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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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) 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/MAPbI₃ interface, resulting from the interfacial reaction between the deposited metal and iodine ions from MAPbI₃. It is found that the Schottky barrier height at the metal/MAPbI₃ 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 MAPbI₃ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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,³²⁻³⁴ 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.³⁶⁻³⁹ For example, Peng *et al.* and Gu *et al.* observed Ohmic conduction behavior in devices with an Au/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) interface,^{36,37} 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,

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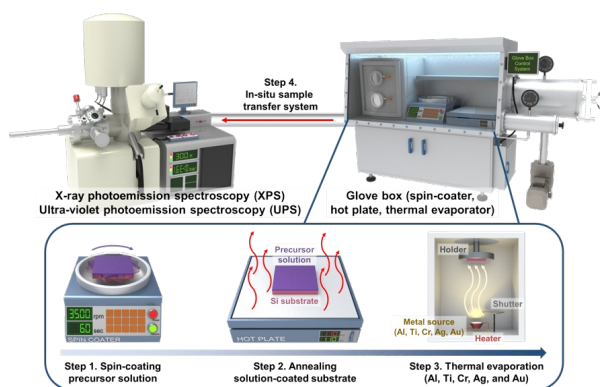
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highly surface sensitive X-ray photoemission spectroscopy (XPS) has proven to be an appropriate characterization technique for the evaluation of physical and chemical interface properties of halide perovskites without the need for an externally applied 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/MAPbI₃ interfaces by means of photoelectron spectroscopy. Formation of a pristine interface was enabled by using a glovebox equipped with a thermal evaporator and a direct transfer system to an XPS measurement chamber without exposing the samples to ambient air at any point. The common metal electrodes Al, Ti, Cr, Ag, and Au were selected to investigate the relationship of metal/MAPbI₃ interfaces as low and high work function metals from 4.1 to 5.2 eV. We found that a substantial amount of metallic lead (Pb⁰) is formed at the interfaces irrespective of metal electrode material. In addition, by chemical profiling we detect metal-iodine compounds at the interface indicating that the formation of Pb⁰ aggregates can be attributed to the chemical reaction between iodine in MAPbI₃ and the interfacing metal layer. The Pb⁰ aggregates induce Fermi-level pinning at the metal/MAPbI₃ interfaces, suggesting that the Fermi-level pinning at MAPbI₃ is mainly determined by the interfacial trap states rather than metal-induced gap states. The charge neutrality level of MAPbI₃ is consistent with the energy level of Pb⁰-related defects, which are nonradiative recombination sites. These results clearly show that the Pb⁰ aggregates play a key role in deteriorating charge transfer efficiency and determining the electrical properties of metal/MAPbI₃ interfaces. This study provides new insights for designing high performance halide perovskite-based electronic and optoelectronic devices.



Scheme 1 Schematic illustration for preparation and characterization process of metal/MAPbI₃ thin films.

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

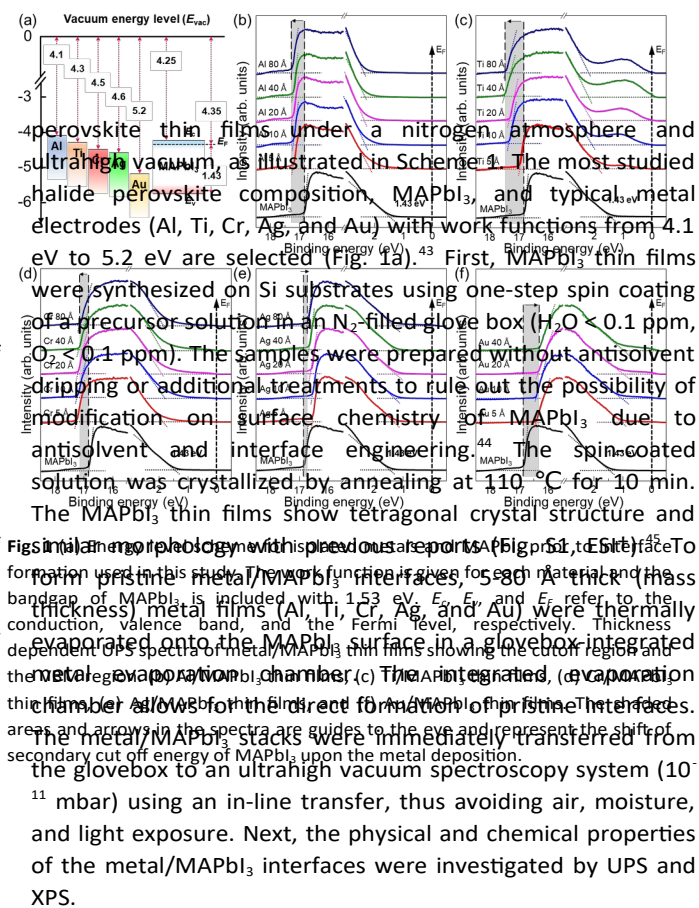


Fig. 1 (a) The energy level with this previous reports (Fig. S1, ESI†) for formation used in this study. The work function is given for each material and thickness of MAPbI₃ is included with 1.53 eV. E_c , E_v , and E_f refer to the conduction, valence band, and the Fermi level, respectively. Thickness dependence of the metal/MAPbI₃ interfaces showing the secondary cutoff energy of the metal/MAPbI₃ thin films. (b-f) The integrated UPS spectra of metal/MAPbI₃ thin films. The shaded areas and arrows in the spectra are guides to the eye and represent the shift of secondary cut off energy of MAPbI₃ upon the metal deposition. The metal/MAPbI₃ stacks were immediately transferred from the glovebox to an ultrahigh vacuum spectroscopy system (10⁻¹¹ mbar) using an in-line transfer, thus avoiding air, moisture, and light exposure. Next, the physical and chemical properties of the metal/MAPbI₃ interfaces were investigated by UPS and XPS.

Fig. 1b–f show 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 cut off energy was determined by linear extrapolation of the leading edge of the spectra.⁴⁶ The shifts of secondary cut off energy are highlighted with shaded areas and arrows in the spectra. The vacuum level (VL) is obtained from the difference between the secondary cutoff energy and the photon energy (21.22 eV). For bare MAPbI₃ 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 ($E_f - E_v$) is 1.43 eV, comparable to those previously reported in literature.^{41,47} With a bandgap of 1.53 eV (Fig. S2, ESI†), the surface of MAPbI₃ 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/MAPbI₃ 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 metal/MAPbI₃ saturate at 3.94 eV, 3.71 eV, 4.02 eV, 4.48 eV, and 4.90 eV for Al, Cr, Ti, Ag, and Au, respectively. The VL shift at the metal/MAPbI₃ interfaces reveals that charge transfer occurs between the deposited metals and MAPbI₃ thin films.⁴⁸ Al, Ti, and Cr deposition on MAPbI₃ leads downward VL shift, indicating that electrons are transferred from Al, Ti, and Cr to MAPbI₃. On the other hand, the upward VL shift with Ag and Au deposition means electron transfer occurs from MAPbI₃ thin films to the metal (Ag and Au). The valence band maximum (VBM) is determined by a linear extrapolation of valence band onset subtracted to the background around Fermi level.⁴⁶ The valence band spectra show the similar trend

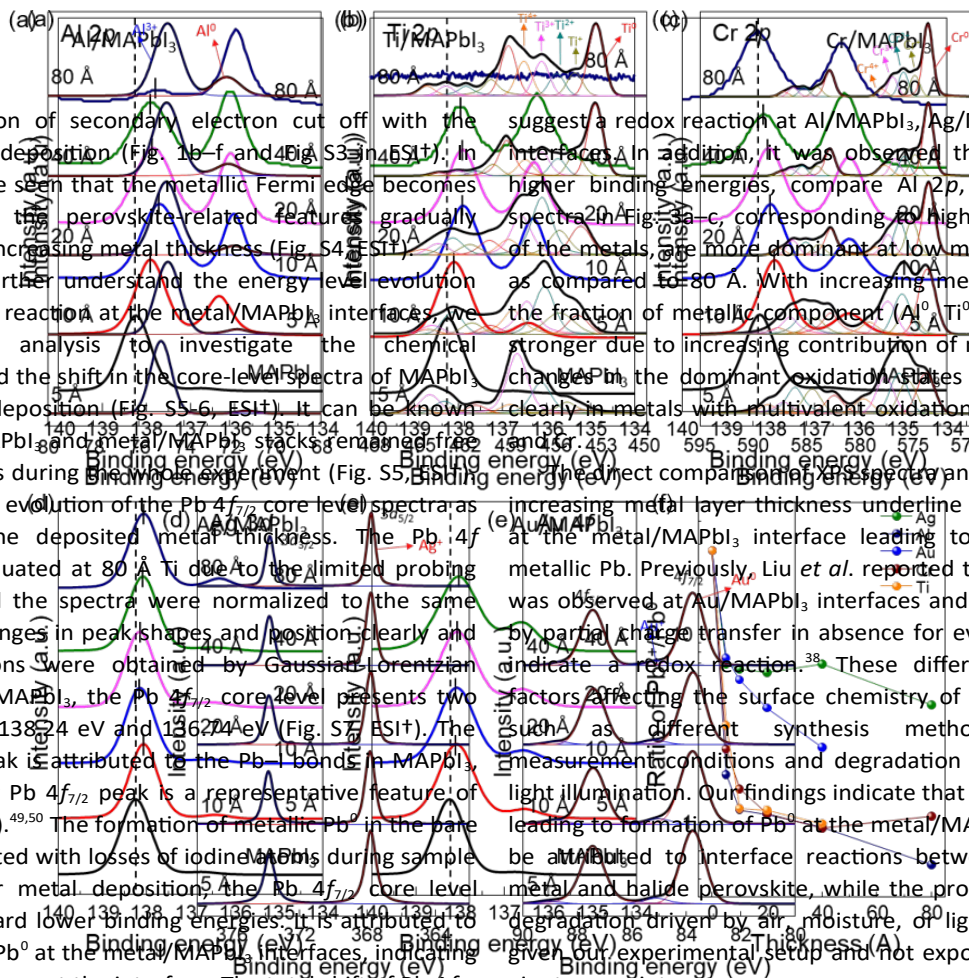


Fig. 2 The evolution of Pb 4f_{7/2} XPS peaks of the metal/MAPbI₃ thin films as a function of the deposited metal thickness. (a) Al/MAPbI₃ thin films, (b) Ti/MAPbI₃ thin films, (c) Cr/MAPbI₃ thin films, (d) Ag/MAPbI₃ thin films, (e) Au/MAPbI₃ thin films. The dashed line peaks in the core level spectra of MAPbI₃ thin films are the theoretical peaks in the Au/MAPbI₃ thin films.

induced by the metal deposition. Notably, it is evident that the metallic Pb⁰ peak (136.74 eV) becomes pronounced with increasing metal thickness. To evaluate the relative amount of Pb⁰, the evolution of the ratio of Pb²⁺ to Pb⁰ (Pb²⁺/Pb⁰) as a function of deposited metal thickness is plotted in Fig. 2f. For bare MAPbI₃, the Pb²⁺/Pb⁰ is 27.77. The Pb²⁺/Pb⁰ is drastically decreased after 5 Å layer of metal deposition and saturates at 0.59 (Al), 0.98 (Ti), 1.07 (Cr), 4.21 (Ag), and 2.51 (Au) with increasing the deposited metal thickness, respectively. This trend indicates that Pb⁰ becomes enriched at the metal/MAPbI₃ interface possibly due to charge transfer between the deposited metal layers and MAPbI₃ thin films.

To provide further information on the interaction between the deposited metal layers and the MAPbI₃ 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/MAPbI₃ interfaces resulting from the charge transfer between the deposited metal and MAPbI₃ thin films. For example, we can find the dominant Al³⁺ (74.7 eV) and Ag⁺ (367.8 eV) peaks in Al 2p and Ag 3d_{5/2} spectra, which are associated to the Al and Ag component in aluminium halides and silver halides, respectively (Fig. 3a,d).⁵¹ The Au 4f_{7/2} spectra can be deconvoluted into two distinct components centered at 83.8 eV and 85.1 eV, which are ascribed to Au⁰ and Au⁺, respectively (Fig. 3e).⁵² The oxidized Al, Ag, or Au layers on MAPbI₃ and the formation of Pb⁰ through reduction of Pb²⁺

suggest a redox reaction at Al/MAPbI₃, Ag/MAPbI₃, Au/MAPbI₃ interfaces. In addition, it was observed that the peaks with higher binding energies, compare Al 2p, Ti 2p, and Cr 2p spectra in Fig. 3a-c, corresponding to higher oxidation states of the metals, are more dominant at low metal thickness (5 Å) as compared to 80 Å. With increasing metal layer thickness, the fraction of metallic component (Al⁰, Ti⁰, and Cr⁰) becomes stronger due to increasing contribution of neutral metals. The dominant oxidation states can be seen more clearly in metals with multivalent oxidation states, here for Ti increasing metal layer thickness underline the redox reaction at the metal/MAPbI₃ interface leading to the formation of metallic Pb. Previously, Liu *et al.* reported that no metallic Pb⁰ was observed at Au/MAPbI₃ interfaces and this was explained by partial charge transfer in absence for evidence that would indicate a redox reaction.³⁸ These differences are due to factors affecting the surface chemistry of halide perovskites, such as different synthesis methods, uncontrolled measurement conditions and degradation by air exposure or light illumination. Our findings indicate that the charge transfer leading to formation of Pb⁰ at the metal/MAPbI₃ interfaces can be attributed to interface reactions between the deposited metal and halide perovskite, while the probability for MAPbI₃ degradation driven by air moisture, or light is relatively low given our experimental setup and not exposing the sample to air at any point.

Fig. 3 The evolution of the core level spectra of Al 2p, Ti 2p, Cr 2p, Ag 3d and Au 4f core level spectra of the metal/MAPbI₃ thin films as a function of the deposited metal thickness. (a) Al 2p, (b) Ti 2p, (c) Cr 2p, (d) Ag 3d, (e) Au 4f core level spectra of the metal/MAPbI₃ thin films. The dashed line peaks in the core level spectra of MAPbI₃ thin films are the theoretical peaks in the Au/MAPbI₃ thin films.

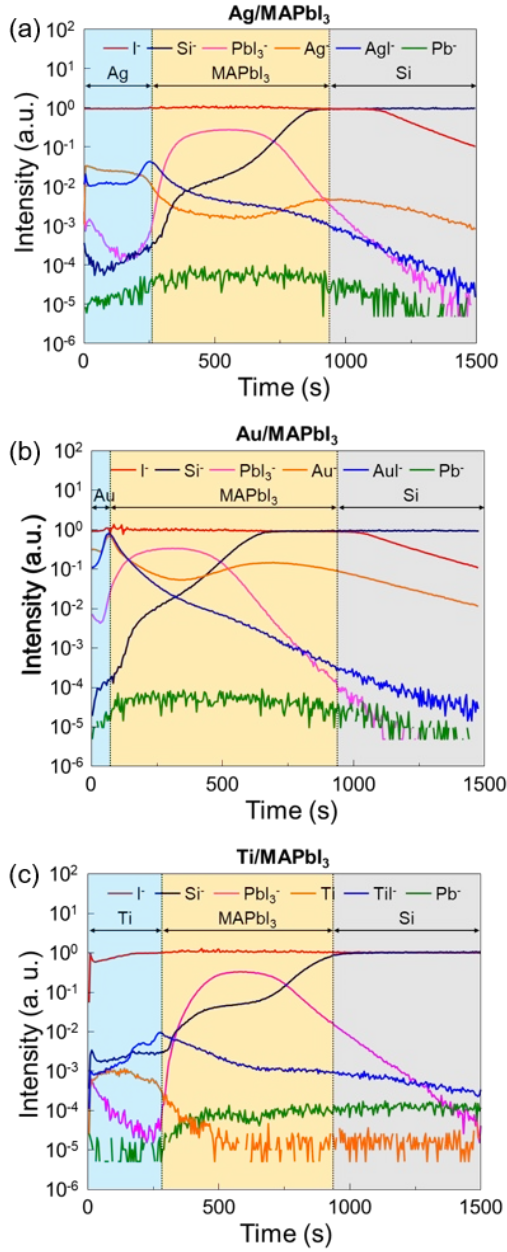
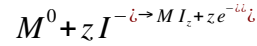


Fig. 4 ToF-SIMS depth profiles of (a) the Ag/MAPbI₃, (b) the Au/MAPbI₃, and (c) the Ti/MAPbI₃ stacks.

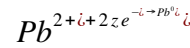
To further investigate the underlying interfacial chemistries of the metal/MAPbI₃ interfaces, time-of-flight secondary ion mass spectroscopy (ToF-SIMS) is employed to study the elemental distribution in the metal/MAPbI₃ stacks. Fig. 4 shows the ToF-SIMS depth profiles of relative element distributions in Ag/MAPbI₃, Au/MAPbI₃, and Ti/MAPbI₃ stacks. The boundaries of each layer were identified by the intensity of detected ions, as reported in previous studies.^{53,54} Ag⁺, Au⁺, and Ti⁺ ions are selected to identify the deposited metal layers, Pb⁺ for Pb⁰ aggregates, Pbl₃⁻ for the MAPbI₃ thin films, Si⁻ for the substrates. The maximum signals of AgI⁻, AuI⁻, and TiI⁻ are observed at the Ag/MAPbI₃, Au/MAPbI₃, and Ti/MAPbI₃ interfaces, indicating a chemical reaction between the deposited metals and iodine from the MAPbI₃ surface. The

formation of metal-iodine compounds is attributed to thermodynamically stronger bonds as compared to metal-metal bonds.⁴³ In addition, the ToF-SIMS result of the bare MAPbI₃ film (Fig. S8, ESI[†]) reveals that the concentration of Pb⁰ is higher in the bulk than at the surface, which is in good agreement with the Pb⁰ distribution in bare MAPbI_{3-x}Cl_x films reported by Sadoughi *et al.*⁵⁰ However, the concentration of Pb⁰ at metal/MAPbI₃ interfaces is comparable with that at bulk MAPbI₃. It indicates that a substantial amount of Pb⁰ is existed at metal/MAPbI₃ interfaces, consistent with XPS results.

Overall, our XPS and ToF-SIMS results provide evidence that the redox reaction between MAPbI₃ and all investigated metals occurs. It has been reported that thermodynamically unfavorable reactions can occur at metal/semiconductor, especially metal/Pb(Zr,Ti)O₃ interface, due to the heat of condensation of metal atoms.⁵⁵⁻⁵⁷ However, the formation of metal-iodine bond is thermodynamically favor due to the negative formation enthalpy and energy barrier,⁴³ resulting in the formation of Pb⁰ state at metal/MAPbI₃ interfaces (Table S1, ESI[†]). Generally, it is believed that Ag has higher reactivity with halide perovskite compared to other metals.^{28,58,59} 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 MAPbI₃ 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 Pb²⁺ in MAPbI₃ to Pb⁰.



(1)



(2)

It has been reported that Pb⁰ in pristine halide perovskites acts as a donor-like surface state, which pins E_F at the surface.^{41,42} Thus we speculate that the Pb⁰ formed at the metal/MAPbI₃ 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 4f_{7/2} core level shifts in the metal/MAPbI₃ interfaces using the following equation:⁶⁰

$$\phi_B = E_g - E_V^i + (E_{core}^i - E_{core}^{metal}) = E_g - (E_{core}^{metal} - E_{VC}) \quad (3)$$

where ϕ_B is the SBH, E_g is the bandgap of MAPbI₃ (1.53 eV), E_{core}^{metal} is the binding energy of the core level peak after metal deposition, E_{core}^i is the initial binding energy of the core level

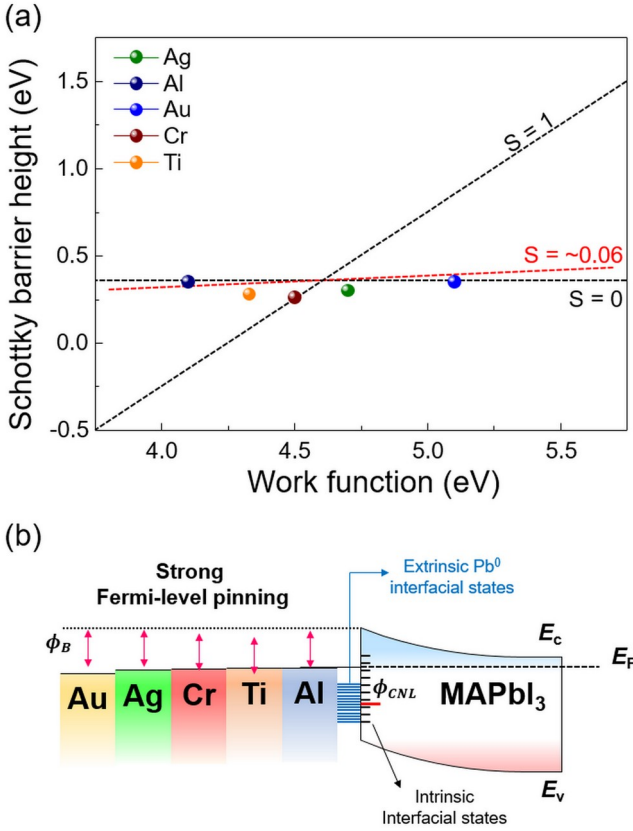


Fig. 5 (a) Extracted Schottky barrier heights of MAPbI₃ for the various metal work functions, showing the pinning factor $S \sim 0.06$ when the deposited metal thickness is 40 Å (red dashed line). (b) Band diagram of metal/MAPbI₃ interfaces with five different metals.

peak (138.24 eV), E_v^i is the initial binding energy of the VBM of MAPbI₃, and E_{VC} is equal to $(E_{core}^i - E_v^i)$.

The extracted SBH values of the metal/MAPbI₃ 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 (ϕ_{CNL}), we perform a linear fit using the Schottky-Mott law and the Sze model.⁶¹ 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/MAPbI₃ interfaces is 0.06 when the thickness of the deposited metal layer is 40 Å and the ϕ_{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/MAPbI₃ interface, therefore an ohmic contact cannot be formed between MAPbI₃ and the metals investigated here (Fig. 5b).

We also calculated the density of the gap states (D_g) at the metal/MAPbI₃ 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†).⁶¹⁻⁶² The calculated gap D_g are the sum of the density metal-

induced gap states (D_{MIGS}) and interface trap states (D_{IT}), the D_g , D_{MIGS} , and D_{IT} are estimated to be 2.09×10^{15} , 4.16×10^{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/MAPbI₃ interfaces. Strikingly, the density of calculated gap states at the metal/MAPbI₃ interfaces is two orders of magnitude larger than the previously reported surface state density of bare MAPbI₃ ($\sim 10^{13} \text{ eV}^{-1} \text{ cm}^{-2}$).⁶³ Probably, the formation of Pb⁰ due to the redox reaction between the deposited metal and iodine in MAPbI₃ contributes to the difference in D_g . This result indicates that the metal/MAPbI₃ interfaces suffer from low charge transfer efficiency due to the Pb⁰-interface trap state-induced strong Fermi-level pinning. Therefore, to enable efficient charge transport at the meal/MAPbI₃ interfaces, the redox reaction resulting in the formation of extrinsic interface trap state should be suppressed.

Furthermore, our experimental ϕ_{CNL} of MAPbI₃ is in agreement with the theoretical value of the Pb⁰-related defect energy levels of MAPbI₃.⁶⁴ It means that the Pb⁰ trap states at the metal/MAPbI₃ interfaces can act as nonradiative recombination sites, resulting in performance degradation of halide perovskite-based devices.⁵⁰ 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.⁶³ 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 Pb⁰-interface trap states at the metal/MAPbI₃ 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.^{53,65}

Conclusions

In summary, we have experimentally investigated the evolution of interfacial properties and Fermi-level pinning at the interface between MAPbI₃ and Al, Ti, Cr, Ag, and Au. XPS measurements indicate accumulation of Pb⁰ at the metal/MAPbI₃ interfaces with subsequently increasing metal layer thickness. The formation of Pb⁰ aggregates at the interfaces is attributed to the interfacial reaction between the deposited metal and iodine ion from MAPbI₃, confirmed by ToF-SIMS analysis. Based on the core level shift in metal/MAPbI₃ interfaces, we obtained the effective Schottky barrier heights and the pinning factor between the metals and MAPbI₃. The pinning factor of MAPbI₃ is 0.06, indicating that Schottky barrier heights at the metal/MAPbI₃ interfaces are independent with metal work function. The charge neutrality level of MAPbI₃ is 4.62 eV less than 0.3 eV from the E_F , consistent with Pb⁰-related defects energy levels of MAPbI₃. The Pb⁰ aggregates have a detrimental impact on efficient transport and transfer of electrons and photogenerated carriers at the metal/MAPbI₃ interfaces, as they act as interface trap sites and nonradiative recombination sites. This research suggests that the electrical properties of metal/MAPbI₃ interfaces are dominated by Pb⁰-related defects

in MAPbI₃, 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

CH₃NH₃PbI₃ (MAPbI₃) films were fabricated on p-type Si substrates using one-step spin coating method in a N₂-filled glove box. The MAPbI₃ precursor solution was prepared by MAI (≥ 99%, Sigma-Aldrich) and PbI₂ (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 MAPbI₃ precursor solution, ultraviolet (UV)-O₃ surface treatment was conducted on p-type Si substrates to make the surface of substrates hydrophilic to obtain a uniform and large-grain MAPbI₃ film. The MAPbI₃ 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 MAPbI₃ 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 MAPbI₃ 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/MAPbI₃ interface characterization

The morphology and crystal structure of MAPbI₃ thin films were characterized by scanning electron microscope (SU-70, Hitachi) and X-ray diffraction (D-8 Advance, Bruker Miller). The absorption spectra of MAPbI₃ 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)/MAPbI₃ thin film samples in glove box were transferred into ultrahigh vacuum chamber for UPS and XPS measurement system via a ultra-high vacuum tube (<10⁻⁸ mbar). The XPS, and UPS analyses were conducted using advanced in-situ nanosurface analysis system (AISAS, KBSI, Korea). XPS 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 (E_F) of the analyzer. A time-of-flight secondary ion mass spectroscopy (IONTOF, Germany) used for chemical depth profile of Ti/MAPbI₃, Ag/MAPbI₃, and Au/MAPbI₃ interfaces with Cs⁺ primary ions (1 keV, 100 nA, 500 × 500 μm²) for the erosion and a Bi⁺ pulsed primary ion beam (30 keV, 1 pA, 100 × 100 μm²) 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.

Acknowledgements

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