Supporting Information for:

"Depth-dependent electronic band structure at the Au / $CH_3NH_3PbI_{3-x}Cl_x$ junction"

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1. Thickness of perovskite films determined by AFM and XPS

To elucidate the electronic structure at the perovskite/Au interfaces, it is necessary to know the exact thicknesses of perovskite layers. Although the thickness of spin-coated films has been generally determined by AFM, it is hard to measure accurately the thickness of films over few nanometers. To more exact estimation of thicknesses, we have performed by both AFM and XPS measurements. The XPS method was examined the attenuation of the substrate-related Au 4f emission lines. The layer thickness (d) for each deposition was estimated from[1,2]

Concentration of Solutions (wt%)	Thickness (nm)	
	AFM	XPS
3.2	30.9	3.93
6.3	33.9	12.71
12.5	71.4	33.44
25	112.2	57.00
50	125	116.34

Table S1. The film thicknesses of all perovskite films measured by AFM and XPS.

$$d = -l\left[ln\left(\frac{I}{I_0}\right)\right]$$

where l is the mean free path of the emitted electrons, I is the intensity measured on each perovskite layer and I_0 is the intensity measured on the bare Au substrate. The ratio $\frac{I}{I_0}$ was obtained from the Au 4f peak areas. The mismatch of AFM and XPS results observed is

probably due to the big grain sizes of perovskite crystalline as the perovskite thickness is increased. The thicknesses are an average measurement of coverage and the thickness error is approximately ± 20% of the last digit.

2. Cl 2p XPS spectra of perovskite films

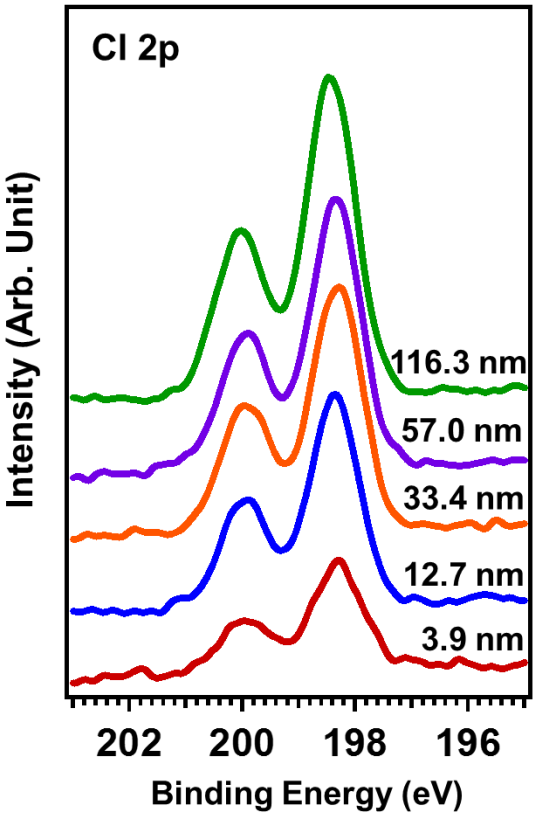

Figure S1. Cl 2p XPs spectra of perovskite films.

3. Supplemental AFM images

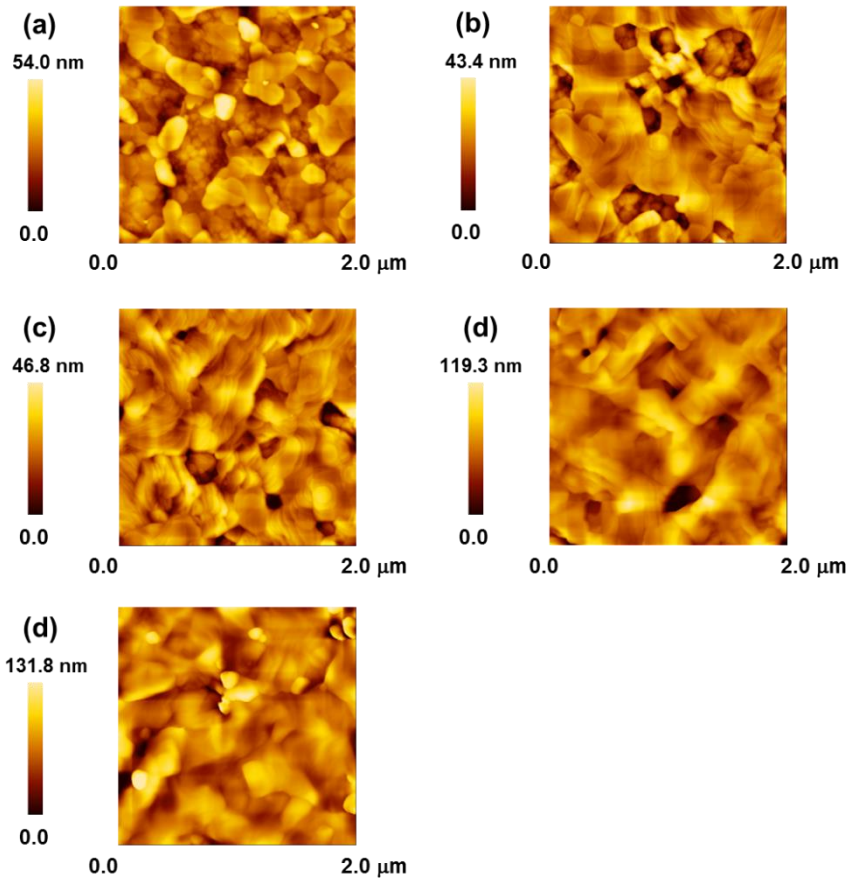

Figure S2. Topographic images (size: 2 μm × 2 μm) of (a) 3.9, (b) 12.7, (c) 33.4, (d) 57.0, and (e) 116.3 nm $CH_3NH_3PbI_{3-x}Cl_x$ films.

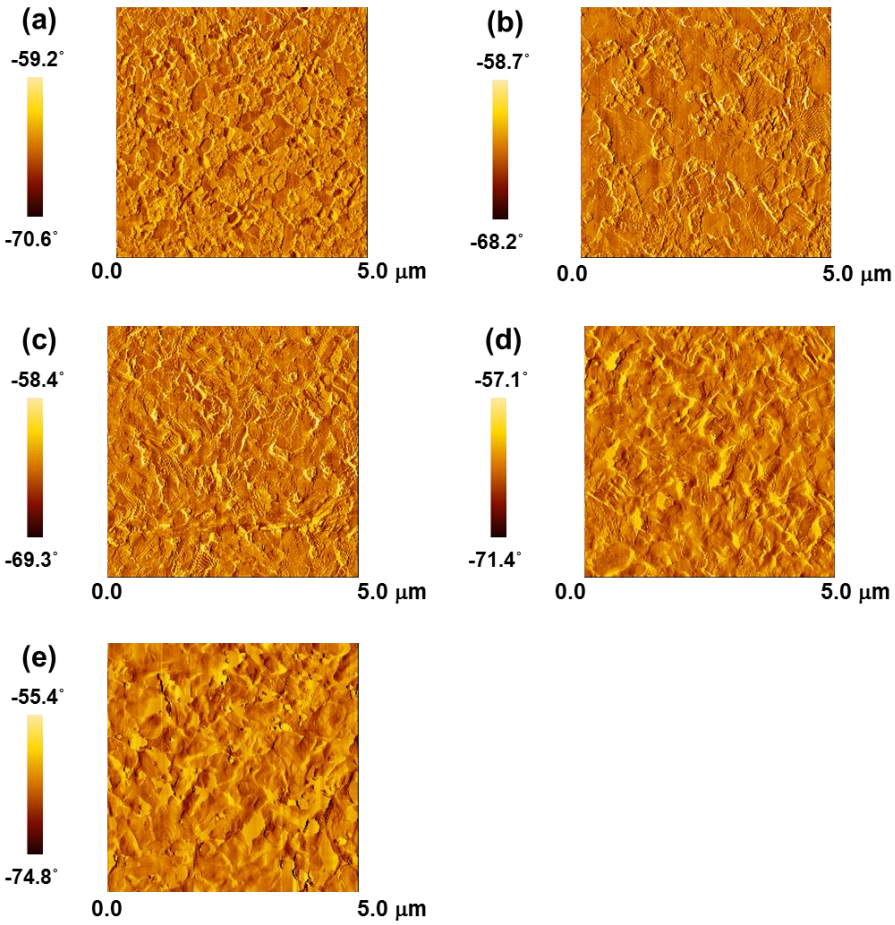

Figure S3 Phase images (size: 5 μm × 5 μm) of (a) 3.9, (b) 12.7, (c) 33.4, (d) 57.0, and (e) 116.3 nm $CH_3NH_3PbI_{3-x}Cl_x$ films.

4. Grain Size Analysis of AFM images

Grain sizes were analyzed using Gwyddion 2.52 data analysis software,[3] which has been reported in the literature as a functional, open-source software package capable of performing quantitative analyses of AFM data.[4] Grain sizes were calculated by opening topographic AFM image files were with width: 5 µm and height: 5 µm; assigning grain areas using the "mark by threshold" tool; adjusting height ratios to match the grain areas in the images and calculating average grain sizes using the summary tool (Data Process-Grains-Summary).

The results of the grain size analysis are shown as images in Figure S4.

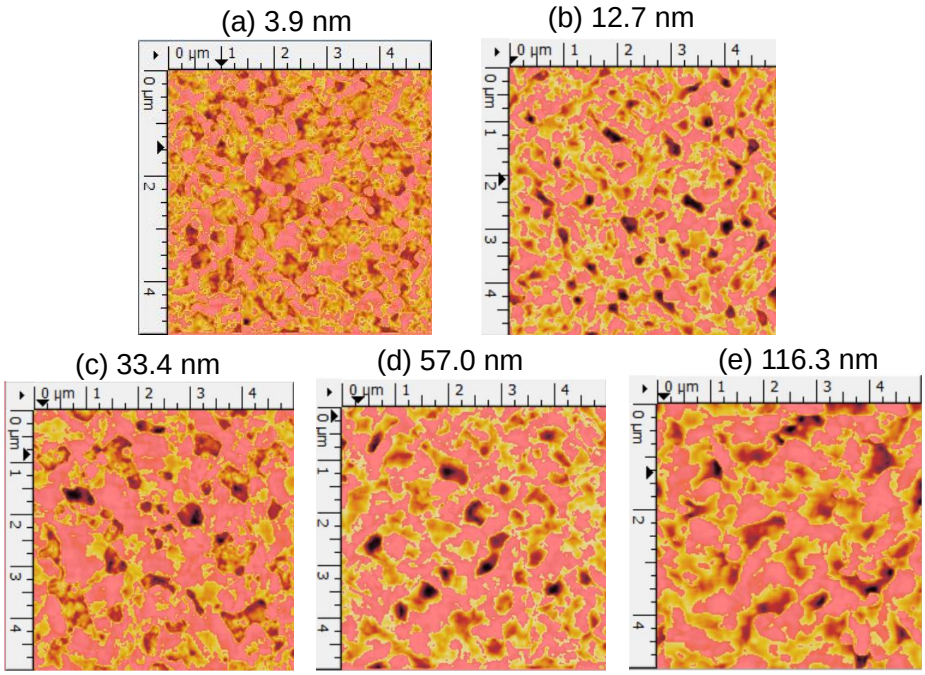

Figure S4 AFM images used to calculate grain sizes (size: 5 µm × 5 µm) for (a) 3.9, (b) 12.7, (c) 33.4, (d) 57.0, and (e) 116.3 nm thick $CH_3NH_3PbI_{3-x}Cl_x$ films.

Table S2. Summary of grain sizes for $CH_3NH_3PbI_{3-x}Cl_x$ films with different thickness.

Thickness [nm]	Mean grain size [nm]
3.9	124.9
12.7	147.6
33.4	153.2
57.0	168.9
116.3	214.3

References.

1. J. H. Seo, R. Yang, J. Z. Brzezinski, B. Walker, G. C. Bazan, T.-Q. Nguyen Advanced Materials, **2009**, 21, 1009.
2. N. Dam, M. M. Beerbom, J. C. Braunagel, R. Schlaf, Journal of Applied Physics, 2005, 97, 024909.
3. http://gwyddion.net/ Accessed 2019/02/07.
4. D. Nečas, P. Klapetek, *Cen. Eur. J. Phys.* **2012**, *10*, 181.