Intact Metal/Metal Halide van der Waals Junction Enables Reliable Memristive Switching with High Endurance

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Organic–inorganic or inorganic metal halide materials have emerged as a promising candidate for a resistive switching material owing to their ability to achieve low operating voltage, high on–off ratio, and multi-level switching. However, the high switching variation, limited endurance, and poor reproducibility of the device hinder practical use of the memristors. In this study, a universal approach to address the issues using a van der Waals metal contact (vdWC) is reported. By transferring the pre-deposited metal contact onto the active layers, an intact junction between the metal halide and contact layer is formed without unintended damage to the active layer caused by a conventional physical deposition process of the metal contacts. Compared with the thermally evaporated metal contact (EVC), the vdWC does not degrade the optoelectronic quality of the underlying layer to enable memristors with reduced switching variation, significantly enhanced endurance, and reproducibility relative to those based on the EVC. By adopting various metal halide active layers, versatile utility of the vdWC is demonstrated. Thus, this vdWC approach can be a useful platform technology for the development of high-performance and reliable memristors for future computing.
halide layer might hinder the formation of a reproducible, clean, and uniform junction at the interface\cite{28,29} and thus the reliable operation of the memristor devices. However, the side effects of the deposition process have rarely been considered for metal halide memristors.

Herein, we adopt the van der Waals metal contact (vdWC) approach to form an intact junction between the metal contact and the underlying metal halide active layer. The vdWC was formed by transferring the pre-deposited metal contact onto the active layer. It retained the high optoelectronic quality of the underlying active layer without degradation, enabling reproducible metal halide memristors with reduced switching variation, and significantly enhanced endurance relative to those based on a conventional thermally evaporated metal contact (EVC). Furthermore, the general applicability of the vdWC approach is demonstrated by adopting various metal halide active layers, which ensures the versatile utility of vdWC for high-performance memristive applications.

2. Results and Discussion

2.1. Formation of Intact van der Waals Metal Contacts

The memristors were fabricated based on solution-processed hexagonal formamidinium lead triiodide (\(\delta\)FAPbI\(_3\)) thin films with the structure of Si/Pt/FAPbI\(_3\)/Ag.\cite{30} On top of the FAPbI\(_3\) films, Ag metal contacts are formed by either conventional thermal evaporation (EVC) or physical lamination of the pre-deposited metal contacts through van der Waals force (vdWC), as depicted in Figure 1a. Photographs of the devices based on vdWC are shown in Figure 1b where most of the vdWCs are successfully transferred onto FAPbI\(_3\) films. An optical microscopy image with higher magnification in Figure 1c confirms a well-defined Ag electrode array formed by the transfer process.

To investigate the possible physical and chemical interactions between the metal contacts and the underlying FAPbI\(_3\) layer, optical microscopy (upper panels) and the corresponding photoluminescence (PL) mapping images (middle panels) are shown in Figure 1d–g where a line scan of the PL intensity is shown in the lower panels. The PL emission spectrum of the \(\delta\)FAPbI\(_3\) film spans from \(\approx\)650 to 900 nm (Figure S1, Supporting Information), probably due to the charge carrier funneling from \(\delta\)FAPbI\(_3\) to trace \(\alpha\)-FAPbI\(_3\) in the film.\cite{31} PL mapping images were obtained before (Figure 1d,f) and after peeling off the deposited metal contacts using adhesive tape (Figure 1e,g). Before peeling off the metal contacts, the film region covered by EVC or vdWC was clearly visible as dark spots (middle panels of Figure 1d,f). After the EVC was peeled off, the PL intensity was notably lower in the region where the deposited Ag was located (the region enclosed with white dashed lines in Figure 1e) than in the region without metal contacts. This implies that the EVC deposition process possibly degrades the optoelectronic quality of the underlying FAPbI\(_3\) films, resulting in nonradiative recombination.\cite{31} In contrast, after the vdWC was peeled off, the region where the vdWC was transferred showed a PL intensity comparable to that of the region without metal contacts (Figure 1g), indicating that the FAPbI\(_3\) layer under the vdWC remained intact.

Time-of-flight secondary ion mass spectrometry (TOFSIMS) was performed to study the depth distribution of the deposited metal atoms in the FAPbI\(_3\) memristors (Figure 2a,b). In the device with EVC, Ag atoms seem to penetrate the bulk FAPbI\(_3\) layer, which makes the boundary between the Ag and FAPbI\(_3\) layer unclear (Figure 2a).\cite{32} In particular, the relative intensity of Pb in the top electrode region is comparable to that of Ag, suggesting that severe physical and/or chemical interactions occur between the Ag and FAPbI\(_3\) layers. This can be attributed to the bombardment of the FAPbI\(_3\) surface by the thermally excited metal atoms, which provide sufficient thermal and kinetic energy for the metal atoms to diffuse into and/or react with the underlying FAPbI\(_3\) layer during the thermal evaporation process. For the devices with vdWC in Figure 2b, the Ag and FAPbI\(_3\) layers were clearly distinguishable, indicating a well-defined planar van der Waals heterojunction formed between the vdWC and FAPbI\(_3\) layers.

To investigate possible changes in the surface morphology and electrical properties of the underlying FAPbI\(_3\) layer with different top metal contacts, conductive atomic force microscopy (c-AFM) images of bare FAPbI\(_3\) film and the FAPbI\(_3\) films after peeling off the EVC or vdWC (hereafter referred to as EVC-off and vdWC-off, respectively) were compared (Figure 2c–e). Optical microscopy (upper panel), topography (middle panel), and c-AFM images (lower panel) are shown for each sample. The regions where the metal contacts were peeled off are marked with red dashed lines in the optical microscopy images in Figure 2d,e, and the regions highlighted with a black solid square are analyzed through c-AFM measurements. Compared with the bare FAPbI\(_3\) film (Figure 2c), the EVC-off film exhibited significantly altered surface morphology and electrical characteristics (Figure 2d). The scanned images show an increase in the surface roughness and inhomogeneous conductivities of the EVC-off film, which is more evident in the line scan profiles of the topography and conductivity in Figure 2f,g. This might be due to residual Ag having chemical interactions with the FAPbI\(_3\) layer and/or damaged underlying FAPbI\(_3\) layer during the thermal evaporation and peeling-off process. The residual Ag on the FAPbI\(_3\) film was detected using X-ray photoelectron spectroscopy (XPS) in Figure S2 (Supporting Information). Clear Ag 3d peaks were observed from the EVC-off film surface, and chemical shifts of the Pb 4f, I 3d, and N 1s peaks relative to those in the bare film suggest that there are chemical interactions between the residual Ag and the FAPbI\(_3\) layer. The unintended chemical interactions between the EVC and the FAPbI\(_3\) layer can alter the electrical and electronic properties of the FAPbI\(_3\) layer, which hampers the utilization of the intrinsic properties of FAPbI\(_3\). Indeed, the UV photoelectron spectroscopy (UPS) data in Figure S3 (Supporting Information) show that the positions of the energy band edges and Fermi level for the EVC-off sample are different from those measured in the bare FAPbI\(_3\) film. For the region where the vdWC is peeled off, we identified that the FAPbI\(_3\) film surface morphology and conductivity are almost unchanged compared with those of the bare FAPbI\(_3\) film (Figure 2e–g), which is consistent with the PL mapping data in Figure 1.
2.2. Memristors Based on van der Waals Metal Contacts

The current–voltage (I–V) curves of the FAPbI₃ memristors based on the EVC and vdWC are shown in Figure 3a,b, respectively. Bipolar resistive switching behavior was observed for both devices based on the FAPbI₃ films with an average thickness of 208 ± 15 nm. When the first positive voltage sweep (0 V → 0.6 V → 0 V, compliance current of 10⁻² A) is applied, the resistance is changed from a high-resistance state (HRS) to a low-resistance state (LRS), which is a set process that forms CFs. Upon application of a negative voltage sweep (0 V → −0.6 V → 0 V, compliance current of 10⁻¹ A), a reset process occurs where the resistance is changed from LRS to HRS by rupturing the CFs. For the device based on EVC, the CFs are formed at ≈ 0.27 V, which is substantially lower than ≈ 0.49 V for that based on vdWC (black dashed lines in Figure 3a,b). After the forming process, the next ten scans were conducted with a lower positive bias voltage (0 V → 0.35 V → 0 V → −0.6 V → 0 V).
but the same compliance current. As shown in Figure 3a, the device based on EVC showed comparable set voltages for the first forming scan and the next ten scans. In contrast, there is a clear difference in the set voltages for the first forming scan and the next ten scans for the vdWC device. The relatively low forming voltage of the EVC device could be caused by thermally evaporated Ag atoms that penetrated and reacted with the FAPbI₃ layer, resulting in the formation of unintended chemical bonding and relevant defects.[26,27] The (reacted) Ag atoms in the FAPbI₃ layer reduced the activation energy for electrochemical metallization (ECM) and valence change of the FAPbI₃ layer, thus facilitating the migration of Ag atoms and iodide vacancies at a relatively low bias voltage (Figure S4a, Supporting Information). In contrast, vdWC hardly generates additional defects during the transfer process. Thus, Ag atom penetration at the well-defined van der Waals heterojunction in the vdWC device requires a higher bias voltage than that in the EVC device (Figure S4b, Supporting Information).[33,34]
resulting in a higher forming voltage for the vdWC device than for the EVC device. During additional ten scans, the average set voltages of EVC and vdWC devices were $0.18 \pm 0.048$ and $0.17 \pm 0.029$ V, respectively. The well-defined van der Waals junction between the vdWC and FAPbI$_3$ layers probably enables more reproducible formation of the CFs, and thus a narrower distribution of set voltages (Figure S4, Supporting Information). In the case of reset voltages, the average and deviation for both devices were comparable ($-0.22 \pm 0.042$ and $-0.19 \pm 0.049$ V for EVC and vdWC devices, respectively). The comparable reset voltages indicate that the sizes and orientations of the formed CFs were similar, irrespective of the contact layer.[35]

In Figure 3c, the time-resolved current decay curves, $i(t)$ are measured to estimate the concentration of mobile ions (defects) in the EVC and vdWC devices. As the total current is the sum of the electronic current ($I_{\text{electronic}}$) and ionic current ($I_{\text{ionic}}$), $I_{\text{ionic}}$ was obtained by subtracting $I_{\text{electronic}}$ from the total current. While $I_{\text{electronic}}$ can flow through the electrodes, mobile ions accumulate at the interfaces between the FAPbI$_3$ layer and the electrodes. Consequently, $I_{\text{electronic}}$ has a steady-state value ($I_{\text{ss}}$), whereas $I_{\text{ionic}}$ is transient. Therefore, we estimated the migrated mobile ion concentration using the equation[36–38] given by:

$$\text{migrated ion concentration} = \frac{\int_i(f - I_{\text{ss}})dt}{\text{volume of the perovskite layer}}$$

The migrated ion concentrations for each device are shown in Figure 3c. The lower total migrated ion concentration of the vdWC device at a given time suggests that the mobile ionic
defect density in the vdWC device was lower than that in the EVC device. This supports the thermal evaporation process of the Ag metal contact generated additional defects in the underlying FAPbI₃ layer. We also compared the defect densities of the EVC and vdWC devices based on non-reactive gold contacts using space charge limited current (SCLC) measurements (Figure S5, Supporting Information). Since we used an identical FAPbI₃ layer, the trap-filling voltage ($V_{TFL}$) should be linearly proportional to the trap density in the film.

The average $V_{TFL}$ of EVC devices (0.50 ± 0.092 V) is 1.6 times higher than that of vdWC one (0.31 ± 0.083 V), indicating that trap density in the EVC device is 1.6 times higher than that in the vdWC one. This indicates that not only the reactive nature of the Ag atom but also physical damage by the thermally excited metal atoms causes defects in the underlying FAPbI₃ layer during the thermal evaporation process.

To study the conduction mechanism in both devices, plots of log $I$–log $V$ in the LRS and ln($I$)/$V^{1/2}$ in the HRS are analyzed in Figure 3d,e. In the LRS, the carrier transport mechanism of both EVC and vdWC devices is ohmic conduction, as confirmed by the linear relationship between the current and voltage. With a slope of 0.96, vdWC forms a more ideal ohmic junction with the underlying FAPbI₃ than the EVC dose (slope ≈0.91, Figure 3d). In the HRS, the conduction mechanism for both devices was Schottky emission, as evidenced by the linear relationship between ln $I$ and $V^{1/2}$ (Figure 3e) [40,41]. Interestingly, the slope of the plot for EVC is much lower than that of vdWC devices. The Schottky barrier is expected to be formed at the interface between FAPbI₃ and Pt owing to the large difference in the work function. The Schottky emission equation is given by:

$$I = A' T^2 \exp \left[ -\frac{q(\varphi_B - \sqrt{q V/(4 \pi \varepsilon_0 d)})}{kT} \right]$$

where $I$ is the current, $A'$ is the effective Richardson constant, $T$ is the absolute temperature, $q$ is the electron charge, $k$ is the Boltzmann constant, $\varphi_B$ is the Schottky barrier height, $V$ is the external voltage, $\varepsilon_0$ is the optical dielectric constant, $\varepsilon_0$ is the permittivity in a vacuum, and $d$ is the Schottky barrier thickness [40,41]. According to the equation, the $d$ is inversely proportional to the slope as $d \propto \left( \frac{1}{\text{slope}} \right)$. Therefore, the $d$ is thinner for the device based on EVC than that based on vdWC. We speculated that the migrated ionic defects generated by thermal evaporation in the EVC device might compensate for the built-in potential to decrease the Schottky barrier thickness in the EVC device. To further verify our speculation, the In $I$–$V^{1/2}$ curves of the devices at different temperatures are shown in Figure 3f. A notable difference was observed in the temperature-dependent slope change in the In $I$–$V^{1/2}$ curves. While the slope decreased as the temperature increased for the vdWC device, it increased anomalously for the EVC device. We attributed the anomalous increase in the slope, and thus reduced the barrier thickness with increasing temperature, to the heat-induced activation of the defect migration pronounced in the EVC device. For both devices, the linear relationship between ln($I$)/$T^2$ and 1000/$T$ is observed with different bias voltages from 0.05 to 0.15 V (Figure S6, Supporting Information), which confirms the Schottky emission conduction in HRS of both EVC and vdWC devices.

In Figure 4, the reproducibility of resistive memory operation of the devices based on the EVC and vdWC is compared. For each condition, the histograms for operating voltages of 350 devices on seven different substrates fabricated in the same batch are shown in Figure 4a,b. Consistent with the data in Figure 3a,b, an average forming voltage for vdWC devices is 0.36 ± 0.049 V, higher than 0.27 ± 0.051 V of EVC one (Figure 4a; Table S1, Supporting Information). In the histogram of the set voltage, the vdWC device (0.16 ± 0.036 V) has a relatively narrower distribution than the EVC device (0.19 ± 0.050 V, Figure 4b). The relatively poor reproducibility of the EVC device was observed from the device to the other devices on the same substrate, as well as from the substrate to the other substrate.

The position-dependent evaporation rate, and thus the energy of the Ag atom, probably causes penetration and reaction of the Ag atom in the underlying FAPbI₃ layer to varying degrees, causing such a wide distribution in the set voltage. Thus, the vdWC device, which is free from such damage, shows a relatively uniform junction and thus operating voltage.

The cumulative probabilities of the HRS and LRS resistances of the 350 cells for both the EVC and vdWC devices are demonstrated in Figure 4c,d. The average LRS and HRS resistances of the EVC device are 109.2 ± 44.3 Ω and 1.52 × 10⁸ ± 1.52 × 10⁷ Ω, respectively (Figure 4c; Figure S7a, Supporting Information), while those of the vdWC devices are 69.4 ± 34.8 Ω and 5.4 × 10⁸ ± 2.61 × 10⁷ Ω, respectively (Figure 4d; Figure S7b, Supporting Information). The formation of reproducible van der Waals hetero-junctions without generating additional defects during the fabrication process could be the origin of the much narrower distribution of the LRS and HRS resistances of the vdWC device compared with those of the EVC device. Notably, a large proportion of the EVC devices suffer from a serious reaction between the EVC and FAPbI₃ layer, and these devices show anomalously higher resistance (lower current) than EVC devices with less reaction and vdWC devices, probably because of the increase in series resistance of the degraded metal contact and formation of the insulating AgI₃ layer (Figure S8, Supporting Information). Especially in the HRS without CFs, the conductance was largely decreased. To investigate the batch reproducibility, the box plots for the set and reset voltages of the devices from three different batches are presented in Figure 4e (the box plot for the forming voltage of the devices is shown in Figure S9, Supporting Information). As summarized in Tables S2–S4 (Supporting Information), the vdWC devices fabricated in the different batches have relatively less operating deviation, especially for the set voltage, compared to the EVC devices.

The on–off switching cycle endurance of the devices is shown in Figure 5a. While the EVC device failed after ~650 cycles of operation, the vdWC device remained operable up to 2100 cycles, a more than 3-fold improvement in endurance. The major reset failure reported is likely due to the formation of permanent conducting filaments involving a large number of metal atoms or anion vacancies [42,43]. When a voltage is applied, the Ag atoms in the EVC can easily migrate into the FAPbI₃ layer through chemical bonding to participate in the formation
of CFs. As the number of operation cycles increases, more migration of the metal atoms can occur. Finally, permanent metal filaments that cannot be ruptured cause switching failure in EVC devices. In this regard, the dramatically improved endurance of the vdWC device is owing to the well-defined van der Waals heterojunction with relatively high activation energy for Ag atom penetration, which prevents the formation of permanent CFs.

To evaluate the storage stability, the I–V characteristics of the devices were tracked for 30 days (Figure 5b,c). The vdWC device retained more consistent I–V characteristics than the EVC device. After 10 days, the HRS resistance of the EVC device sharply increased, which can be attributed to the aforementioned reaction of the EVC with the FAPbI₃ layer. The relatively severe reaction between the EVC and FAPbI₃ layer was confirmed by X-ray diffraction (XRD) measurements, where the appearance of an AgI peak with a higher intensity was observed for the EVC device (Figure S10, Supporting Information). The optical microscopy images in Figure S11, (Supporting Information) further show more reactive interactions between the EVC and FAPbI₃ layers than between the vdWC layers. The formation of insulating AgI might cause the increase in series resistance and thus alteration in distribution of the applied electric field, as well as the generation of additional defects. All these factors could affect the operating characteristics of the EVC device and degrade device reliability. Temperature-dependent I–V characteristics of both devices were measured to study their thermal stability (Figure 5d,e). In vdWC devices, a relatively stable set/reset operation was observed across all temperatures tested, whereas an incomplete reset of the EVC device occurred at 356 K. As the temperature increases, the migration of Ag atoms and their reaction with other defects in the EVC might be further promoted to generate permanent CFs that induce an incomplete reset of the device. We observed that the device with a more serious reaction between the EVC and FAPbI₃ layers suffers from relatively poor thermal stability. In other words, a few EVC devices with relatively less reaction between the EVC and FAPbI₃ layers showed better thermal stability (Figure S12, Supporting Information), supporting the detrimental effects of the damage caused by the direct metal contact.

Figure 4. Statistical operation property analysis. Operating voltage of the 350 devices based on EVC and vdWC in the same batch; a) forming voltage, b) set voltage, and reset voltage. Cumulative probabilities for the on/off ratio of 350 devices based on the c) EVC and d) vdWC in the same batch. e) A box plot for operating voltages of the 30 devices based on EVC and vdWC fabricated in three different batches (denoted as B1, B2, B3).
deposition on the thermal stability of the devices. Similar to the operation characteristics, various thermal stabilities of the EVC devices were observed from device to device in the same substrate, as well as from substrate to substrate. Retention capability with on–off ratio higher than $10^7$ was confirmed for the vdWC devices with a reading voltage of 0.05 V (Figure S13, Figure 5. Stability of the memristors. a) The endurance measurement of Si/Pt/FAPbI$_3$/Ag devices based on EVC (upper panel) and vdWC (lower panel). Applied voltage pulses = 0.25 V, pulse width = 640 µs, compliance current (CC) = 1 mA for set and applied voltage pulses = -0.42 V, pulse width = 1 ms, CC = 100 mA for reset, reading voltage = 0.03 V. b,c) Time-dependent current–voltage ($I$–$V$) characteristics of the devices measured for 30 days (inset: HRS and LRS resistance values of the devices with different aging time). d,e) The $I$–$V$ characteristics of the devices measured at different temperatures. b,d) EVC device and c,e) vdWC device.
Supporting Information). The multi-level storage ability of the vdWC devices was also demonstrated with different compliance current levels ranging from 1 to 0.01 mA (Figure S14, Supporting Information) with a retention time of 1000 s.

2.3. Universal Application of van der Waals Metal Contacts

To confirm that the proposed vdWC approach is universally applicable, memristor devices based on different active materials are tested in Figure 6. I–V characteristics of the EVC and vdWC devices based on 2D (PEA)$_2$PbI$_4$ perovskite are shown in Figure 6a,b. Similar to the FAPbI$_3$ memristor devices, the vdWC-based (PEA)$_2$PbI$_4$ memristor device showed a higher forming voltage (~0.35 V) than that of the EVC device (~0.21 V), indicating a well-defined van der Waals heterojunction between the vdWC and (PEA)$_2$PbI$_4$ layer. In addition, the device based on vdWC demonstrated a higher HRS resistance and narrower distribution of set/reset voltages. These results can be attributed to the well-defined van der Waals heterojunction between the vdWC and (PEA)$_2$PbI$_4$ layers without the generation of additional defects. The poor junction between the EVC
and (PEA)₂PbI₄ layers might be the origin of the larger operating voltage deviation and lower HRS resistance of the EVC device. In particular, the EVC device showed gradual reset characteristics with a higher reset voltage, which is attributed to the higher defect concentration and lower activation energy for Ag atom penetration, making the CFs harder to rupture.[33] In Figure 6c,d, operation endurance of the devices was examined. As expected, a well-defined vdWC enabled a significantly improved endurance performance of the vdWC devices (=350 cycles) relative to the EVC devices (=170 cycles).

We further adopted lead-free all-inorganic Cs₃Cu₂I₅ perovskites for the fabrication of vdWC and EVC devices (Figure 6e,f). In the forming I–V scan, distinct dual switching characteristics are observed for both the EVC and vdWC devices, in which charge trapping and ion migration-enabled switching are involved.[48,49] In Figure S15. (Supporting Information) the carrier conduction mechanisms at two different LRS states (LRS1 and LRS2) were investigated. With ohmic/sub-ohmic behavior at the HRS, the switching from the HRS to LRS1 seems to involve a transition from the ohmic to trap-free SCLC region.[48,49] In this region, we can identify that the V_T of EVC device is higher than vdWC one, suggesting that EVC device has a higher defect density than vdWC one. Upon applying a higher bias voltage, a second transition from LRS1 to LRS2 occurred due to the formation of CFs.[48,49] In this case, unlike the FAPbI₃ and (PEA)₂PbI₄ devices based on filamentary-only switching, the forming voltage for the EVC device was higher than that for the vdWC device, which might be due to the association of different switching mechanisms. After the formation step, switching was observed only in the filamentary conduction region. For the EVC device, the HRS/LRS switching characteristics gradually degraded with an increase in the number of voltage scans (Figure 6e). The HRS and LRS are not reproducible but fluctuate with a lower on/off ratio than the vdWC device. The vdWC device shows relatively less switching variation and maintained a higher on/off ratio with consecutive voltage sweeps (Figure 6f).

The endurance performance of the devices is shown in Figure 6g,h. Consistent with the FAPbI₃ and (PEA)₂PbI₄ memristor devices, the endurance of the vdWC device was significantly enhanced to >325 cycles relative to <50 cycles of the EVC device with a superior on/off ratio. These results confirm that the vdWC approach is universally applicable to memristors with various metal halide compositions despite having different switching mechanisms.

3. Conclusions

We reported a vdWC approach for fabricating high-performance and reliable memristors based on metal halide materials. Physical lamination of pre-deposited metal contacts onto the active layer enabled the formation of a well-defined and reproducible van der Waals heterojunction without generating unintended physical and chemical interactions between the metal contacts and the active layer that has been found between the conventional EVC and the underlying active layer. Consequently, while retaining the high optoelectronic quality of the active layer, vdWC enables less switching variation of metal halide memristors and significant enhancement in endurance and reproducibility, compared to those of devices based on EVC. The vdWC approach was found to be universally applicable to the fabrication of memristors based on various active layer compositions, despite having different switching mechanisms. This study provides a promising platform for the development of high-performance and reliable memristors for future computing.

4. Experimental Section

Fabrication of FAPbI₃ Thin Film: A 35 wt.% FAPbI₃ precursor solution was prepared by dissolving 1 mmol of FAI (172 mg, 99.99%, Greatcell Solar), 1 mmol of PbI₂ (461 mg, 99.99%, TCI), and 1 mmol of N-Methyl-2-pyrrolidone (NMP, 99.1 mg, 99.5%, Sigma-Aldrich) in 1080 mg of N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich). The precursor solution was filtered through a 0.2 µm PTFE-H filter before use. The precursor solution was spin-coated on the cleaned Pt-coated Si wafer at 4000 rpm for 30 s to which 0.2 mL of diethyl ether (>99.7%, Sigma-Aldrich) was poured after 10 s of spinning. The as-spun films were annealed on a hot plate at 110 °C for 10 min.

Fabrication of (PEA)₂PbI₄ Thin Film: The 0.5 M PEA₂PbI₄ perovskite solution was prepared by dissolving 2 mmol of phenethylammonium iodide (PEA, 498 mg (>99%, Greatcell Solar) and 1 mmol of PbI₂ (461 mg, 99.99%, TCI) in 0.2 mL of DMF. The precursor solution was filtered through a 0.2 µm PTFE-H filter before use. The precursor solution was spin-coated on the cleaned Pt substrate at 4000 rpm for 60 s. On the spinning substrate, 0.3 mL of toluene (99.8%, anhydrous, Sigma Aldrich) was dropped after 48 s. The as-spun film was annealed at 75 °C for 30 min on a hotplate.

Fabrication of Cs₃Cu₂I₅ Thin Film: The 0.5 M of Cs₃Cu₂I₅ perovskite solution was prepared by dissolving 1.8 mmol of cesium iodide (CsI, 467 mg, 99.99%, Sigma-Aldrich), and 1.2 mmol of copper iodide (CuI, 228 mg, 99.99%, Sigma-Aldrich) in 1.2 mL of dimethyl sulfoxide (DMSO, anhydrous, >99.9%, Sigma-Aldrich). The precursor solution was filtered through a 0.2 µm PTFE-H filter before use. The precursor solution was spin-coated on the cleaned ITO substrate at 4000 rpm for 30 s to which 0.2 mL of diethyl ether (>99.7%, Sigma-Aldrich) was poured after 20 s of spinning. The as-spun films were annealed on a hot plate at 100 °C for 10 min.

Metal Contact Fabrication: For the deposition of vdWC, the metal contacts were pre-deposited on a Si wafer. The Si wafer was cleaned via successive sonication in detergent, acetone, and ethanol baths. A 100 nm-thick Ag or Au layer was deposited on the cleaned Si wafer by electron-beam evaporation using a patterned metal shadow mask. The metal-contact-deposited Si wafer was post-treated with hexamethyldisilazane (HMDS, 99%, Sigma-Aldrich). Specifically, the Si wafer was placed in a glass bottle containing 3 mL of HMDS, and the sealed bottle was heated at 120 °C for 30 min. The HMDS-treated Si wafers were washed with isopropanol and dried at 80 °C. Subsequently, a polymethyl methacrylate (PMMA, Micro Chem, 495PMMA A8) solution was spin-coated at 2000 rpm for 40 s, followed by annealing on a hot plate at 180 °C for 10 min. The Au or Ag/PMMA layer was exfoliated using thermal release tape and attached to the active layer film surface. Since the HMDS-functionalized metal contacts have a weak interaction with the PMMA overlayer, they can be easily released from the PMMA by van der Waals interactions with the targeting layer. To enhance the adhesion of the transferred layer, 30 µL of chloroform (>99%, Sigma Aldrich) was dropped onto the active layer film surface prior to the transfer. After the film was heated at 90 °C for a few seconds to remove the thermal release tape: Finally, the PMMA layer was removed with chloroform. For the formation of EVC, a 100 nm-thick Ag or Au layer was directly deposited on the active layer films by thermal evaporation under 2.0 × 10⁻⁶ torr with a deposition speed of 0.1–0.6 Ås⁻¹.

Device Characterization: Steady-state PL spectra were measured using a spectrometer equipped with a 464 nm excitation laser source...
(Hamamatsu Quantauros-Tau C1367-12). The PL mapping images were collected using a customized PL microscope, consisting of a microscope (Zeiss Axios Imager.A2m), an external LED light source (CoolLED pE-300 Lite Light source), and a CCD camera (Andor Technology Zyla5.5) with a light filter setup (Chroma Technology 19008-AT-Auramine Longpass) to irradiate excitation light of 440 nm blue light. The excitation light intensity was adjusted to 65 mW cm$^{-2}$ with an exposure time of 200 ms. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) data were obtained by TOF-SIMS-5 (ION-TOF) using a 1 keV oxygen-ion beam sputter gun and a 25 keV Bi$^+$ primary ion beam. The local topology and conductivity were investigated using conductive atomic force microscopy (C-AFM, Park Systems, NX10) in contact mode under an N$_2$ atmosphere with a glovebox cage system (Mbraun, MB10 Compact). X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (Rigaku Smartlab SE) with Cu K$_\alpha$ radiation ($\lambda = 1.5406$ Å). X-ray photoelectron spectroscopy (XPS) and UV photoelectron spectroscopy (UPS) spectra were collected using a Thermo Fisher ESCALAB250 surface analysis system with a micro-focused Al K$_\alpha$ X-ray for XPS and a He I discharge light X-ray for UPS. The current-voltage characteristics of the devices were measured using a probe station equipped with a Keithley 4200 under moderate vacuum ($\sim$10$^{-2}$ torr).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.

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