

# Self-Organized Superlattice and Phase Coexistence Inside the Perovskite Solar Cell Thin Film

Tae Woon Kim<sup>1</sup>, Ludmila Cojocaru<sup>2</sup>, Satoshi Uchida<sup>1</sup>, Tomonori Matsushita<sup>1</sup>, Takashi Kondo<sup>1</sup> and Hiroshi Segawa<sup>1</sup>

<sup>1</sup> RCAST, The University of Tokyo  
4-6-1, Komaba, Meguro-ku  
Tokyo 153-8904, Japan

Phone: +81-3-5452-5298 E-mail: uchida@rcast.u-tokyo.ac.jp

<sup>2</sup> Albert-Ludwigs University of Freiburg  
Georges-Kohler-Allee 105, 79110  
Freiburg im Breisgau, Germany

## Abstract

It is newly identified that the tetragonal and cubic phases coexist at room temperature in the perovskite solar cell thin film, and is also confirmed that superlattices composed of a mixture of tetragonal and cubic phases are self-organized without a compositional change

## 1. Introduction

Recently, organometal halide perovskite solar cells (PSCs) have received great attention. The power conversion efficiency (PCE) of PSCs have shown a dramatic increase and certified PCEs adopting mixed organic cations and halide anions have reached up to 22%. The PCE is considerably affected by photovoltaic property of each component of a PSC. Particularly, because crystal quality of materials is strongly concerned with the electronic properties such as carrier transport, investigation of detailed crystallographic information of the perovskite light absorber is essential. In this research work, we will report a microstructural observation about phase coexistence in the perovskite light absorber through transmission electron microscope (TEM) observation.

## 2. Experimental

For the crystallographic information of the organometal halide perovskite, planar type thin film perovskite solar cells (Au/Spiro-MeOTAD/MAPbI<sub>3</sub>/TiO<sub>2</sub>/FTO/Glass) were fabricated through spin-coating method. A pure methylammonium lead iodide (MAPbI<sub>3</sub>) layer was formed through spin-coating method assisted by antisolvent in a planar type PSC (Au/Spiro-MeOTAD/MAPbI<sub>3</sub>/TiO<sub>2</sub>/FTO/Glass). MAPbI<sub>3</sub> precursor solution used is 1.4 M and the spin-coated MAPbI<sub>3</sub> film was annealed at 100°C for 30 min.

## 3. Results and discussion

It is widely believed that each phase of the organometal halide perovskite solely exists with orthorhombic phase < 165K < tetragonal phase < 327K < cubic phase. Nevertheless we observed that the tetragonal and cubic phases coexist at room temperature and identified that superlattices composed of mixture of tetragonal and cubic phases are self-organized without a compositional change.

Figure 1 shows a high resolution (HR) TEM image of the

perovskite light absorber at room temperature and Fourier transformed electron diffraction patterns (EDP) from regions A and B. As is seen at Figure 1, coexistence of tetragonal and cubic structures in the perovskite layer is identified.

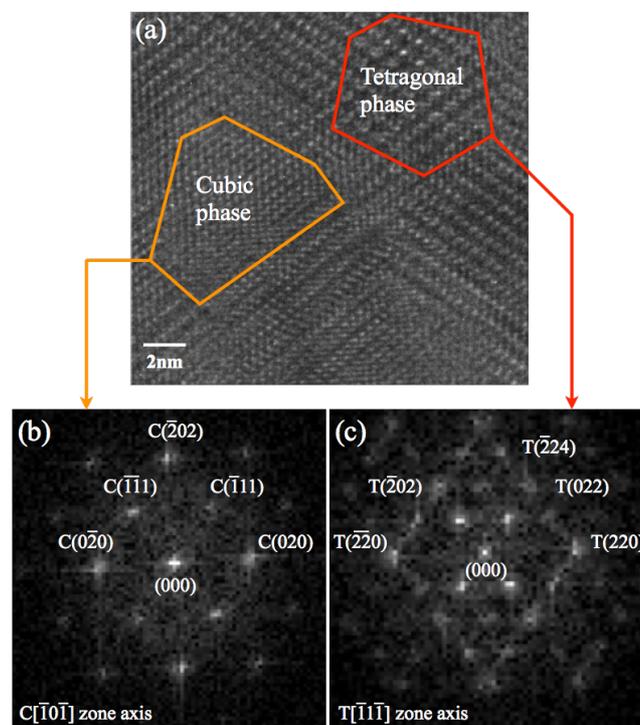


Fig. 1 TEM images (Hitachi HF-3300, 300KeV), a) HRTEM ( $\times 1,000K$ ) image showing the coexistence of the tetragonal and cubic nano domains. b) Fourier transformed diffraction pattern (FTDP) at small area (6.5nm $\times$ 6.5nm) for cubic C[101] zone axis and c) tetragonal T[111] zone axis.

Figure 2 a is a HR( $\times 1,000K$ ) TEM image of thin film MAPbI<sub>3</sub> perovskite layer containing asymmetric lattice structures (black dot rectangle) and their FFT is shown in Figure 4b. In Figure 4b, we can observe additional satellite diffraction spots (green circles) generating asymmetric half period along C[111] in typical C[101] zone axis diffraction pattern (red circles) of cubic phase. To investigate the asymmetric half period in the diffraction pattern with  $d$ -spacing, we refined

black solid rectangle of Figure 2a through Fourier filtering and reconstruction technique with 4 diffraction spots of red and green solid circles in Figure 2b. Figure 2c shows the results of the refined HR TEM image along with C[111̄] (blue arrow). As shown here we can clearly recognize *d*-spacing of C(111̄) (3.71 Å) and T(202̄) (3.58 Å), and confirm tetragonal/cubic stacking sequence which means existence of double-layer superlattice.

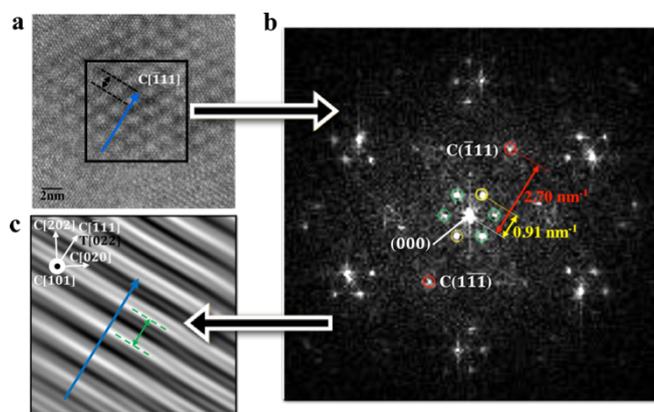


Figure 2. HR TEM image, FFT and refined HRTEM image for analysis of triple-layer superlattice. a) HR ( $\times 1,000K$ ) TEM image including triple-layer superlattice. b) FFT from black rectangle of Figure 3a showing additional satellite diffraction spots generated by triple-layer superlattice. c) Refined HR TEM image obtained through Fourier filtering and reconstruction technique.

Note that single crystal organometal halide perovskite does not contain the phase coexistence and superlattices different from the multi-crystalline films. The differences of microstructural configuration in the single crystal and the multi-crystalline films may provide another possible approach to explain the unsolved puzzling questions between them.

Figure 3 is an example of schematic illustration of super lattice with phase coexistence with cubic and tetragonal.

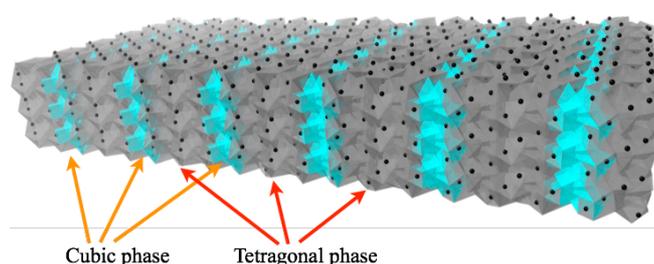


Fig. 3 Schematic illustration of super lattice with phase coexistence with cubic and tetragonal.

### 3. Conclusion

In conclusion, we confirmed coexistence of tetragonal and cubic phase, and existence of self-assembled triple- and double-layer superlattices in the thin film organometal halide perovskite solar cells for the first time. According to our analysis, the origin of the superlattice is coexistence of phases,

because the superlattices are only composed of mixture of tetragonal and cubic planes without any compositional change. Formation of the superlattice is achieved by only intrinsic structural transition without artificial modifications and, therefore, most phenomena concerned with the structural superlattice are expected to spontaneously and automatically occur in context with situation. Surprisingly, the spontaneous phenomena are observed. The organometal halide perovskite self-adjusts their microstructural configuration and self-organizes buffer layers inside crystal or at hetero-interface by introducing the self-assembled superlattices. We believe, this report will be a vital cornerstone to bring the PCEs of the organometal halide perovskite solar cells one step closer to theoretical maximum point and redefine possibility of the organometal halide perovskite as promising materials for not only solar cell but also various application.

### Acknowledgements

This research work was supported by NEDO funding

### References

- [1] T.W. Kim, S.Uchida, T. Matsushita, L. Cojocaru, R. Jono, K. Kimura, D. Matsubara, M. Shirai, K. Ito, H. Matsumoto, T. Kondo and H. Segawa, *Advanced Materials*, 1705230 (2018).