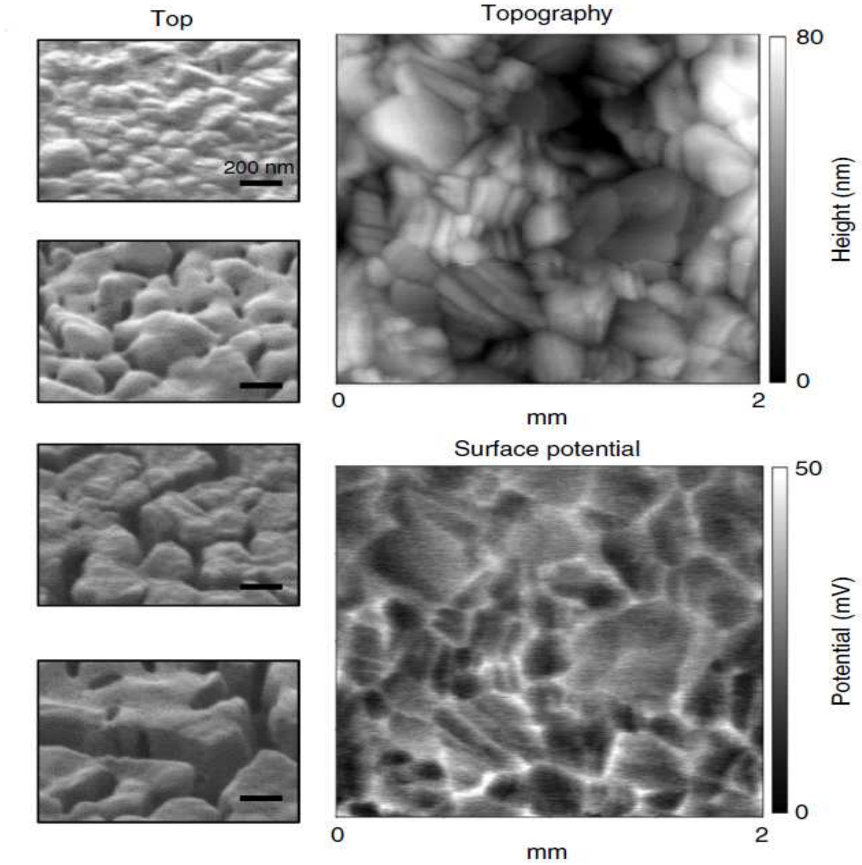


Figure 3 First column represents change in surface taken by SEM as times past and also shows the film degraded mainly along grain boundary. Second column is surface topography and surface potential. ref[1]

Here I want to propose dynamics of charges along grain boundary should have something to do with degradation mechanism along with device performance. Scientifically speaking, grain boundary is where defects prevail and banding of electronic structure takes place. Violation of periodicity in lattice chain gives birth to abnormal charge distribution and phenomenon. In addition to this, low activation energy for crystallization gives rise to increase in degree of freedom in crystallization process.

Although many of scientists have attempted to understand this, they ended up with more perplexing puzzle since light based spectroscopy and microscopy created different types of degradation on sample. To prevent this undesired phenomenon, atomic force microscopy was used in a novel way to unravel science behind this irreversible process with expecting it could become technology for centuries to come.

Chapter 2

Theory & background knowledge

2.1 Perovskite lattice structure

2.2 Fabrication process

2.3 Electrical Force microscopy

2.1 Perovskite structure

Crystal structure is paramount of importance in understanding degradation mechanism since its shape and geometry on surface as well as in bulk completely changed as it is proceeded. 2.1 chapter will be devoted to explaining electronic structure and polarization property based on Perovskite structure. Next page will be shown two possible lattice structures of Perovskite according to XRD data in figure 4.

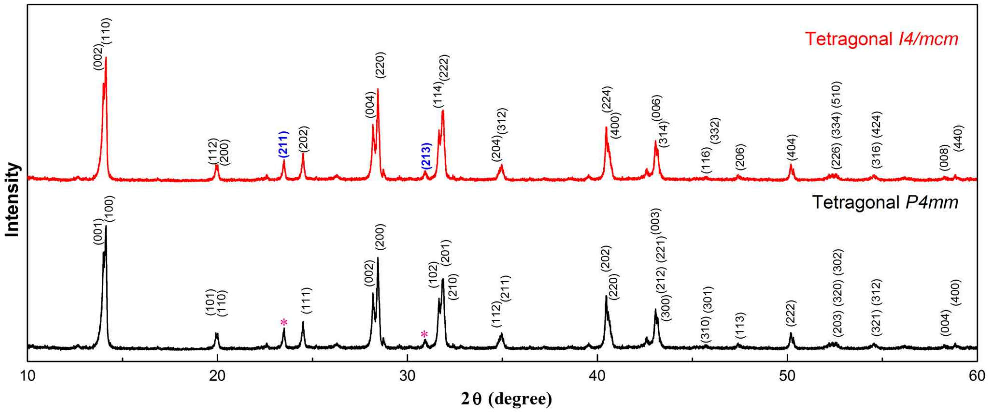


Figure 4 X-ray Diffraction microscopy of power Perovskite and possible space groups of lattice are tetragonal I4/mcm and tetragonal P4mm, ref[2]

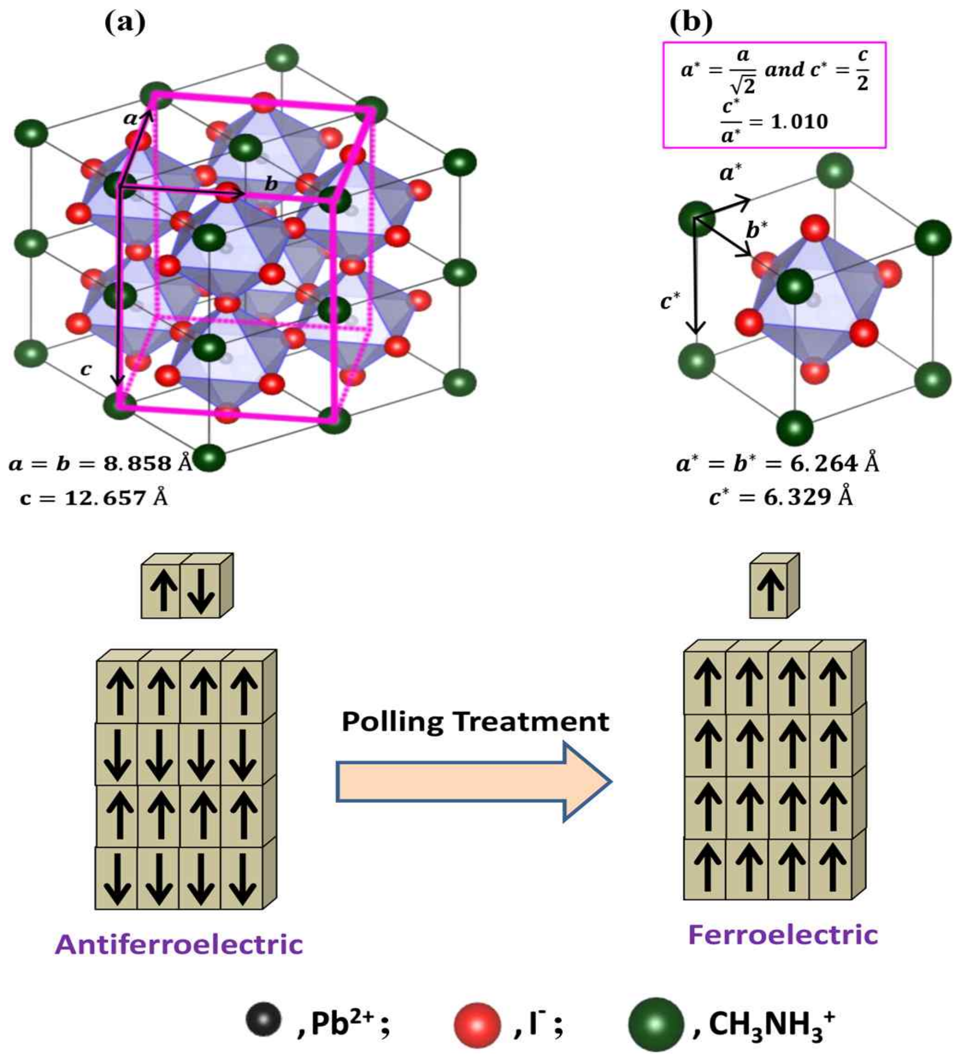


Figure 5 (a) I4/mcm unit cell and super lattice 4-ABX3 holds antiferroelectric nature of the lattice and (b) P4mm (disordered 1-ABX3) unit cell presents ferroelectricity of Perovskite, ref[2]

It was reported that local dipole direction can be aligned in parallel by poling effect, ref [2] Polling effect is driven by light and octahedron gets disordered so that organic tetragonal can become unit cell.

Disordered octahedron can be quantified by tolerance factor. Tolerance factor, t, is defined by ion radius of A, Iodide, and X, lead. Equation is as following.

Equation 1

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

Since the structure tolerates distortion, degree of freedom when the crystallization takes place has increased. Following diagram plots valence band shift depending on tolerance factor. Region (I) is where I/Pb is allowable and (ii) is progress toward (iii) PbI_2 formation.

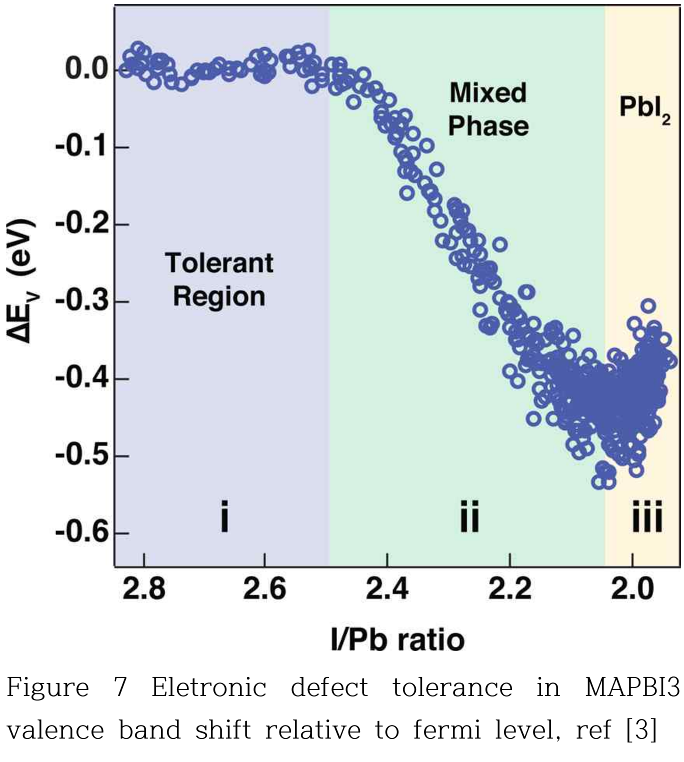


Figure 7 Eletronic defect tolerance in MAPBI3 valence band shift relative to fermi level, ref [3]

2.2 Fabrication process

Mixing methylammonium iodide and lead iodide with solvent dimethyl formamide and solvent dimethyl sulfoxide is legitimate way to produce uniform solution. It is followed by applying tens of micro-liter solution on top of extremely-cleaned and ozone treated substrate. Then, dropping about milli-liters of ether from the top the substrate rotating around 3000 rpm. Then, the sample is ready to crystallize and coated uniformly. Placing the specimen on hot plate at 100℃ for few minutes generate polycrystalline film as thin as hundreds of nanometers. The below image shows well enough.

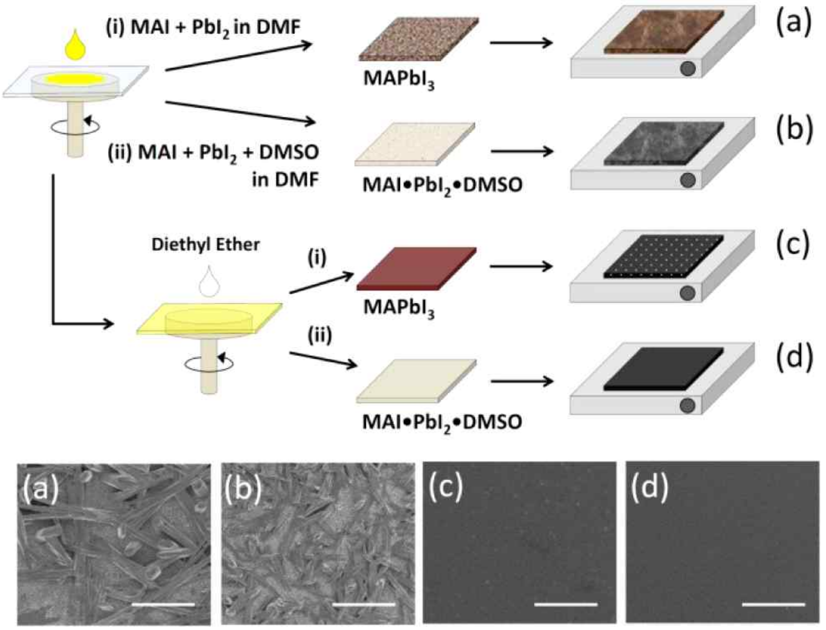


Figure 8 Developments of spin coating method (a), (b) were carried out without dripping anti solvent and (c),(d) with ether as anti solvent, ref[4]

Homogeneous film was coated and it is illustrated in the figure 8 and figure 9 (a), (b).

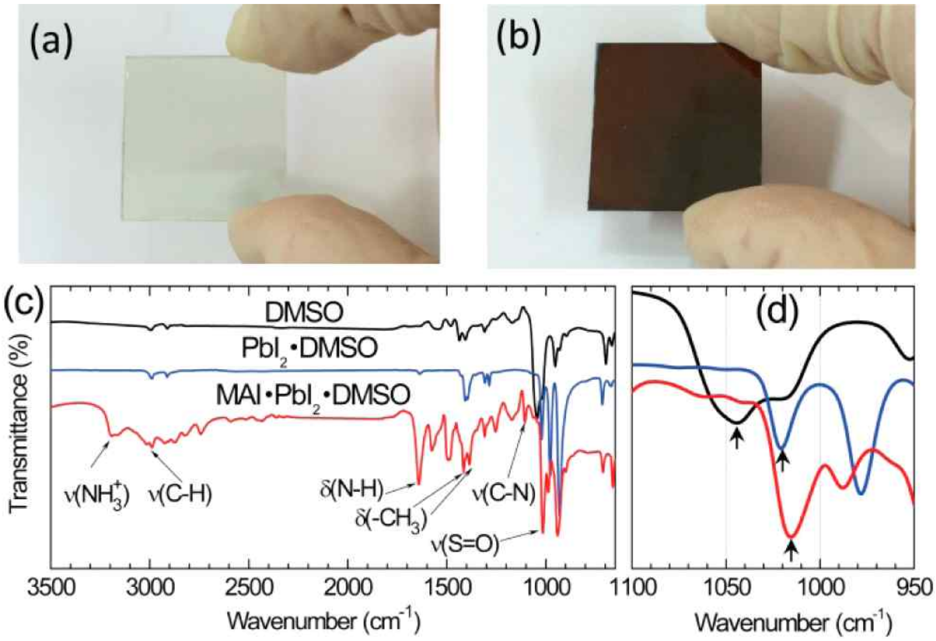
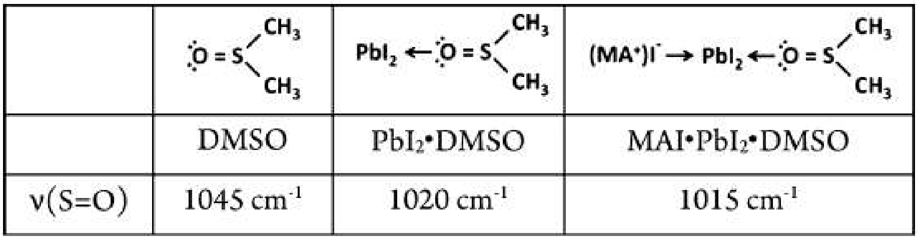


Figure 9 (a) Transparent film indicates adduct of PBI2 with Lewis base DMSO and iodide in MAI. (b) Annealed film and c) Fourier transform infrared spectrometer of adduct phase (d) highlighed wave number region, ref[4]

An adduct (from the Latin adductus, "drawn toward" alternatively, a contraction of "addition product") is a product of a direct addition of two or more distinct molecules, resulting in a single reaction product containing all atoms of all components. The resultant is considered a distinct molecular species. [wikipedia]

It is reported that PbI2 is Lewis acid since it can bear a pair of electrons from other molecules like oxygen, nitrogen and sulfur containing bases. If the pair of electrons is moved from base to acid, adduct can be formed between Lewis base and Lewis acid. [ref 4] As PbI2 is mixed with DMSO, it favorably forms adduct by bridging O atom and PbI2 since S=O bonding holds large polarity. MAI is also a strong donor and it is likely to create another adduct boding so that three different molecules can behave like one molecule. In addition, the solubility of PbI2 is greatly enhanced when MAI is added.

This network can be studied with fourier transform infrared spectroscopy and it is grounded on harmonic motion for diatomic model.

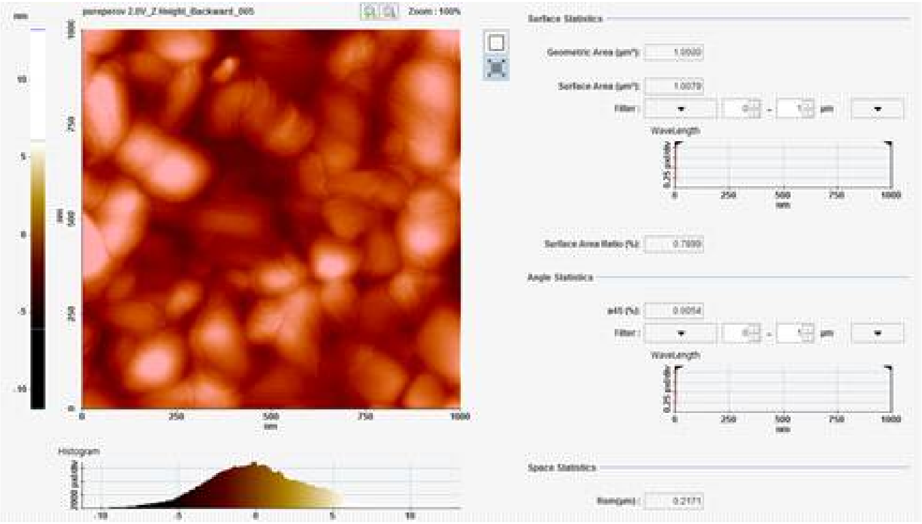


	DMSO	PbI_2•DMSO	MAI•PbI_2•DMSO
ν(S=O)	1045 cm^{-1}	1020 cm^{-1}	1015 cm^{-1}

Figure 10 Vibrational frequency change in (a) S=O bonding when (b) Lewis acid is added and along © with MAI, ref[4]

Since ether is not miscible with DMSO and dissolves DMF completely, it can effectively make homogeneous adduct all across the substrate. DMSO evaporates quickly when the substrate is kept at higher temperature. It starts to crystallize at around 100 degree Celcius.

Considerable amounts of defects is tolerable in crystallization, its electronic structure are heavily dependent on the condition it is created. Accordingly, it is expedient to estimate the amounts of defects and how they are dispersed on the surface of spin coated perovskite.



Surface Statistics

Geometric Area (µm²): 1.0000

Surface Area (µm²): 1.0079

Filter: 0 - 1 µm

Surface Area Ratio (%): 0.7899

Angle Statistics

ø45 (%): 0.0054

Filter: 0 - 1 µm

Space Statistics

Rsm(µm): 0.2171

Figure 11 Grain boundary is well illustrated in image taken by atomic force microscopy.

‘

2.3 Electrical Force microscopy

It is still at elementary stages in understanding relationship between surface defects and optoelectronic properties of the material. This article suggests atomic force microscopy (AFM) for powerful tool in disclosing this relation. First chapter accounts for principles of electrical force microscopy installed in AFM, which is followed by dynamics of crystallization. The last chapter describes actions of charges on the exterior region of HHP.

For scanning topography of surface, frequency variation around first resonance frequency was approximated as following where F is force exerted on the cantilever and k stands for spring constant.

Equation 2

$$\triangle f_1 \simeq f_1 \frac{\partial F}{k \partial z}$$

Electrostatic force of materials is built on its intrinsic electron energy levels constructed by its overlaps of elemental orbital. Namely, it can be considered as fermi-energy level or quasi-electron energy level. Relative energy difference between sample and tip of Atomic force microscopy will be simplified to U_{Dc} in this paper.

By superimposing on U_{DC} an alternating current of frequency w with amplitude of U_{AC},electrostatic force, Fes can be separated from signal of topography. Denoting potential of stationary charge as CPD (contact potential difference), which is mainly caused adsorbates and oxidation effect, three spectral components of Fes will be obtained as following.

Equation 3

$$F_{d\cdot c} = -\frac{\partial(C)}{\partial(z)}\left(\frac{1}{2}U_{d\cdot c} - CPD\right)^2 + \frac{U_{a\cdot c}^2}{4}$$

Equation 4

$$F_w = \frac{\partial C}{\partial z}(U_{d\cdot c} - CPD)U_{a\cdot c}Sin(wt)$$

Equation 5

$$F_{2w} = \frac{\partial C}{\partial z}\frac{U_{a\cdot c}^2}{4}cos(2w)$$

where C is capacitance between cantilever and the sample. Notably, frequency of each of the terms are different from one another.

2.3.1 Frequency Mode of EFM

CPD can be measured in two technical ways. Firstly, change in amplitude of the cantilever at w is a direct measure of magnitude of the static force. The other mode is detecting gradient of the force by observing the variations in frequency w of the cantilever oscillation.

Since the first mode is proven to be heavily affected by geometry of the tip by Kikukawa [1], this paper will be based on frequency mode of electrostatic force microscopy to exclude unnecessary effect.

Equation 5

$$\triangle f_1(w) \propto \frac{\partial F_w}{\partial z} = \frac{\partial^2 C}{\partial z^2}(U_{d\cdot c} - CPD)U_{a\cdot c}\sin(wt)$$

As represented in equation, unless z be fixed at constant height, second derivative of capacitance will also be included in equation 5. To do the job, appropriate frequency range of w should be chosen. The lower limit of w is determined by whether the cantilever begins oscillating On contrary, the coupling between topography and CPD becomes decreased when frequency further increases. This tendency can be induced by decreasing Uz at increasing frequency w in figure 1.

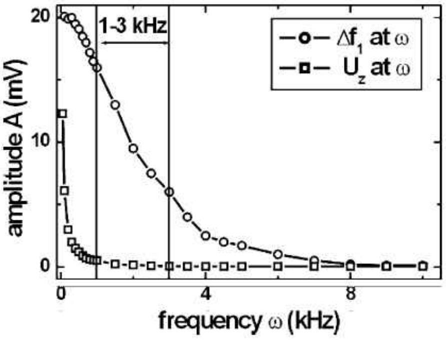


Figure 12, ref [5]

Meanwhile, the upper limit of frequency range is governed by bandwidth of the modulator in circuit system. The width drawn in figure 1 shows the range of frequency in which amplitude of electrostatic force falls off. Apparently, the oscillation of piezo voltage, Uz, attenuates at higher rate with respect to frequency. Accordingly, topography and surface potential can be scanned at the same time without interfering each other.

Chapter 3

Data and analysis

3.1 Redistribution of charge under illumination on surface of film

3.2 Charge redistribution and degradation

3.1 Redistribution of charge under illumination on surface of film

3.1.1 Ions and electrons

Defects is essential in understanding deviations of intrinsic material property such as band gap and electric polarizability. This is largely because defect is where certain ions are at absence and electronic structure is distorted from that of defect free region. On surface of the material, defect is predominantly distributed and our focus of research is to elucidate charges.

Grain boundary necessarily accompanies defects, which is open space for charges. As demonstrated in figure 13b, several bright jumps are situated particularly along grain boundaries (13a). These jumps are at not distinctive in figure 13c. EFM phase is a measure of polarization directions and implies these jumps do not deviate from neighboring polar directionality.

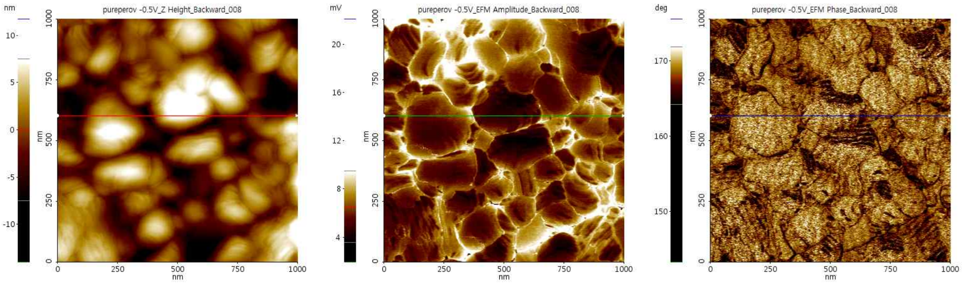


Figure 13 Perovskite film surface under light a) topograpy b) Electrical force microscopy c) phase

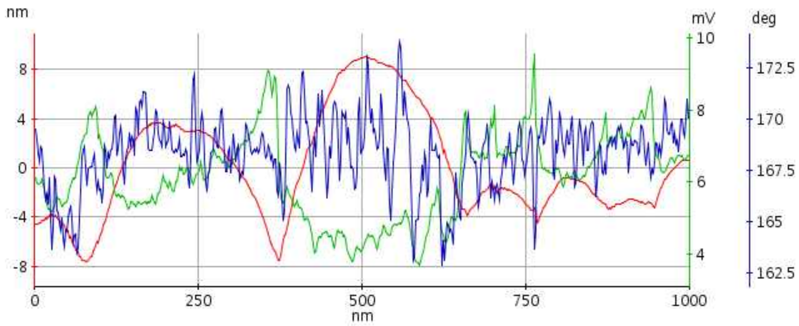


Figure 14 Line scan of figure 14

Dark areas in EFM amplitude (13b) bears dark area in EFM phase image. Taking a line scan from image as seen in figure 14, a little decrease in amplitude and phase implies that grains are composed of different domains. Judging from difference in degree, angle between domains could be subtle but clear. Concept of domain will be explained after two pages.

3.1.2 Domains

Increasing voltage to 1.67V grouping behavior came back and the jumps disappeared. Groupings in figure 14b and 14c are in good agreement.

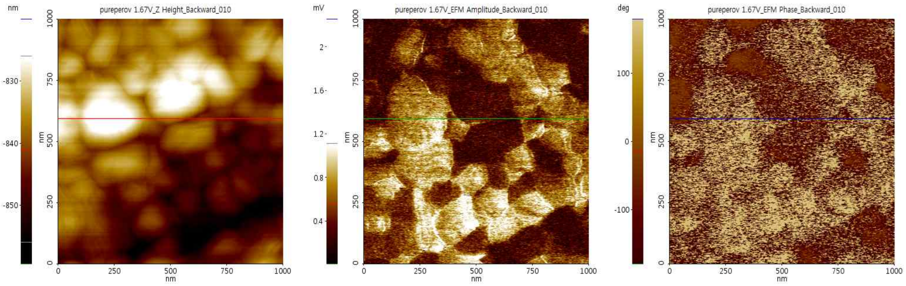


Figure 15

Taking one line scan image from figure 9, the region of larger amplitude is around 180°and the darker region is the opposite of brighter region, which refers that their orientations are completely opposite.(figure 10)

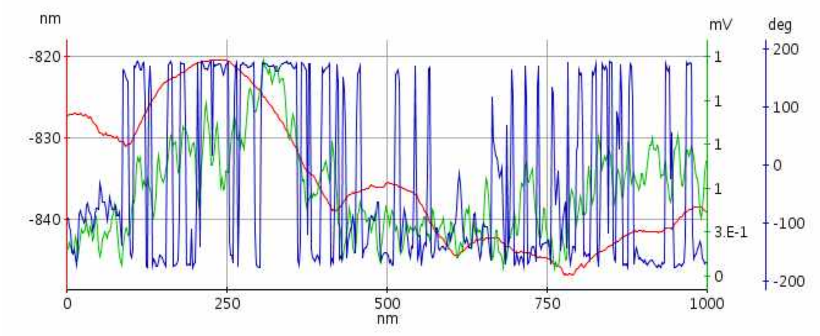


Figure 16

Clusters of lattices that have the same polarization defines a domain. Below image schematically explains domain, and domain wall within one grain. Domains could be anti-parallel and vertical to one another when there is no external bias. If you apply bias all domains can become.

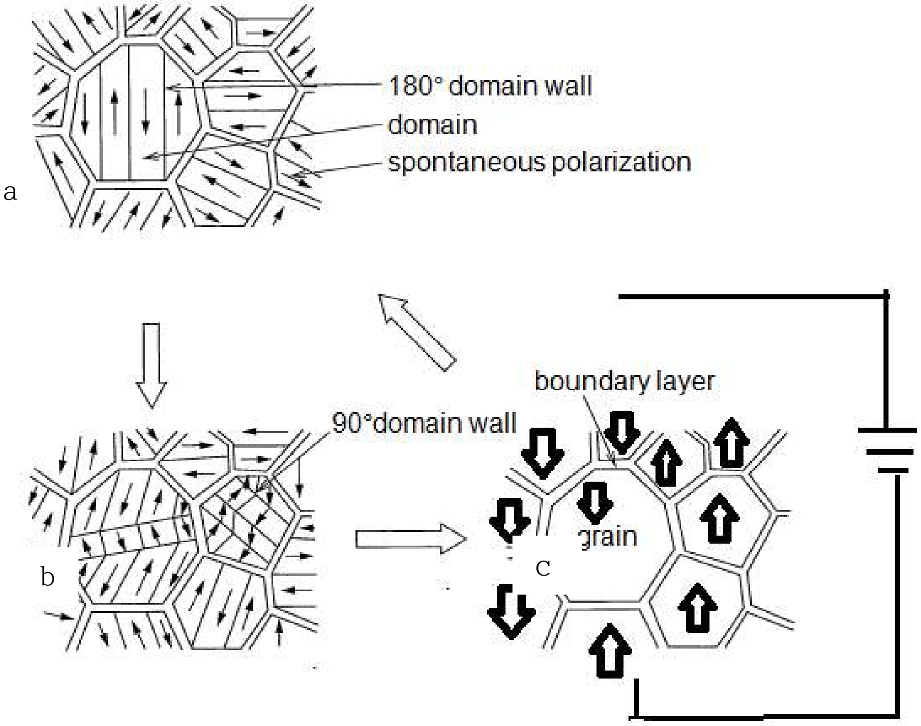


Figure 17 a) Definition of domain and domain wall b) When domains are vertical to one another c) When all domains are parallel in one grain.

Normally happens at low temperature due to crystal phase change from cubic to tetragonal structure lattice. If it were a single grain, it would have behave like this. Average effect of neighboring domains create strong polarization.

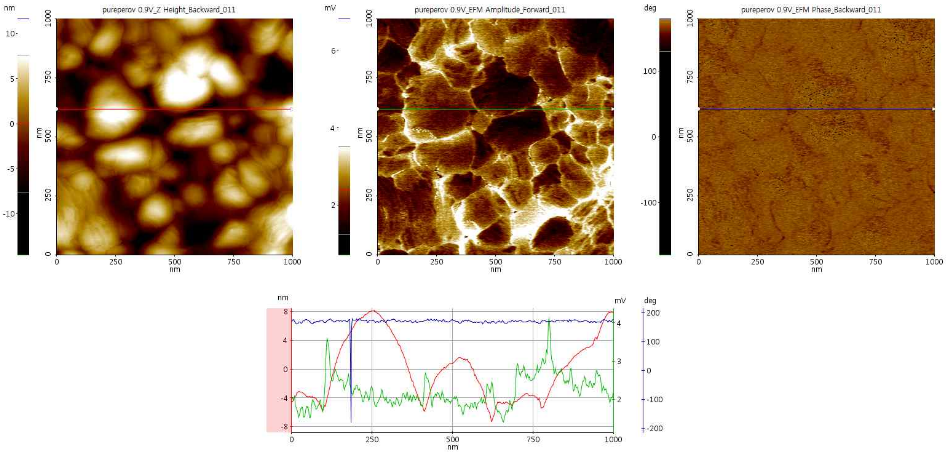


Figure 18 perovksite film surface potential at 0.9V

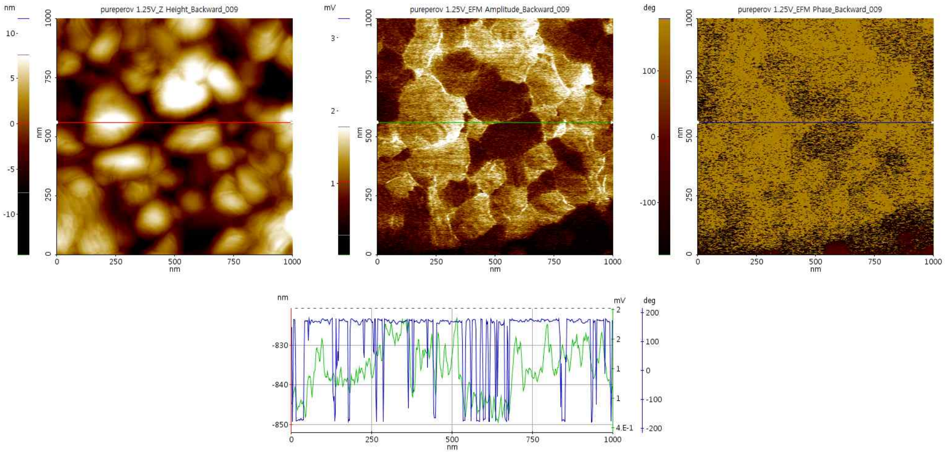


Figure 19 perovksite film surface potential at 1.2V

3.2 Charge redistribution and degradation

Monitoring one spot of film continuously for three days is a scientific way to unravel degradation mechanism of organic-metal halide Perovskite under strong light. Images below are topography and surface potential of $MaPbI_3$ film coated on bare glass for three days. For each day, the scanning was conducted three times with 6 hours of interval.

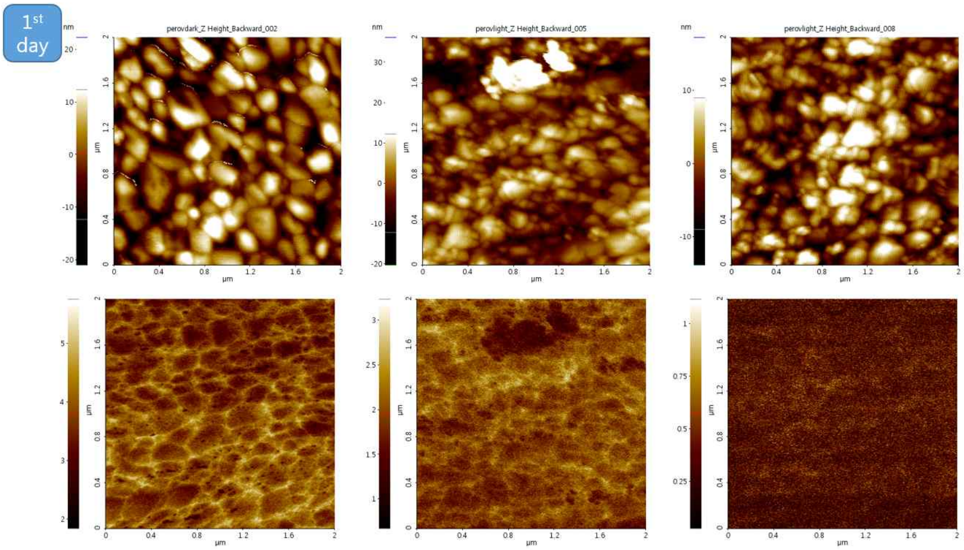


Figure 20

On the first day, preferred surface potential that was initially spread across surface became homogeneous as time flew. The distribution of potential became completely dissipated and homogeneous. Summing up this potential and multiply with electron charge would yield energy took for the sample to degrade partially.

On the second day of observation, the grain showed a sort of grouping behavior that was explained in chapter 4.1. This grouping behavior persisted for a day and eventually disappeared on the 3rd day when the sample totally degraded and turned into yellow. (Figure 22 and Figure 23)

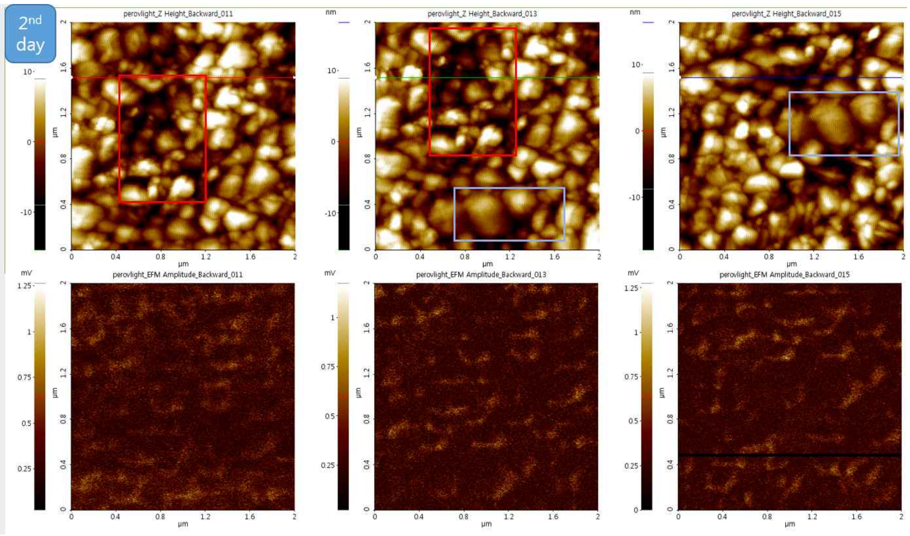


Figure 21

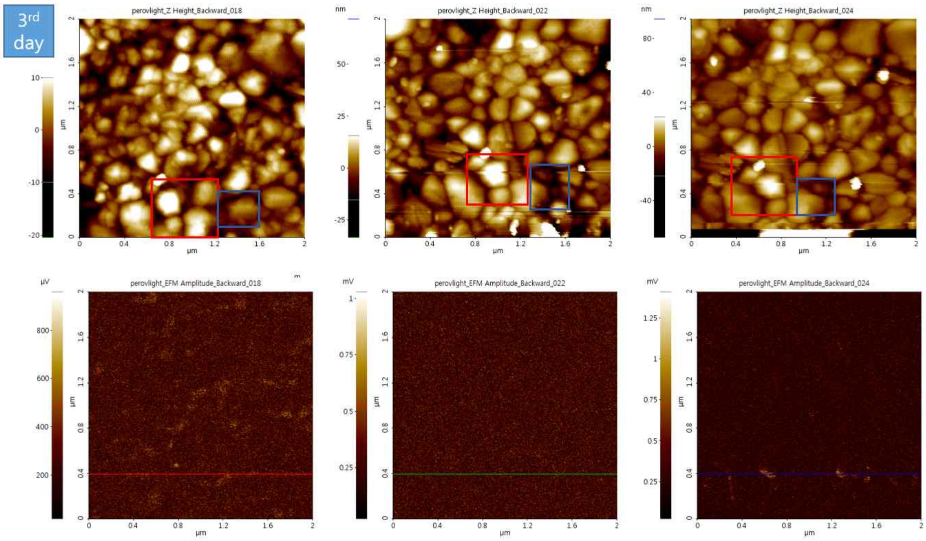


Figure 22

Chapter 4

4.1 Conclusion

4.2 Future work

4.3 Reference

4.4 Supporting information

4.1 Conclusion

What makes it degrade when illuminated with visible range light? Electrons absorb energy of photon and fills higher energy band. Freed electrons in conduction band possess longer life time than excited electrons of other kinds of semiconductors. Extended life time causes accumulation of electrons and supplies energy for ions to hop over to defect sites. Migration takes place and effective measurement of distribution of ions was performed with EFM.

When the defect is occupied by ions, discrepancy between grain boundary and bulk greatly reduces so the electrical potential along the boundary vanishes. Then, it is ready to form polarization domain without external bias. It still needs to be verified why polarization domain is prior step in decomposing the sample to PbI2 and turns to yellowish powder.

It is reported that (100) plane of lattice is intrinsically non-charged but other planes are others are charged. EFM images in figure13 can be considered as some grains nonparallel to (100) plane are mixed with parallel grains (dark area). Under mixed state, to further balance the effects of charge, ions generated from oxygen and hydrogen in ambient air would drive the process to the end. Even though binding energy of organic compound is different from every facet of grains, exchange of energy between the grains related by their polarizability lead them to termination of life of the sample.

4.2 Future work

Different states of adduct or surface passivation can be extensively studied with methodology introduced in this article. Adduct formation may effectively vary mapping of polarization distribution, amounts of defects, and relative orientations of grains.

Heat transfer direction other than bottom heating hot plate is planned to be investigated. Film is formed by dynamics between evaporation of adduct solvents and the way heat is conducted or conveyed. The films will be carefully examined with AFM.

Polarization domain is possible to be modeled based on DFT calculation. It is at extreme difficulty to quantify amounts of defects and network different grains. By taking some parts of wave functions off, electronic variations in electronic structure can be drawn.

4.3 Reference

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2) Antiferroelectric to ferroelectric switching in Perovksite and its potential role in effective charge separation in solar cells. G.A Sewvandi. at PRA.
3) Defect tolerance in methylammonium lead triiodide Perovskite. K.X Steirer. at Acs.E.Letters
4) Highly Reproducible Perovskite Solar Cells with Average Efficiency of 18.3% and Best Efficiency of 19.7% Fabricated via Lewis Base Adduct of Lead(II) Iodide. N. Ahn Jacs.
5) Amplitude or frequency modulation-detection in Kelvin probe force microscopy S. Glatzel. at Applied Surface Science 210 (2003) 84-89
6) Understanding the physical properties of hybrid Perovskites for photovoltaic applications. Huang J., at. Rev. Matejr. 2, 17042 (2017).

4.4 Supporting information

Figure 23

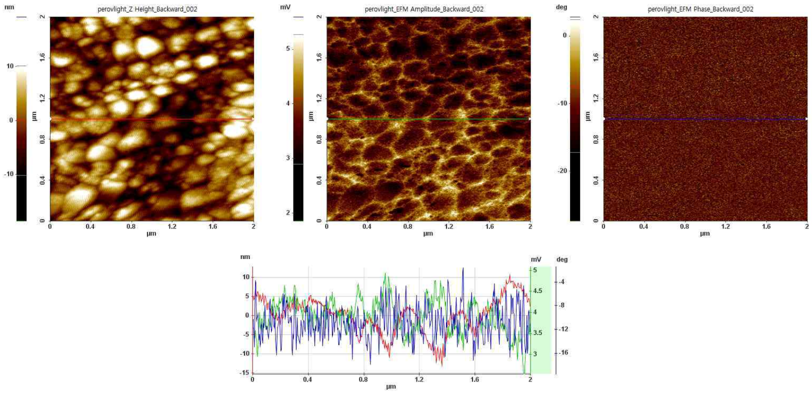


Figure 24

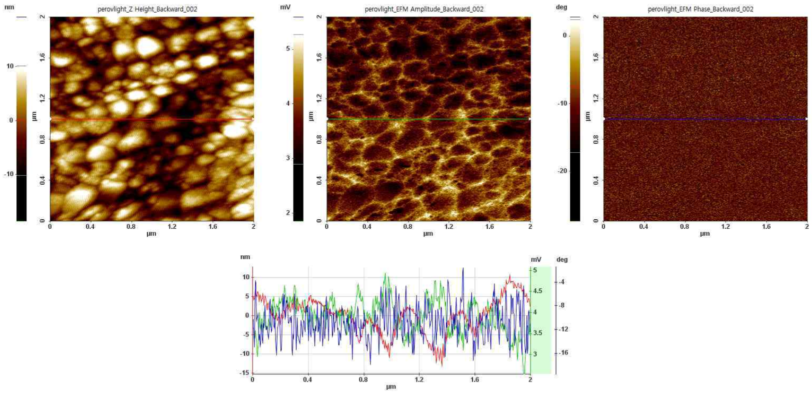


Figure 25

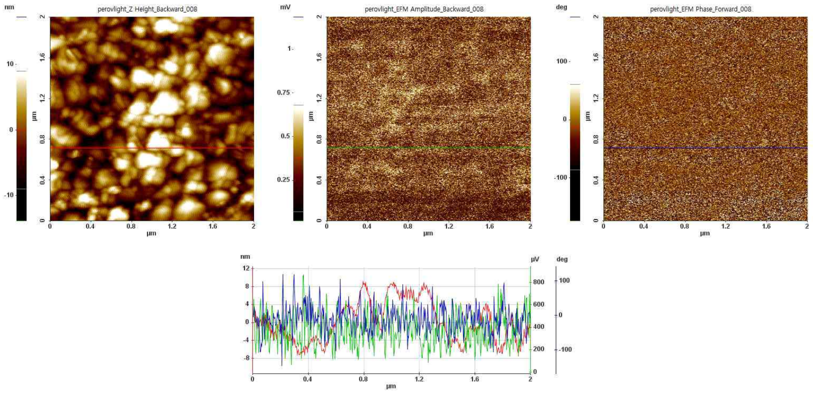


Figure 26

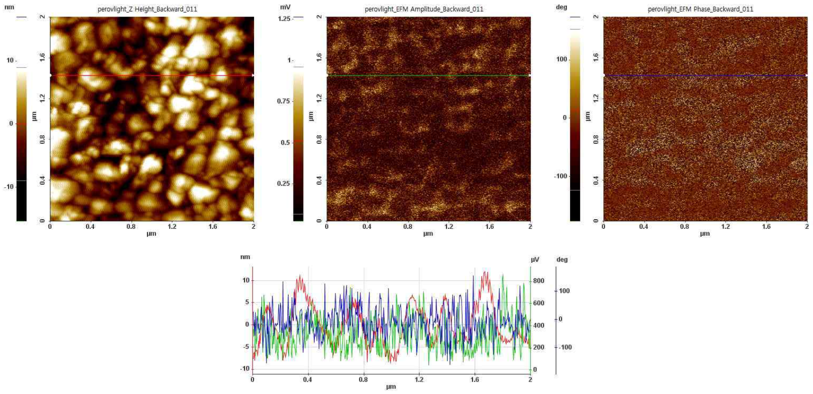


Figure 27

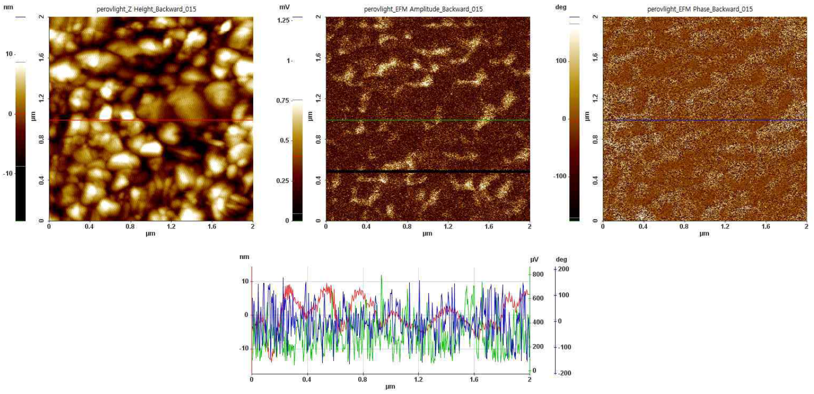


Figure 28

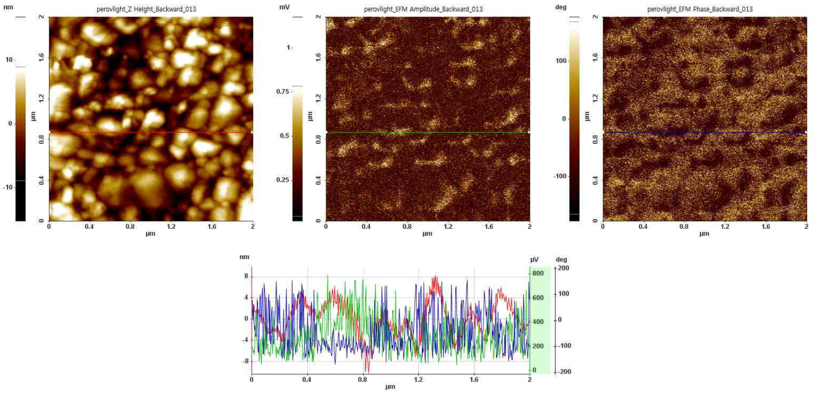


Figure 29

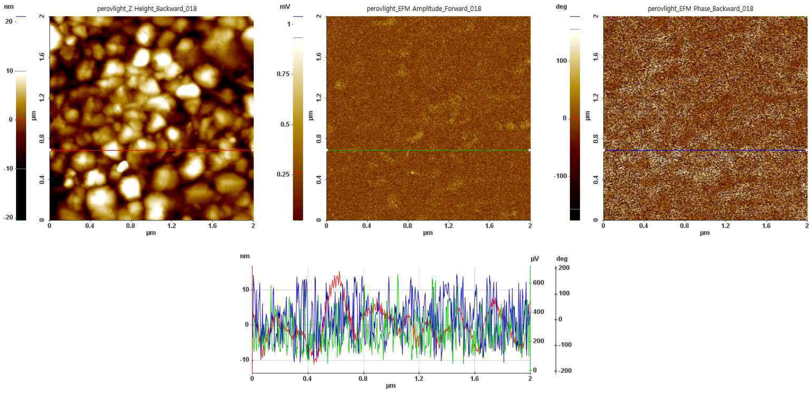


Figure 30

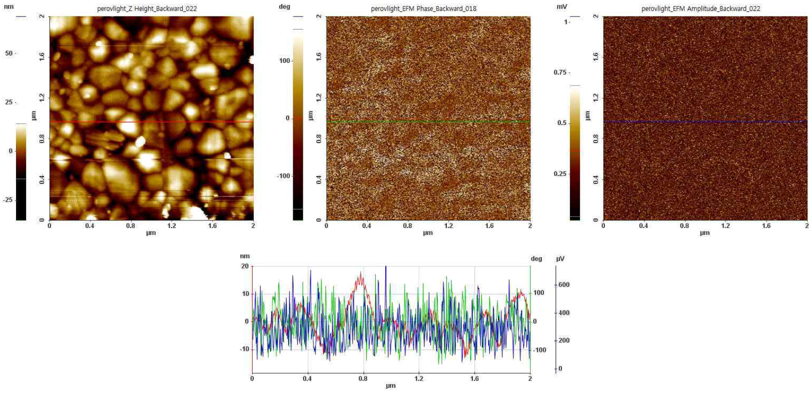
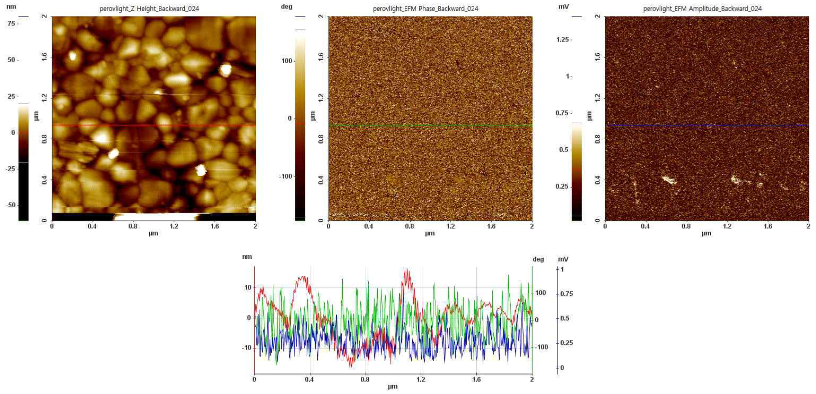


Figure 31


perovlight_Z Height_Backward_024
nm
75
50
25
0
-25
-50
perovlight_EFM Phase_Backward_024
deg
100
0
-100
perovlight_EFM Amplitude_Backward_024
mV
1.25
1
0.75
0.5
0.25
0
0.4
0.8
1.2
1.6
2
µm
nm
10
0
-10
deg
100
0
-100
mV
1
0.75
0.5
0.25
0
µm

표면 전하의 재분배와 도메인 등장을 통한 페로브스카이트 열화현상 규명

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초 록

페로브스카이트 태양전지의 효율이 실리콘 태양전지에 준할 만큼 상승했지만, 빛에 노출도니 상황에서 안정성은 상용화 까지 가기에 큰 걸림돌이다. 최근에 페로브스카이트 박막의 그래인 가장자리에 쏠려있는 전하와 열화현상이 밀접한 관련이 있음이 연구되었다 이에 이 논문에서는 페로브스카이트 격자와 공정에 대해서 깊이 있게 소개한다. 이는 공정시 필름의 생성 자유도가 높은 이유가 결함-용인 성질을 띄는 격자구조와 밀접한 관련이 있음을 설명하는 내용을 나타낸다. 표면에 있는 결함들을 탐구하기 위해서 우리는 AFM과 EFM을 이용하여 물성의 변화를 표면에서 관측한다. EFM은 효과적으로 표면의 전하를 토포 이미지로부터 분리해 낼 수 있는 기술이다. 이를 통해 극성 도메인이 외부 전압을

가해주었을 때 생긴다는 사실을 확인 하였다. 그리고 이 도메인 형성에 따라서 그레인 경계의 전하들이 움직이는 모습을 설명하고 더 나아가 열화 현상이 진행되는 과정에서 모습을 실시간으로 연속적으로 측정하였다. 특히 열화가 진행되면서 극성 도메인이 등장했다가 사라지는 현상을 보았다는 점이 주목 할 만하다.

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keywords : perovskite, EFM. polarization, charge, surface potential

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