Electronic Supplementary Information

Strong Fermi-Level Pinning at Metal Contacts to Halide Perovskites

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Method for fitting to estimate the pinning factor and estimation of the density of gap states, metal-induced gap states, and interfacial gap states

Based on the Schottky−Mott rule, Schottky barrier height (ϕ_B) at an ideal case of metal/n-type semiconductor is expressed as[1]

$$\phi_B = \phi_m - \chi \tag{1}$$

where ϕ_B is the Schottky barrier height, ϕ_m is the work function of metal, and χ is the electron affinity of the semiconductor. However, for real applications, the ϕ_B value can be deviated from the Schottky−Mott rule due to Fermi-level pinning originating from gaps states at the interface. By introducing a pinning factor (*S*) and charge neutrality level (ϕ_{CNL}), the effective ϕ_B can be expressed using following equation.

$$\phi_B = S(\phi_m - \phi_{CNL}) + (\phi_{CNL} - \chi) = S\phi_m + b \tag{2}$$

$$\phi_{CNL} = \frac{\chi + b}{1 - S} \tag{3}$$

By linear fitting of ϕ_B-ϕ_m curve, we can derive the value of *S*. In addition, the pinning factor *S* can be expressed as follow according to the Sze model,[2]

$$S = \left(1 + \frac{q^2 D_g d}{\varepsilon_r \varepsilon_0}\right)^{-1} \tag{4}$$

$$d = \frac{h^2}{2\pi a m_0 E_g} \tag{5}$$

$$D_g = \frac{(1 - S)\varepsilon_r \varepsilon_o}{S d q^2} \tag{6}$$

where q is the elementary charge, D_g is the density of gap states, d is the penetration depth. ε_r is the dielectric constant of the semiconductor, ε_0 is the permittivity of the vacuum, h is the Planck constant, a is the lattice constant, m_0 is the electron rest mass, and E_g is the band gap of the semiconductor. Here, we used the previously reported static dielectric constant for $MAPbI_3$ (24.1).[3,4] The *d*-value of 0.31 nm was obtained using the lattice constant value of approximately 1 nm (a ≈ 1 nm) because a corresponded to 0.8855 nm and c corresponded to 1.2659 nm for $MAPbI_3$.[5] The D_g is estimated to be 6.75×10^{15} eV^{-1} cm^{-2}.

Considering $D_g = D_{MIGS} + D_{IT}$, we also evaluated the D_{MIGS} and D_{IT} using the following equations.[6]

$$D_{MIGS} = \frac{2}{\pi a^2 E_g} \tag{7}$$

$$D_{IT} = D_g - D_{MIGS} \tag{8}$$

Using the above equations, the D_g and D_{IT} at metal/$MAPbI_3$ interfaces are estimated to be 4.16×10^{13} and 6.71×10^{15} eV^{-1} cm^{-2}, respectively. It indicates that the interface trap states, rather than the metal-induced gap states, mainly cause the strong Fermi-level pinning at metal/$MAPbI_3$ interfaces.

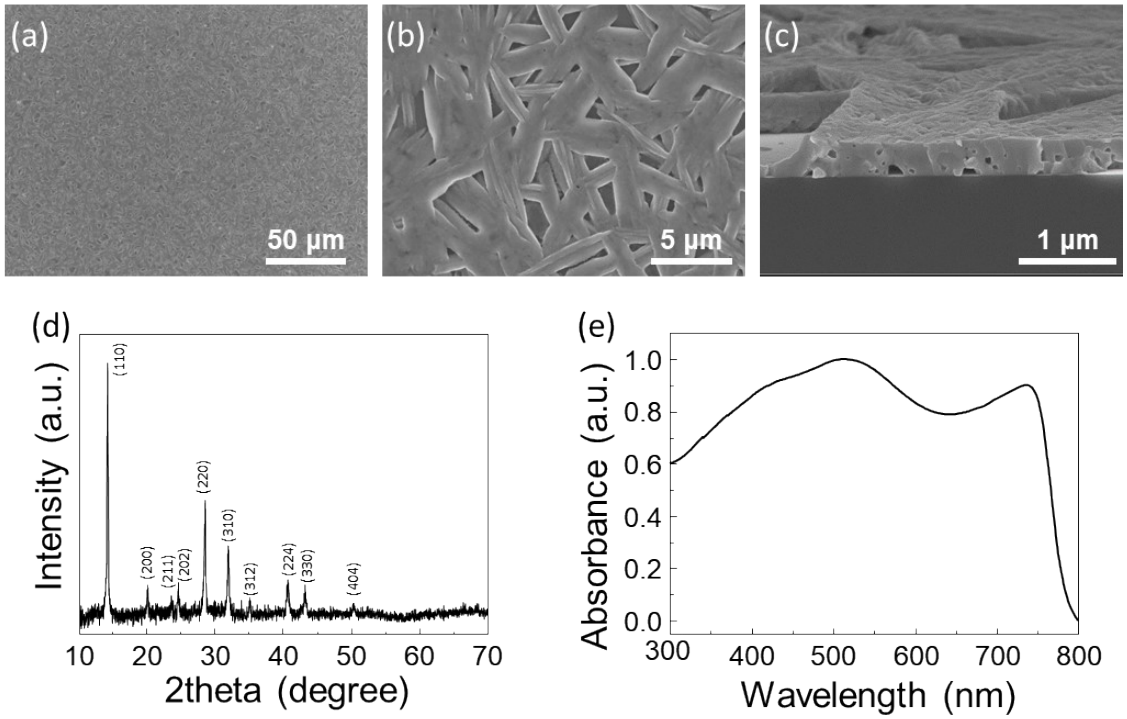

Fig. S1 (a,b) Plain-view and (c) cross-section view scanning electron images of $MAPbI_3$ thin films. (d) XRD pattern of the $MAPbI_3$ thin films. (e) UV-Vis absorption spectrum of $MAPbI_3$ thin films.

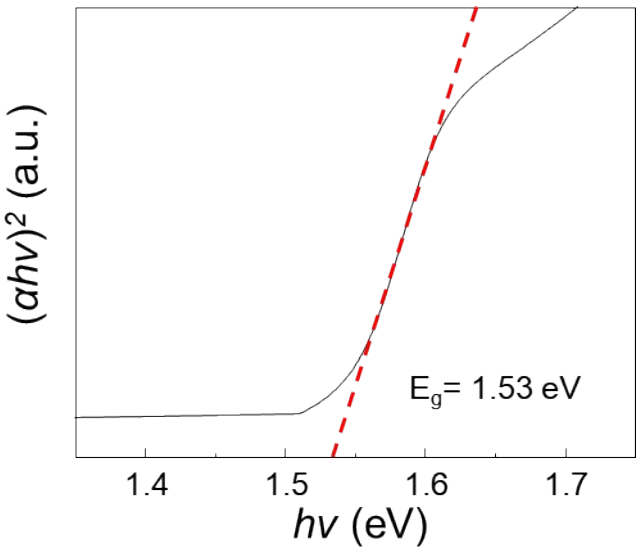

Fig. S2 Tauc plot of $MAPbI_3$ thin films.

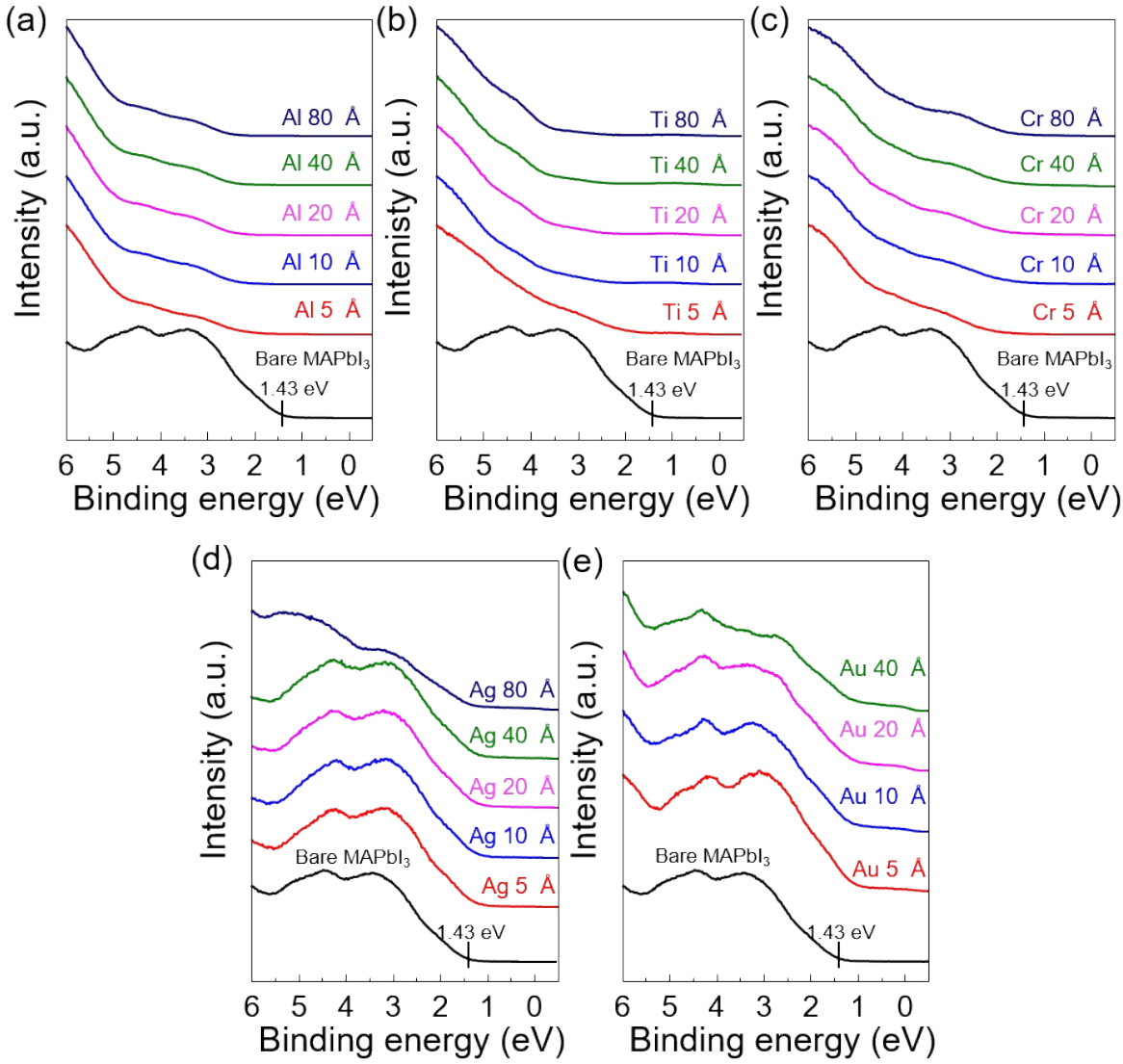

Fig. S3 Thickness depedent UPS sepctra of metal/$MAPbI_3$ thin films showing the VB edge region.

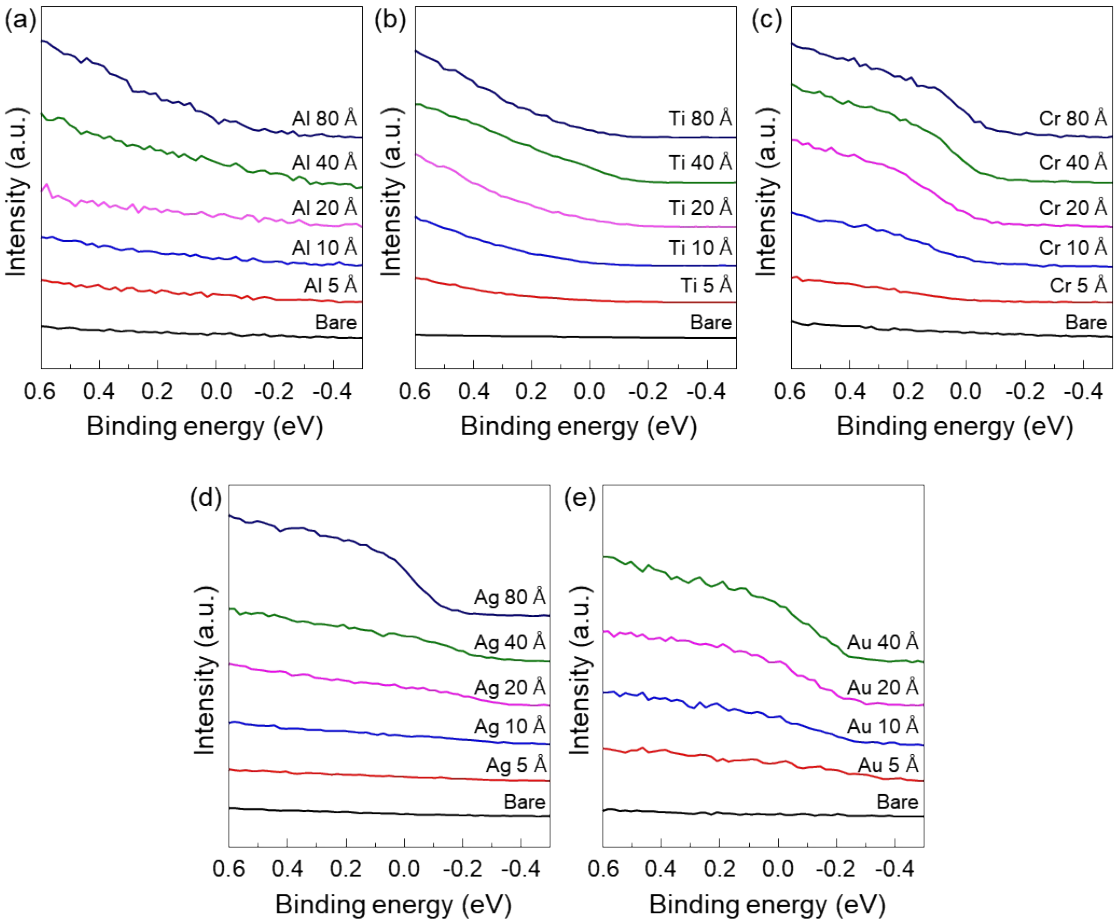

Fig. S4 Thickness dependent UPS spectra of metal/$MAPbI_3$ thin films showing the local enlarged view of the valence band edge region near E_F.

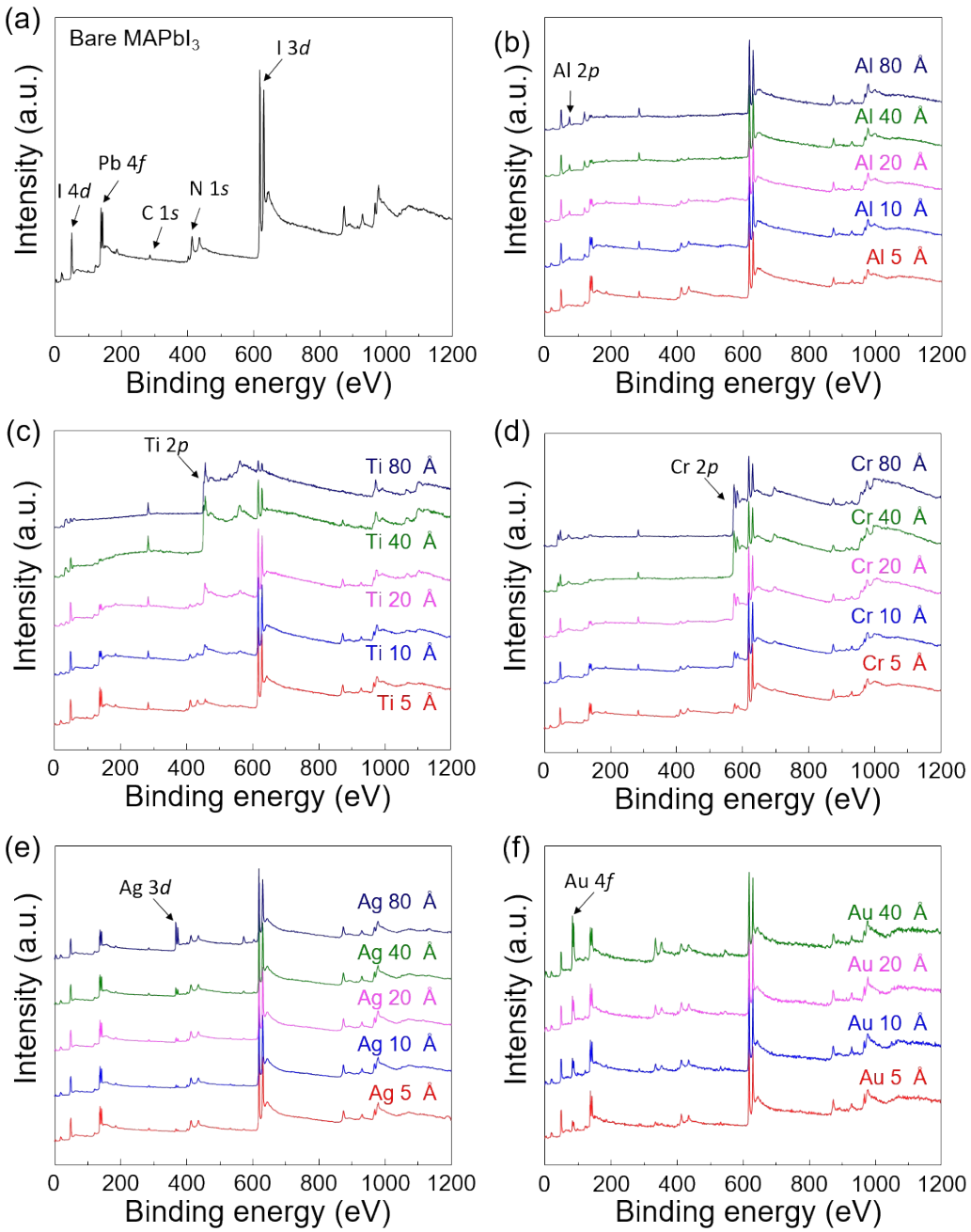

Fig. S5 XPS survey spectra of (a) bare $MAPbI_3$ thin film and (b-f) metal/$MAPbI_3$ as function of metal deposition thickness on $MAPbI_3$. (b) Al/$MAPbI_3$ thin films, (c) Ti/$MAPbI_3$, (d) Cr/$MAPbI_3$, (e) Ag/$MAPbI_3$ and (f) Au/$MAPbI_3$ thin films.

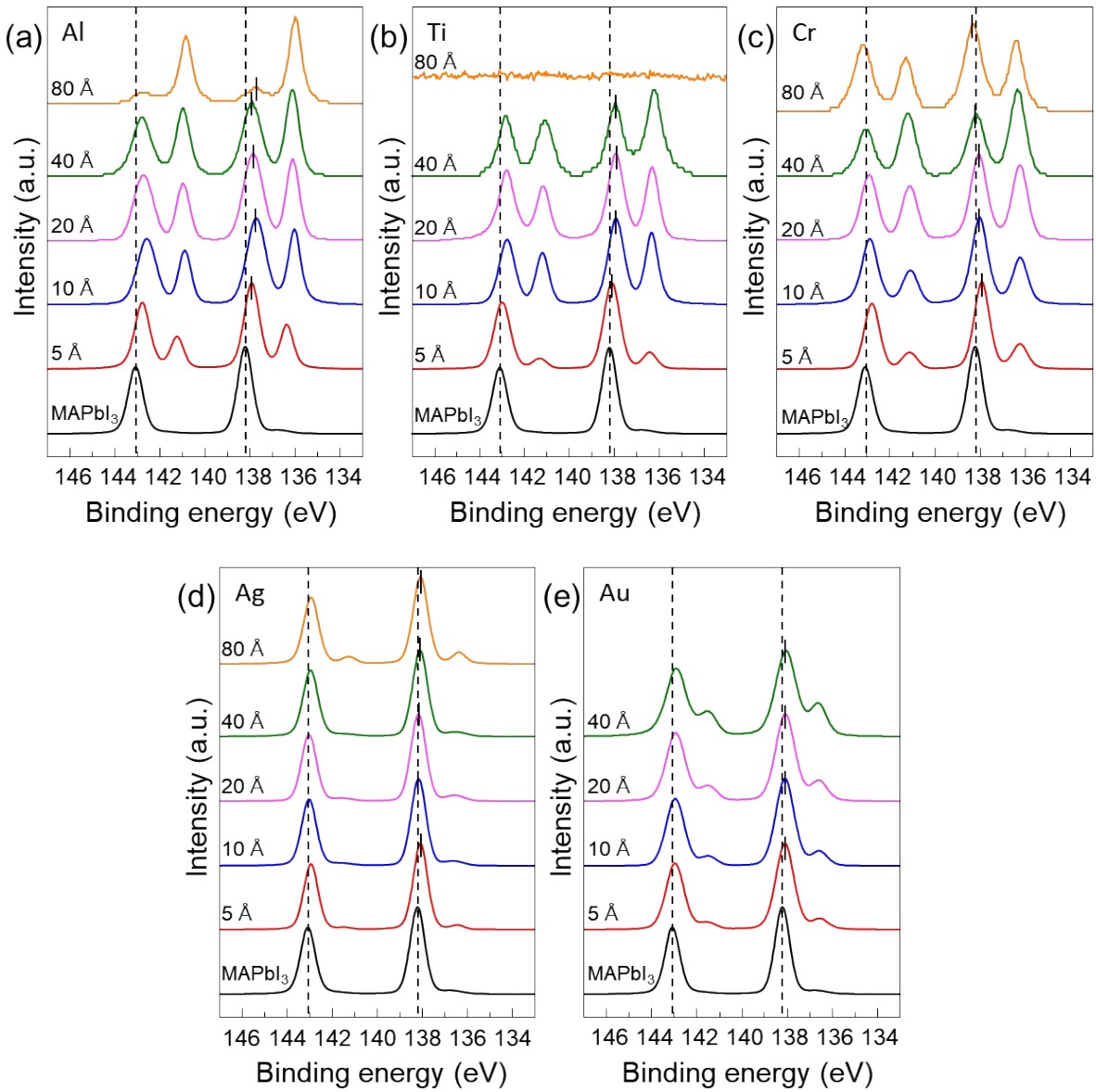

Figure S6. The evolution of Pb 4f core level spectra of (a) the Al/$MAPbI_3$ thin films, (b) the Ti/$MAPbI_3$ thin films, (c) the Cr/$MAPbI_3$ thin films, (d) the Ag/$MAPbI_3$ thin films, and (a) the Au/$MAPbI_3$ thin films, with increasing the deposited metal thickness.

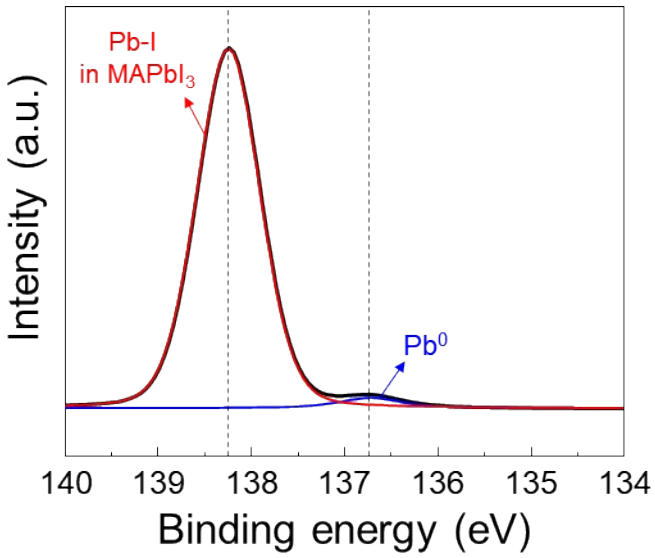

Fig. S7 The Pb $4f_{7/2}$ core level spectrum of bare $MAPbI_3$ thin films.

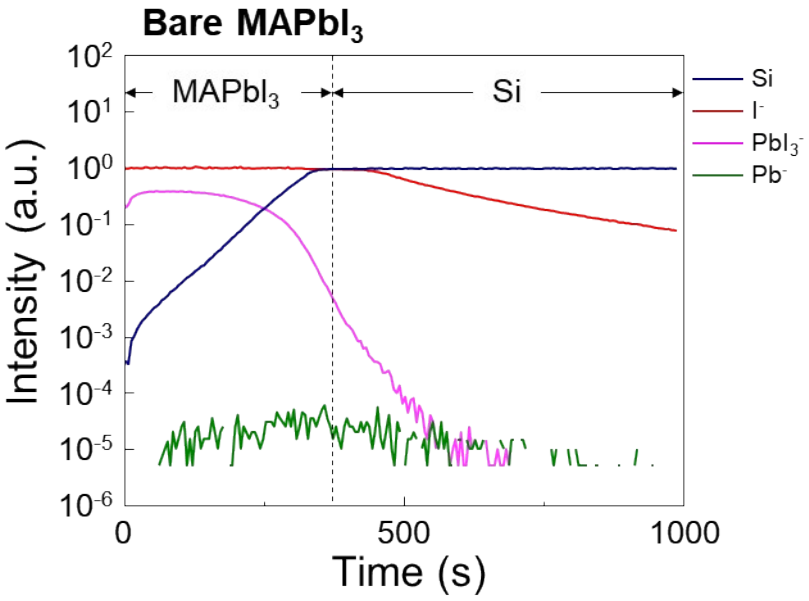

Fig. S8 ToF-SIMS depth profiles of the bare $MAPbI_3$ thin films.

Metal	Metal-Metal bond energy (E_{M-M}, kJ/mol)	Metal-Iodine bond energy (E_{M-I}, kJ/mol)	Energy barrier ($\Delta E = E_{M-M} - E_{M-I}$, kJ/mol)	Standard enthalpy of formation
Al	264.3	369.9	-105.6	-302.9 (AlI_3)
Ti	117.6	306	-188.4	-375.7 (TiI_4)
Cr	152	287	-135	-205.0 (CrI_3)
Ag	162.9	234	-71.1	-61.8 (AgI)
Au	226.2	276	-49.8	0 (AuI)

Table S1 Summary of the bond energies and standard enthalpies for metals.[7-9]

References

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