Electrical metal contacts formed with 2D materials strongly affect device performance. Here, we used scanning transmission electron microscopy (STEM) and energy-dispersive spectroscopy (EDS) to characterize the interfacial structure formed and physical damage induced between MoS2 and the most commonly used metals, Ti, Cr, Au, and Pd. We further correlated the electrical performance with physical defects observed at the 2D interfacial structure. The contact resistances were higher in the order of Ti, Au, Pd, and Cr contacts, but all 4-point probe mobilities measured with metals in contact with identical quadrilayer MoS2 were \( \sim 65 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1} \), confirming the reliability of the devices. According to the STEM and EDS analyses, the Ti contact gave rise to a van der Waals gap between the clean quadrilayer MoS2 and the Ti contact. By contrast, Cr migrated into MoS2 while Mo and S counter-migrated into the SiO2 substrate. Au and Pd formed glassy layers that resulted in the migration of Mo and S into the Au and Pd electrodes. These interfacial structures between MoS2 and contact metals strongly correlated with the electrical performance of 2D MoS2 FETs, providing practical guidelines to form van der Waals contacts.

In recent studies of 2D materials, electrical metal contacts have been found to present serious technical challenges. Mostly, researchers have deposited metals directly onto the top/surface of 2D materials to form metallic electrodes. From the early papers on graphene to recent reports of a “magic angle” graphene superlattice, such top metal contacts have been predominantly used.1,12 However, the electrical contact between a metal and a 2D semiconductor interferes with researchers’ ability to demonstrate the quantum mechanical performance unique to 2D devices, e.g., quantum transport, superconductor, and valley transport devices.13,14 In particular, the absence of surface dangling bonds at the 2D interfaces gives rise to a van der Waals tunnel barrier and weakens intra-layer atomic bonding.15,16 Surprisingly, semiconducting 2D materials cause high contact resistances, stubborn polarity, and an uncontrollable Schottky barrier height (SBH), which are related to strong Fermi-level pinning.17,18 That is, if a van der Waals gap exists as a tunnel barrier at the interface, Fermi-level pinning is expected to be alleviated because of the reduced charge dipole between the metal and the semiconductor.19,20 Apparently, the van der Waals gap, acting as a tunnel barrier, has not existed clearly at the interface between 2D materials and contacting metals. Atomic vacancies and defects can induce much stronger Fermi-level pinning than that theoretically expected.17,21–24

Several innovative approaches to achieving good metal contact have recently been proposed. A one-dimensional electrical contact gave rise to greatly improved electronic
performance for graphene and Fermi level depinning enabling ambipolar performance for MoS\textsubscript{2}.\textsuperscript{25,26} Inserting hexagonal boron nitride (h-BN) or a polymeric dopant interlayer replacing a van der Waals gap can reduce the contact resistance and SBH between a metal and MoS\textsubscript{2}.\textsuperscript{27–30} Liu \textit{et al.} reported that evaporated metals physically damage the MoS\textsubscript{2} surface, whereas a transferred metal that functions as a van der Waals contact on MoS\textsubscript{2} clearly contributes to Fermi-level de-pinning and to the formation of a van der Waals gap.\textsuperscript{31} Wang \textit{et al.} recently reported that gold-capped indium can also form a low-resistance van der Waals contact \textit{via} direct metal deposition and post-annealing.\textsuperscript{32}

In this work, we explored the interface formed between 2D materials and metals. Scanning transmission electron microscopy (STEM) and energy-dispersive spectroscopy (EDS) were used to investigate the atomic structure at the van der Waals interface, the physical damage that occurred during evaporation, and the existence of a van der Waals gap. Additionally, device properties of MoS\textsubscript{2} obtained from various metal contacts were examined \textit{via} measurements of the electrical characteristics of MoS\textsubscript{2} FETs.

**Results and discussion**

**Electrical characteristics of MoS\textsubscript{2} FETs**

As metal electrodes, Ti, Cr, Au, and Pd were chosen to be tested and compared because these materials have been extensively used and studied.\textsuperscript{13,16,17,31,33} Ti and Cr have relatively low metal work functions of approximately 4.5 eV and show good adhesion to SiO\textsubscript{2} substrates. In particular, Ti is known to react with MoS\textsubscript{2} and form an alloy at the interface.\textsuperscript{34} However, Ti and Cr have lower conductivities than Au and Pd. Because Au and Pd have high metal work functions (>5 eV), they can be used in high-performance p-type transistors.\textsuperscript{31,33} Unlike Ti, Au does not react with MoS\textsubscript{2}.\textsuperscript{13} To ensure good adhesion and conductivity, double-stack metals (Cr/Au, Ti/Au) are often used for forming contacts.\textsuperscript{1,12,17} In terms of the metal work function and conductivity, we think that these metals can be very good candidates for investigating and comparing the electrical performance and physical interaction of metals with MoS\textsubscript{2}, the detailed properties of the metals are summarized in Table S1.\textsuperscript{†}

As shown in Fig. 1, we fabricated a MoS\textsubscript{2} transistor with various metals on an identical MoS\textsubscript{2} flake to ensure a fair comparison. We used TEM to observe the quadrilayer MoS\textsubscript{2} and characterize any physical damage that occurred during metal evaporation. The MoS\textsubscript{2} layers were exfoliated onto a 285 nm SiO\textsubscript{2} onto which a p++ Si substrate was used for global back gating. Plasma treatment was performed to etch the MoS\textsubscript{2} to obtain a device structure with the same length and width for each metal contact. Electrodes were patterned \textit{via} electron-beam lithography using a poly(methyl methacrylate) (PMMA) mask. All four of the aforementioned metal electrodes with a 1 \textmu m width had various channel lengths of 2, 4, and 8 \textmu m for transfer line measurement (TLM), and these electrodes were also used for four-point probe (4pp) measurement for measuring the contact resistance ($R_C$) and the four-point probe mobility ($\mu_{4pp}$) because the $R_C$ is one of the most critical parameters for quantifying metal contact properties. All of the metal deposition processes were conducted at the same pressure and deposition rate because these parameters can affect the device performance.\textsuperscript{35} The base pressure was 10$^{-8}$ Torr, and the depo-
position rate was varied in the range from 0.02 to 0.1 nm s\(^{-1}\). We observed that the vacuum pressure during Au and Pd evaporation increased to \(10^{-7}\) Torr while the deposition was carried out. We used only single-elemental metal layers instead of hybrid stacked metals (Ti/Au, Cr/Au) for the precise detection of the chemical composition by EDS. Fig. 1c shows the electron-beam current \((I_{\text{e-beam}})\) and temperature during evaporation. Au and Pd required electron beam currents and a temperature greater than those required by Cr and Ti. Note that when metals evaporate under vacuum, the vapor pressure and temperature of metal atoms are expressed by the Clausius-Clapeyron equation.\(^{36}\) Based on the kinetic theory of ideal gases, we estimated the kinetic energy of each metal atom as shown in Fig. S1 and Table S2.\(^{†}\)

After device fabrication, the electrical properties were measured under vacuum conditions. Fig. 2a–d show the measured drain current \((I_D)\) vs. gate voltage \((V_G)\) for the MoS\(_2\) transistors with different channel lengths for each of the four metals. All of the obtained transfer curves show n-type behavior. Although all of the electrodes were formed on the identical MoS\(_2\), the current levels of the Ti and Au contacts are much higher than those of the Cr and Pd contacts. The current level of the Cr contact is particularly low. The transfer curves in the logarithmic scale and the output curves are shown in Fig. S3.\(^†\)

In the output curves, only the Ti contact shows a linear slope, implying the formation of an ohmic contact; the Cr, Au, and Pd contacts exhibit Schottky contact behavior. The current levels of the Au and Ti contacts are similar, but their behaviors differ. On the basis of the transfer curves in Fig. 2, we calculated the two-terminal field-effect mobility using eqn (1). Note that two-terminal mobilities are dependent on the channel resistance and the contact resistance.

\[
\mu = \frac{dI_D}{dV_G} \frac{L}{W} \frac{C_{\text{OX}}}{V_{\text{th}}} 
\]

Here, \(L\) and \(W\) are the channel length and width, respectively, and \(C_{\text{OX}}\) is the capacitance of the dielectric oxide (1.15 × 10\(^{-8}\) F cm\(^{-2}\) for 285 nm SiO\(_2\)). All of the obtained mobilities and threshold voltages \((V_{\text{th}})\) are shown in Fig. 3b. The threshold voltages were deduced from the linear fit of the transfer curves. A comparison of the two-terminal mobilities reveals that Ti exhibits the highest mobility, followed by Au, Pd, and Cr. A large variation in the mobility of Au is indicated by large error bars.

To extract the contact resistance, we used both measurements in the 4pp configuration and TLM. The contact resistance values (green squares) obtained from the 4pp configur-
ation are also plotted in Fig. 2e–h. For the 4pp measurements, the drain voltage was applied to the outer electrodes and the voltage drop between the inner electrodes was measured by comparing the applied voltage. On the basis of the measured voltage drop and current flow, we estimated both the channel resistance and the contact resistance. The contact resistance of Ti contacts measured via TLM was approximately 41 kΩ μm, with a small error bar and a value similar to the contact resistance obtained from 4pp measurements (32 kΩ μm). In the case of TLM, the linearly increasing trend with increasing channel length \( (L) \) was not clearly observed for metals other than Ti (Fig. S4†). This deviation from the linear behavior becomes more obvious for high contact resistances and introduces a larger measurement error. To indicate the deviation from linearity and the scattering of the TLM data, we show the error bars in the linear fitting used to obtain the contact resistances from TLM (red squares) in Fig. S4.† The contact resistances (black squares) obtained from measurements in the 4pp configuration are also plotted together. Other metal contacts show high contact resistances and large error bars compared with those of the Ti contact. The contact resistance of the Au contact from TLM even shows a negative value, implying that high contact resistances were extracted inaccurately by TLM. By contrast, when contact resistances were low, the TLM approach was found to be more accurate than the 4pp measurements because of the enhanced reliability in the linearity between the total resistance and the channel length.35

In Fig. 3a, the ratios of contact resistance from the Ti, Au, Pd, and Cr contacts with respect to the total resistance are 32%, 69%, 90%, and 99%, respectively. The high values of the ratio indicate that contact resistance dominates device performance, so it was difficult to obtain the linear dependence of the channel length on the current level: see Fig. 2. On the basis of these results, we calculated the 4pp mobilities by excluding the contact resistance and analyzed the electrical properties of the MoS2 channel. Interestingly, the 4pp mobilities for all of the metals were similar at approximately 60–70 cm² (V s)⁻¹, as shown in Fig. 3b. This result indicates that, irrespective of the metals tested, the identical MoS2 flake shows the same channel properties, confirming that our measurements are reliable.

**TEM and EDS analyses**

After performing electrical measurements, we deposited 30 nm-thick Pt onto all of the metal contacts and MoS2 channels, followed by focused ion beam (FIB) milling for the cross-sectional characterization of the interface via TEM and EDS. Fig. 4 shows TEM pictures of the interfaces. Interestingly, the structures of MoS2 under different metals differ substantially from each other even though an identical MoS2 flake was used. The Ti contact shows a clear and uniform MoS2 channel with a clear boundary (Fig. 4a), indicating that the structure of the MoS2 layer was well preserved. However, in the case of the Cr contact, the MoS2 layer was observed vaguely, likely because of the damage that occurred during the electron-beam evaporation of metal atoms. We took into consideration that the FIB milling can also damage 2D materials.38 However, identical MoS2 was used with various metal contacts; thus, the damage under the Cr contact was clearly not caused by the FIB milling. Unlike the other metal contacts, the Au and Pd contacts give rise to a glassy layer shown as a bump on the MoS2 layer (Fig. 4c).31 For the Au and Pd contacts, the MoS2 layer maintained its layer structure; however, Au and Pd atoms apparently diffused into the layer, as reported by Liu et al.31

To analyze the chemical composition of the interface more clearly, we treated it with a high-energy electron beam shower, followed by STEM and EDS analyses. Fig. 5 shows the STEM images of the interface formed between each metal and MoS2, along with the corresponding EDS results. The STEM images show clear quadrilayer MoS2 under all of the metal contacts. Each EDS line profile was obtained along the vertical yellow lines in Fig. 5e–h. Notably, EDS recorded X-ray spectra gener-
ated from the electron shell of an atom via a high-energy electron beam. In the case of the Mo, Pd, and Au atoms, the outer L electron shell was detected, whereas the inner K electron shell was detected for S, Ti, and Cr atoms.

Interestingly, the EDS results show different distributions of the various elements. In the case of the Ti contact, the boundary between the Ti metal and MoS\(_2\) is clearly observed; however, the other metal atoms diffuse into the MoS\(_2\) layer. These results are consistent with the previously discussed TEM results and electrical characteristics. In Fig. 5e, a clear boundary is observed between Ti and MoS\(_2\) in the EDS and STEM images, indicating the presence of a van der Waals gap in the inset of Fig. 5a. According to the optimized geometry of the interface between a metal and 2D materials expected from density functional theory (DFT) calculations, the Au–MoS\(_2\) contact gives rise to a van der Waals gap and the Ti–MoS\(_2\) bond length is shorter than those between other metals and MoS\(_2\), indicating that it is very likely that covalent bonding and ohmic contacts are formed.\(^{13,15,24}\) However, the interfaces observed in this work are different from the ideal interface used for the DFT calculations. The formation of Ti\(_x\)S\(_y\) and TiO\(_x\) from the reaction between MoS\(_2\) and Ti was reported.\(^{14}\) Fig. S5† shows detailed EDS and STEM. The overlap between the spectral peaks of Ti and S atoms was observed in a small part of the contact area. Detecting O atoms in TiO\(_x\) was difficult because EDS can only detect atoms with high atomic numbers, and therefore electron loss energy spectroscopy (EELS) was adopted to detect oxygen, as shown in Fig. S6.† But the oxygen peak was hard to detect at the interface between Ti and MoS\(_2\), unlike the clear oxygen peak from the SiO\(_2\) substrate. McDonnell \textit{et al.} reported that high vacuum (~10\(^{-6}\) mbar) conditions during Ti deposition prevented Ti atoms from reacting with MoS\(_2\).\(^{34}\) We expected this clean and clear interface between Ti and MoS\(_2\) to result in high mobilities and a low contact resistance. As shown in Fig. 5f, the Cr atoms diffused into the MoS\(_2\) layer and even further into the SiO\(_2\) substrate; Mo and S atoms were also detected in the SiO\(_2\) substrate. This result may indicate that Cr atoms “drag” Mo and S atoms into the SiO\(_2\) substrate. Ti and Cr have similar properties, and both are well known to be effective adhesion layers; however, the TEM results and the electrical property measurements of FETs differ substantially between Ti and Cr. Au and Pd atoms are detected in the MoS\(_2\) layer (Fig. 5g), but their concentration is lower than that of Cr atoms (Fig. 5f). Interestingly, Mo and S atoms are detected deep in the Au and Pd electrodes (Fig. 5g and h). During metal evaporation, the electron beam currents and temperature for Au and Pd are greater than those used for the other metals (Fig. 1c). We

![Image of TEM images](image-url)
speculate that the impinging Au and Pd atoms with high energy perturb the atomic structure of MoS$_2$, resulting in the relocation of Mo and S atoms and the formation of the glassy layer. As evidence, Cr atoms were also detected in the MoS$_2$ layer, whereas no Mo and S atoms were detected deep in the electrode. Because both Cr and Ti contacts were evaporated at a low electron-beam current, we propose that a high electron-beam current induces the relocation of MoS$_2$ deep into the electrode. More EDS results are shown in Fig. S5 to S9.

To compare the atomic distribution of Mo and S, we plotted all the EDS data for Mo and S atoms for each metal (Fig. S10†). The different distribution of Mo and S atoms under each metal is clearly observed. The Mo and S atoms penetrated the SiO$_2$ substrate along with Cr atoms during Cr deposition and appeared deep in the Au electrode during Au deposition, although S atoms were comparatively less abundant than Mo atoms.

Unlike the other metal contacts, the Au contact exhibits an unexpected glassy layer (Fig. 4c). Fig. S7† shows the STEM and EDS analyses on this layer. The atomic percentages in the glassy layer are shown in Table S3.† In the glassy layer, more Mo and S atoms are detected than Au atoms, meaning that Mo and S induced the formation of the glassy layer during Au deposition. Consequently, we speculated that the glassy layer induced the inhomogeneity of the Au contact. The atomic structures of metal compounds (Mo with Ti, Cr, Au, and Pd) can be analyzed via phase diagrams for binary mixtures (Fig. S11†), although the binary phase diagrams are based on 3D bulk crystal structures such as face-centered cubic, body-centered cubic, and hexagonal close-packed structures, whereas the crystal structure of 2H-MoS$_2$ is trigonal prismatic in a 2D plane. An alloy of Mo and Au is unlikely to form according to the EDS results. As reported in Table S3,† the atomic percentages of Mo, S, and Au in the middle of the Au electrode are 12%, 23%, and 64%, respectively. The ratio of S is higher than that of Mo. We speculate that gold sulfide (Au$_x$S$_y$) formed rather than the Mo–Au alloy. The metal oxide and sulfide compounds possibly formed through the reaction of MoS$_2$ with the metal electrodes are listed in Table S4.†

As shown in Fig. 3 and 5, the atomic structures under each metal contact are strongly correlated with the electrical performance when a metal serves as the electrode in a FET structure. In order to correlate electrical performance and interfacial structure, we drew band diagrams with or without van der Waals gap so as to enlighten carrier transport mechanisms more clearly, as shown in Fig. 6. The carrier transport at the interface between metal and semiconductor can be explained by thermionic emission and tunneling. See the ESI and Fig. S12† for more details. If a van der Waals gap exists at the interface, carrier transport is dominated by direct tunneling, rather than thermionic emission and Fowler–Nordheim (F–N) tunneling. Fig. 6e and f show an F–N plot to distinguish the carrier transport at the Ti and Pd contacts. In the case of the Ti contact, current shows little change for different temperatures, indicating that direct tunneling occurs dominantly across the van der Waals gap. However, in the case of the Pd contact, current shows strong temperature dependence with F–
N tunneling behavior, indicating that thermionic emission and F–N tunneling occur dominantly without the van der Waals gap. That is, the Ti contact gives rise to the highest mobility with a clear interfacial van der Waals gap, whereas the other metal contacts give rise to damage of the MoS₂ layer, resulting in low electrical performance and a nonuniform interface.

From the perspective of Fermi level pinning, the effect of interfacial structures makes it difficult to predict the relationship between Schottky barrier height and metal work function. For the direct metal deposition on the surface of 2D materials, each metal formed a different interfacial structure which affects device performance more sensitively than its own work function and aggravates the Fermi level pinning of 2D materials. However, when each metal has the same interfacial structure, e.g., one dimensional edge contacts and transferred metal contacts, it is expected that its work function determines polarity and affects device performance, giving rise to a clear depinning effect.

Conclusions

This study demonstrated the electrical properties of a MoS₂ transistor with Ti, Cr, Au, and Pd metal contacts, and their atomic structure at the interface was investigated by STEM and EDS from an identical MoS₂ flake. The mobility and contact resistance were obtained from transfer curves based on TLM and measurements in the 4pp configuration for each metal contact. The TEM and EDS analyses revealed four different types of interfacial atomic structures. The Ti contact gave rise to a clean and clear van der Waals gap between the metal and the MoS₂, whereas the other metal contacts diffused into the MoS₂ layer. In particular, the Cr contact penetrated and dragged Mo and S atoms into the SiO₂ substrate. The Au contact formed with a high electron-beam current formed a glassy layer and relocated Mo and S atoms deep into the electrode, giving rise to inhomogeneity in the mobilities of the device with an Au contact. These results imply that the interfacial structure formed during evaporation affects the electrical performance to a greater extent than the metal work function.

Experimental method

Exfoliation of the MoS₂ flake

MoS₂ was exfoliated by the mechanical exfoliation method. A 285 nm-thick SiO₂ layer on Si was used as a substrate; its dimensions were 1 cm × 1 cm. The SiO₂ was cleaned with acetone (C₃H₆O, 99.5%) and isopropanol (C₃H₈O, 99.5%) for 10 min under ultrasonic vibration. Afterwards, the SiO₂ surface was cleaned using O₂ plasma generated at 20 W for
1 min at 475 mTorr. Multilayer MoS₂ was exfoliated from bulk MoS₂ (HQ graphene) using sticky tape (3 M Scotch tape). The MoS₂ was baked at 100 °C for 10 min to obtain large-area flakes.³⁹

Fabrication of MoS₂ FETs

To pattern electrodes and define the channel, PMMA (950 PMMA A6) was spin-coated onto MoS₂ (4000 rpm, 1 min) and annealed for 90 s at 453 K for hardening. Device structures were patterned via electron-beam lithography (JEOL JSM-7001F for SEM; Raith ELPHY Quantum for lithography). The MoS₂ channel was etched with SF₆/O₂ plasma (SF₆: 10 sccm, O₂: 30 sccm, 20 W, 60 s, 30 mTorr). Each metal electrode (Ti, Cr, Au, and Pd) had various channel lengths of 2, 4, and 8 μm, with a channel width of 12 μm and an electrode width of 1 μm for TLM and 4pp measurements. After patterning, the metal was deposited in an electron-beam evaporator (Korea Vacuum Tech, KVE-E2000). The electrical measurements were conducted using a semiconductor parameter analyzer (Agilent 4155C) in a vacuum chamber (MSTECH M6VC).

STEM and EDS analyses

The specimens were prepared in a FIB system (JEOL, JIB-4601F). Pt (30 nm) was deposited for passivation. All STEM and EDS analyses were performed using Cs-corrected high-resolution TEM (JEOL, JEM ARM 200F).

Conflicts of interest

There are no conflicts to declare.

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Notes and references


