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Strong Fermi-Level Pinning at Metal Contacts to Halide Perovskites

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The performance of halide perovskite-based electronic and optoelectronic devices is often related to interfacial charge transport. To shed light on the underlying physical and chemical properties of CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) in direct contact with common electrodes Al, Ti, Cr, Ag, and Au, the evolution of interfacial properties and Fermi level pinning is systematically studied. Given a unique experimental facility, pristine interfaces without any exposure to ambient air were prepared. We observe aggregation of substantial amounts of metallic lead (Pb$^0$) at the metal/MAPbI$_3$ interface, resulting from the interfacial reaction between the deposited metal and iodine ions from MAPbI$_3$. It is found that the Schottky barrier height at the metal/MAPbI$_3$ interface is independent of the metal work function due to strong Fermi level pinning, possibly due to the metallic Pb$^0$ aggregates, which act as interfacial trap sites. The charge neutrality level of MAPbI$_3$ is consistent with the energy level of Pb$^0$-related defects, indicating that Pb$^0$ interfacial trap states can be nonradiative recombination sites. This work underlines that control of chemical bonding at interfaces is a key factor for designing future halide perovskite-based devices.

**Introduction**

After the first report on organolead halide perovskites (with CH$_3$NH$_3$PbI$_3$ being the forerunner compound) as light absorber materials in 2009,1 there have been numerous efforts to improve performance and stability of halide perovskite-based solar cells.2–6 Unprecedented rapid developments led to power conversion efficiencies (PCE) exceeding 25 % within about a decade of research.7 Therefore, halide perovskites are considered to be promising candidates for solving the impending energy shortage owing to their exceptional optical and charge transport properties.8–12 Moreover, their properties including bandgap, doping concentration, electronic conductivity and ionic conductivity, can be easily tuned through alloying using facile solution synthesis methods.13–15 In this regard, halide perovskites have attracted considerable interest due to their potential applications in optoelectronic and electronic devices,16 such as light-emitting diodes,17 lasers,18 photodetectors,19 field-effect transistors (FETs),20 resistive-switching random access memories (ReRAMs)21 and artificial synapses.22 Interfaces are of utmost importance not only for device functioning but also for device performance and stability.23,24 As an example, the energy level alignment at heterointerfaces such as charge transport layer (CTL)/perovskite or metal/perovskite is critical for efficient charge carrier separation and transport. Most studies thus far have focused on CTL/perovskite interfaces,25–27 while less attention has been given to metal/perovskite interfaces.28–31 The latter, however, is of importance for electronic and optoelectronic devices such as FETs, memories and photodetectors, determining contact resistance, charge transfer behavior and on/off ratio,22–24 as well as in solar cells operating without electron or hole selective contacts in order to reduce device complexity and fabrication cost.35,36 Previous studies have mainly investigated the metal/perovskite interfaces with the motivation of understanding the long-term stability of the halide perovskite-based device where diffusion of metals through CTLs and subsequent reaction with halide perovskites lead to performance degradation.28,29 To this end, there are however, contradicting reports on the contact type of metal/halide perovskite interfaces.30–34 For example, Peng et al. and Gu et al. observed Ohmic conduction behavior in devices with an Au/CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) interface,35–37 while Liu et al. and Lin et al. reported the formation of Schottky contacts at the same material interface.38,39 The discrepancy between various studies might be attributed to different halide perovskite preparation methods leading to different stoichiometries and surface chemistry, measurement conditions, mixed ionic-electronic conduction behavior found in halide perovskites, and uncontrolled exposure to moisture and light irradiation that can impact the metal/halide perovskite interface.19,23,40 Therefore, reliable characterizations of metal/halide perovskite interfaces under well-controlled condition is challenging but needed to understand the pristine interface formation, existence of surface trap states, and energy level alignment which dominate device performance. To do so,
highly surface sensitive X-ray photoemission spectroscopy (XPS) has proven to be an appropriate characterization technique for the evaluation of physical and chemical interface properties of halide perovskites without the need for an externally applied bias voltage.\(^{23,41,42}\)

In this work, we present an experimental study on the interfacial structure evolution and origin of strong Fermi level pinning at pristine metal/MAPbI\(_3\) interfaces. This study provides new insights for designing high performance halide perovskite-based electronic and optoelectronic devices.

Results and discussion

To investigate the physical and chemical status of metal/halide perovskite interfaces without contamination and degradation, we fabricated and characterized metal/halide perovskite thin films under a nitrogen atmosphere and ultrahigh vacuum, as illustrated in Scheme 1. The most studied halide perovskite composition, MAPbI\(_3\), and typical metal electrodes (Al, Ti, Cr, Ag, and Au) with work functions from 4.1 eV to 5.2 eV are selected (Fig. 1f). First, MAPbI\(_3\) thin films were synthesized on Si substrates using one-step spin coating of a precursor solution to an N\(_2\)-filled glove box \((H_2O < 0.1 \text{ ppm}, \text{O}_2 < 0.1 \text{ ppm})\). The samples were prepared without antisolvent dripping or additional treatments to rule out the possibility of modification on surface chemistry by MAPbI\(_3\) due to antisolvent and interface engineering. The spin-coated solution was crystallized by annealing at 110 °C for 10 min. The MAPbI\(_3\) thin films show hexagonal crystal structure and show an abrupt change. For Al, Ti, and Cr, the VL decreases to 3.94 eV, 3.71 eV, 4.02 eV, and 3.94 eV, respectively. As the metal deposition increases, the VL saturates at 3.94 eV for Ag and Au, the VL increases to 4.66 eV and 4.78 eV, respectively. Next, the physical and chemical properties of the metal/MAPbI\(_3\) interfaces were investigated by UPS and XPS.

Fig. 1b–f shows the evolution of the UPS spectra at the secondary cutoff region and valence band region with the gradual deposition of various metal thin films. All the spectra were normalized to the same height. The secondary cutoff shows an abrupt change. For Al, Ti, and Cr, the VL decreases to 3.99 eV, 4.23 eV, and 3.94 eV, whereas, for Ag and Au, the VL increases to 4.66 eV and 4.78 eV, respectively. As the thickness of the metal layers increase to 80 Å, the VL of the metal/MAPbI\(_3\) thin films show an abrupt change. For Al, Ti, and Cr, the VL decreases to 3.99 eV, 4.23 eV, and 3.94 eV, whereas, for Ag and Au, the VL increases to 4.66 eV and 4.78 eV, respectively. As the thicknesses of the metal layers increase to 80 Å, the VL of the metal/MAPbI\(_3\) thin films show an abrupt change. For Al, Ti, and Cr, the VL decreases to 3.99 eV, 4.23 eV, and 3.94 eV, whereas, for Ag and Au, the VL increases to 4.66 eV and 4.78 eV, respectively. To test the secondary cutoff energy and photon energy (21.22 eV). For bare MAPbI\(_3\) thin films, it is found that the work function (WF) is 4.35 eV and the energy difference between the Fermi level and the valence band maximum \((E_v-E_F)\) is 1.43 eV, comparable to those previously reported in literature.\(^{41,42}\) With a bandgap of 1.53 eV (Fig. S2, ESI†), the surface of MAPbI\(_3\) thin films studied in this work exhibits pronounced n-type character in agreement with previous reports.\(^{41,42,47}\) With the subsequent metal deposition of 5 Å, the VL of the metal/MAPbI\(_3\) thin films show an abrupt change. For Al, Ti, and Cr, the VL decreases to 3.99 eV, 4.23 eV, and 3.94 eV, whereas, for Ag and Au, the VL increases to 4.66 eV and 4.78 eV, respectively. As the thicknesses of the metal layers increase to 80 Å, the VL of the metal/MAPbI\(_3\) thin films show an abrupt change. For Al, Ti, and Cr, the VL decreases to 3.99 eV, 4.23 eV, and 3.94 eV, whereas, for Ag and Au, the VL increases to 4.66 eV and 4.78 eV, respectively. As the thicknesses of the metal layers increase to 80 Å, the VL of the metal/MAPbI\(_3\) thin films show an abrupt change. For Al, Ti, and Cr, the VL decreases to 3.99 eV, 4.23 eV, and 3.94 eV, whereas, for Ag and Au, the VL increases to 4.66 eV and 4.78 eV, respectively. As the thicknesses of the metal layers increase to 80 Å, the VL of the metal/MAPbI\(_3\) thin films show an abrupt change. For Al, Ti, and Cr, the VL decreases to 3.99 eV, 4.23 eV, and 3.94 eV, whereas, for Ag and Au, the VL increases to 4.66 eV and 4.78 eV, respectively. As the thicknesses of the metal layers increase to 80 Å, the VL of the metal/MAPbI\(_3\) thin films show an abrupt change. For Al, Ti, and Cr, the VL decreases to 3.99 eV, 4.23 eV, and 3.94 eV, whereas, for Ag and Au, the VL increases to 4.66 eV and 4.78 eV, respectively.
with the evolution of secondary electron cut-off, increasing metal deposition thickness. In addition, it can be seen that the metallic Fermi edge becomes more pronounced and the spectrum becomes gradually attenuated with increasing metal thickness (Fig. S4).

In order to further understand the energy level evolution and the interface reaction at the metal/MAPbI interfaces, we performed XPS analysis to investigate the chemical characteristics and the shift in the core-level spectra of MAPbI after the metal deposition (Fig. 5a–c, ESf†). It can be observed from the spectra that the bare MAPbI spectrum is attenuated at 80 Å due to the limited probing depth of XPS. All the spectra were normalized to the same peak position and normalized to the same intensity as compared to the pristine MAPbI. The Pb 4f spectra of MAPbI thin films, for example, we can find the Pb 4f7/2 peak at 138.24 eV and 136.74 eV (Fig. S7, ES†). The formation of metallic Pb is associated with losses of iodine atoms during sample annealing.47 After metal deposition, the Pb 4f peaks in the Ti/MAPbI thin films are more pronounced, indicating a redox reaction at the Interface possibly due to charge transfer between the deposited metal layers and MAPbI thin films. The oxidized Al, Ag, or Au layers on MAPbI, in addition, it was observed that the peaks with higher binding energies correspond to the oxidized metal layer, while the smaller Pb 4f peaks are located at 136.74 eV (Fig. S7, ES†). The Pb 4f core-level spectra as a function of deposited metal thickness is plotted in Fig. 2f. For bare MAPbI, the Pb 4f core level is associated with losses of iodine atoms during sample annealing.47 After metal deposition, the Pb 4f peaks in the Ti/MAPbI thin films are more pronounced, indicating a redox reaction at the Interface possibly due to charge transfer between the deposited metal layers and MAPbI thin films.

To provide further information on the interaction between the deposited metal layers and the MAPbI thin films, we also obtained the Al 2p, Ti 2p, Cr 2p, Ag 3d and Au 4f core level spectra (Fig. 3). From the evolution of the metal core level spectra, it can be derived that the deposited metals were partially oxidized. It indicates that a redox reaction occurs at the metal/MAPbI interfaces resulting from the charge transfer between the deposited metal and MAPbI thin films. For example, we can find the dominant Al 2p (74.7 eV) and Ag 3d (367.8 eV) peaks in Al 2p and Ag 3d spectra, which are associated to the Al and Ag component in aluminum halides and silver halides, respectively (Fig. 3a,d).52 The Au 4f core-level spectra can be deconvoluted into two distinct components centered at 83.8 eV and 85.1 eV, which are ascribed to Au2+ and Au+ respectively (Fig. 3e).52 The oxidized Al, Ag, or Au layers on MAPbI, and the formation of Pb2+ through reduction of Pb2+...
To further investigate the underlying interfacial chemistries of the metal/MAPbI interfaces, time-of-flight secondary ion mass spectroscopy (ToF-SIMS) is employed to study the elemental distribution in the metal/MAPbI stacks. Fig. 4 shows the ToF-SIMS depth profiles of relative element distributions in Ag/MAPbI, Au/MAPbI, and Ti/MAPbI stacks. The boundaries of each layer were identified by the intensity of detected ions, as reported in previous studies.\textsuperscript{55,54} Al\textsuperscript{3+}, Au\textsuperscript{3+}, and Ti\textsuperscript{4+} ions are selected to identify the deposited metal layers, Pb\textsuperscript{2+} for Pb\textsuperscript{2+} aggregates, Pb\textsuperscript{3+} for the MAPbI thin films, Si for the substrates. The maximum signals of Ag\textsuperscript{1+}, Au\textsuperscript{1+}, and Ti\textsuperscript{1+} are observed at the Ag/MAPbI, Au/MAPbI, and Ti/MAPbI interfaces, indicating a chemical reaction between the deposited metals and iodine from the MAPbI surface. The formation of metal-iodine compounds is attributed to thermodynamically stronger bonds as compared to metal-metal bonds.\textsuperscript{43} In addition, the ToF-SIMS result of the bare MAPbI film (Fig. S8, ESI†) reveals that the concentration of Pb\textsuperscript{0} is higher in the bulk than at the surface, which is in good agreement with the Pb\textsuperscript{5+} distribution in bare MAPbI\_CL films reported by Sadoughi et al.\textsuperscript{40} However, the concentration of Pb\textsuperscript{2+} at metal/MAPbI interfaces is comparable with that at bulk MAPbI. It indicates that a substantial amount of Pb\textsuperscript{2+} is existed at metal/MAPbI interfaces, consistent with XPS results.

Overall, our XPS and ToF-SIMS results provide evidence that the redox reaction between MAPbI, and all investigated metals occurs. It has been reported that thermodynamically unfavorable reactions can occur at metal/semiconductor, especially metal/Pb(Zr,Ti)\textsubscript{3}O\textsubscript{2} interface, due to the heat of condensation of metal atoms.\textsuperscript{55-57} However, the formation of metal-iodine bond is thermodynamically favorable due to the negative formation enthalpy and energy barrier,\textsuperscript{49} resulting in the formation of Pb\textsuperscript{2+} state at metal/MAPbI interfaces (Table S1, ESI†). Generally, it is believed that Ag has higher reactivity with halide perovskite compared to other metals.\textsuperscript{78,58,59} The energy barrier for Ag and standard enthalpy of formation of AgI are less negative than those of Al, Cr and Ti. This trend is in good agreement with our experimental results. The difference between our results and the previous reports is attributed to the sample preparation and measurement methods. Our samples were investigated immediately after metal deposition without exposure to air and moisture, whereas the previous reports focused on the degradation mechanism of Ag/halide perovskite interfaces under air/humid conditions for more than several days. We speculate that the following reactions occur at the interface between MAPbI, and the metal, M (with valency, z) account for the charge transfer of electrons due to the formation of the metal-iodine compounds which reduce Pb\textsuperscript{2+} in MAPbI to Pb\textsuperscript{0}.

\[
M^{z+} + e^{-} \rightarrow M + ze^{-}
\]

(1)

\[
Pb^{2+} + 2e^{-} \rightarrow Pb
\]

(2)

It has been reported that Pb\textsuperscript{2+} in pristine halide perovskites acts as a donor-like surface state, which pins \( E_g \) at the surface.\textsuperscript{41,42} Thus we speculate that the Pb\textsuperscript{0} formed at the metal/MAPbI interface could influence the charge transport behavior. Next, we extract the effective Schottky barrier height (SBH) for electrons, which is one of the important parameters determining charge transfer efficiency, from the Pb\textsuperscript{0} core level shifts in the metal/MAPbI interfaces using the following equation:\textsuperscript{50}

\[
\Phi_B = E_g - E_F + \left( E_{core}^{metal} - E_{core}^{metal} \right) = E_g - \left( E_{core}^{metal} - E_{Vb} \right) \tag{3}
\]
The calculated gap states \((D_{MOS})\) and interface trap states \((D_i)\), the \(D_p\), \(D_{MOS}\), and \(D_i\) are estimated to be \(2.09 \times 10^{-13}\), \(4.16 \times 10^{-13}\), and \(2.05 \times 10^{-15}\) \(\text{eV}^{-1} \text{cm}^{-2}\), respectively. This result indicates that the interface trap states mainly cause the strong Fermi-level pinning at metal/\(\text{MAPbI}_3\) interfaces. Strikingly, the density of calculated gap states at the metal/\(\text{MAPbI}_3\) interfaces is two orders of magnitude larger than the previously reported surface state density of bare \(\text{MAPbI}_3\) \(|10^{13} \text{ eV}^{-1} \text{ cm}^{-2}|\). Probably, the formation of \(\text{Pb}^0\) due to the redox reaction between the deposited metal and iodine in \(\text{MAPbI}_3\) contributes to the difference in \(D_p\). This result indicates that the metal/\(\text{MAPbI}_3\) interfaces suffer from low charge transfer efficiency due to the \(\text{Pb}^0\)-interface trap state-induced strong Fermi-level pinning. Therefore, to enable efficient charge transport at the metal/\(\text{MAPbI}_3\) interfaces, the redox reaction resulting in the formation of extrinsic interface trap state should be suppressed.

![Diagram](image)

**Fig. 5 (a) Extracted Schottky barrier heights of \(\text{MAPbI}_3\) for the various metal work functions, showing the pinning factor \(S \sim 0.06\) when the deposited metal thickness is 40 Å (red dashed line). (b) Band diagram of metal/\(\text{MAPbI}_3\) interfaces with five different metals.**

peak \((138.24 \text{ eV})\), \(E^*_v\) is the initial binding energy of the VBM of \(\text{MAPbI}_3\), and \(E_{VC}\) is equal to \((E_{core}^*_v - E^*_v)\).

The extracted SBH values of the metal/\(\text{MAPbI}_3\) thin films are plotted as a function of the metal work function, as shown in Fig. 5a. The WF and SBH variations depending on the thickness of each metal appear as error bars in the x-axis and in the y-axis. It is apparent that the extracted SBHs are independent of metal work functions. To estimate the pinning factor \(S\) and charge neutrality level \((\phi_{CNL})\), we perform a linear fit using the Schottky-Mott law and the Sze model. The details in the fitting method are described in ESI.† The value of \(S\) varies from 1 for ideal interface without Fermi-level pinning to 0 for a strongly pinned interface. The obtained \(S\) value for the metal/\(\text{MAPbI}_3\) interfaces is 0.06 when the thickness of the deposited metal layer is 40 Å and the \(\phi_{CNL}\) is estimated to be 4.63 eV from the vacuum level, close to the Fermi level and above valance band maximum. This result reveals a strong Fermi-level pinning at the metal/\(\text{MAPbI}_3\) interface, therefore an ohmic contact cannot be formed between \(\text{MAPbI}_3\) and the metals investigated here (Fig. 5b).

We also calculated the density of the gap states \((D_g)\) at the metal/\(\text{MAPbI}_3\) interfaces using the Sze model because the gap states is known to induce Fermi-level pinning at metal/semiconductor junctions (details are given in ESI†). The calculated gap \(D_g\) are the sum of the density metal-induced gap states \((D_{MOS})\) and interface trap states \((D_i)\), the \(D_p\), \(D_{MOS}\), and \(D_i\) are estimated to be \(2.09 \times 10^{-13}\), \(4.16 \times 10^{-13}\), and \(2.05 \times 10^{-15}\) \(\text{eV}^{-1} \text{ cm}^{-2}\), respectively. This result indicates that the interface trap states mainly cause the strong Fermi-level pinning at metal/\(\text{MAPbI}_3\) interfaces. Strikingly, the density of calculated gap states at the metal/\(\text{MAPbI}_3\) interfaces is two orders of magnitude larger than the previously reported surface state density of bare \(\text{MAPbI}_3\) \(|10^{13} \text{ eV}^{-1} \text{ cm}^{-2}|\). Probably, the formation of \(\text{Pb}^0\) due to the redox reaction between the deposited metal and iodine in \(\text{MAPbI}_3\) contributes to the difference in \(D_p\). This result indicates that the metal/\(\text{MAPbI}_3\) interfaces suffer from low charge transfer efficiency due to the \(\text{Pb}^0\)-interface trap state-induced strong Fermi-level pinning. Therefore, to enable efficient charge transport at the metal/\(\text{MAPbI}_3\) interfaces, the redox reaction resulting in the formation of extrinsic interface trap state should be suppressed.

Furthermore, our experimental \(\phi_{CNL}\) of \(\text{MAPbI}_3\) is in agreement with the theoretical value of the \(\text{Pb}^0\)-related defect energy levels of \(\text{MAPbI}_3\). It means that the \(\text{Pb}^0\) trap states at the metal/\(\text{MAPbI}_3\) interfaces can act as nonradiative recombination sites, resulting in performance degradation of halide perovskite-based devices. It has been reported that different surface termination leads to changes in Fermi-level pinning at the surface of pristine halide perovskite due to the different amount of surface states. However, it is uncertain that controlled surface termination of halide perovskite surface can suppress the reaction at the interface between the metal and halide perovskite. To reduce the \(\text{Pb}^0\)-interface trap states at the metal/\(\text{MAPbI}_3\) thin films, an interlayer such as graphene and polymer thin films, which can prevent the reaction between the metal and halide perovskite, should be inserted at the interface.

**Conclusions**

In summary, we have experimentally investigated the evolution of interfacial properties and Fermi-level pinning at the interface between \(\text{MAPbI}_3\) and Al, Ti, Cr, Ag, and Au. XPS measurements indicate accumulation of \(\text{Pb}^0\) at the metal/\(\text{MAPbI}_3\) interfaces with subsequently increasing metal layer thickness. The formation of \(\text{Pb}^0\) aggregates at the interfaces is attributed to the interfacial reaction between the deposited metal and iodine ion from \(\text{MAPbI}_3\), confirmed by ToF-SIMS analysis. Based on the core level shift in metal/\(\text{MAPbI}_3\) interfaces, we obtained the effective Schottky barrier heights and the pinning factor between the metals and \(\text{MAPbI}_3\). The pinning factor of \(\text{MAPbI}_3\) is 0.06, indicating that Schottky barrier heights at the metal/\(\text{MAPbI}_3\) interfaces are independent with metal work function. The charge neutrality level of \(\text{MAPbI}_3\) is 4.62 eV less than 0.3 eV from the \(E_v\), consistent with \(\text{Pb}^0\)-related defects energy levels of \(\text{MAPbI}_3\).

The \(\text{Pb}^0\) aggregates have a detrimental impact on efficient transport and transfer of electrons and photogenerated carriers at the metal/\(\text{MAPbI}_3\) interfaces, as they act as interface trap sites and nonradiative recombination sites. This research suggests that the electrical properties of metal/\(\text{MAPbI}_3\) interfaces are dominated by \(\text{Pb}^0\)-related defects.
in MAPbI$_3$, resulting from the interfacial reaction. It also indicates that control of chemical bonding states, especially metal-iodine reactivity, is a key engineering parameter for designing higher performance halide perovskite-based devices.

**Experimental Section**

**Synthesis and sample preparation**

CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) films were fabricated on p-type Si substrates using one-step spin coating method in a N$_2$-filled glove box. The MAPbI$_3$ precursor solution was prepared by MAI (≥ 99%, Sigma-Aldrich) and PbI$_2$ (99.999% metal basis, Sigma-Aldrich) in molar ratio of 1:1 in anhydrous N,N-dimethylformamide (DMF) for overall concentration of 40 wt%. The mixed precursor solution was stirred for 24 h under 70 °C on a hot plate in a glove box. Before spin-coating of the MAPbI$_3$ precursor solution, ultraviolet (UV)-O$_3$ surface treatment was conducted on p-type Si substrates to make the surface of substrates hydrophilic to obtain a uniform and large-grain MAPbI$_3$ film. The MAPbI$_3$ precursor solution was spun onto the p-type Si substrate at a rate of 4000 rpm for 30 s. The films were annealed on a hot plate at 110 °C for 30 min. For metal deposition, the MAPbI$_3$ films were loaded into an ultra-high vacuum thermal evaporation system, which are integrated with the glove box, and Ag, Al, Au, Cr and Ti were deposited on the MAPbI$_3$ films with an equal deposition rate of 0.1 Å s$^{-1}$. The base pressure of the thermal evaporator was maintained at 10$^{-10}$ mbar and the pressure during metal deposition was less than 5 ×10$^{-7}$ mbar. The thickness of evaporated metal films was monitored by a quartz crystal microbalance and was also confirmed by X-ray reflectivity measurements.

**Metal/MAPbI$_3$ interface characterization**

The morphology and crystal structure of MAPbI$_3$ thin films were characterized by scanning electron microscope (SU-70, Hitachi) and X-ray diffraction (D-8 Advance, Bruker Miller). The absorption spectra of MAPbI$_3$ thin films on glass substrates were measured by an ultraviolet-visible photospectrometer (V-740, JASCO). To avoid air and moisture exposure and contamination, the prepared metal (Ag, Al, Au, Cr and Ti)/MAPbI$_3$ thin film samples in glove box were transferred into ultrahigh vacuum chamber for UPS and XPS measurement system via a ultra-high vacuum tube (<10$^{-10}$ mbar). The base pressure of the ultra-high vacuum chamber for UPS and XPS measurement was performed using an AXIS Ultra DLD model (KRATOS, U.K.) operating at a base pressure of 5×10$^{-10}$ mbar at 300 K with a monochromatic Al Kα line at 1486.69 eV. UPS was performed using a He I (21.2 eV) source. The results were corrected for charging effects using Au 4f as an internal reference. The binding energies of all UPS and XPS spectra were calibrated and referenced to the Fermi level (Ef) of the analyzer. A time-of-flight secondary ion mass spectrometry (IONTOF, Germany) was used for chemical depth profile of Ti/MAPbI$_3$, Ag/MAPbI$_3$, and Au/MAPbI$_3$ interfaces with Cs$^+$ primary ions (1 keV, 100 nA, 500×500 μm$^2$) for the erosion and a Bi$^+$ pulsed primary ion beam (30 keV, 1 pA, 100×100 μm$^2$) for the analysis. Measurements were collected in non-interlaced mode to minimize beam damage from the primary beam.

**Conflicts of interest**

The authors declare no competing financial interests.

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