Uncovering the Effects of Metal Contacts on Monolayer MoS2

Kirstin Schauble, Dante Zakhidov, Eilam Yalon, Sanchit Deshmukh, Ryan W. Grady, Kayla A. Cooley, Connor J. McClellan, Sam Vaziri, Donata Passarello, Suzanne E. Mohney, Michael F. Toney, A. K. Sood, Alberto Salleo, and Eric Pop*

Cite This: ACS Nano 2020, 14, 14798−14808

ABSTRACT: Metal contacts are a key limiter to the electronic performance of two-dimensional (2D) semiconductor devices. Here, we present a comprehensive study of contact interfaces between seven metals (Y, Sc, Ag, Al, Ti, Au, Ni, with work functions from 3.1 to 5.2 eV) and monolayer MoS2 grown by chemical vapor deposition. We evaporate thin metal films onto MoS2 and study the interfaces by Raman spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, transmission electron microscopy, and electrical characterization. We uncover that (1) ultrathin oxidized Al dopes MoS2 n-type (>2 × 10^12 cm^−2) without degrading its mobility, (2) Ag, Au, and Ni deposition causes varying levels of damage to MoS2 (e.g. broadening Raman E’ peak from <3 to >6 cm^−1), and (3) Ti, Sc, and Y react with MoS2. Reactive metals must be avoided in contacts to monolayer MoS2, but control studies reveal the reaction is mostly limited to the top layer of multilayer films. Finally, we find that (4) thin metals do not significantly strain MoS2, as confirmed by X-ray diffraction. These are important findings for metal contacts to MoS2 and broadly applicable to many other 2D semiconductors.

KEYWORDS: MoS2, 2D materials, metal contacts, Raman, XPS, doping, strain

As nanoscale electronic devices decrease in size or as new materials are introduced, the role of their metal contacts becomes increasingly important. For example, contacts to transistors based on organic semiconductors, which are hindered by metal reactivity and poor band alignment, are the largest hurdle for realizing high-frequency operation. Even traditional semiconductors like silicon and germanium suffer from Fermi level pinning at the contacts, which frequently creates an unwanted energy barrier for carrier injection, leading to parasitic contact resistance. As device dimensions and contact areas continue to shrink, these parasitic resistances increasingly limit transistor performance by dominating the total device resistance.

Among new materials, two-dimensional (2D) semiconductors, such as MoS2, show promise toward extreme miniaturization of electronics due to superior electrical properties in atomically thin channels compared to silicon-on-insulator (SOI). However, 2D devices also suffer from Fermi level pinning at the metal interface, potentially causing large Schottky barriers (and contact resistance) both for electron and hole injection. Efforts have been made to depin the Fermi level and tune the Schottky barrier height of contacts to 2D materials by stamp-transferring metal contacts and transferring hexagonal boron nitride (h-BN) as an interlayer, but these approaches are not industrially scalable and have not yet demonstrated improved contact resistance because they introduce an additional van der Waals tunneling resistance. The lowest contact resistance to undoped monolayer MoS2 (~1 kΩ·μm) is currently achieved using electron beam (e-beam) evaporated Au or Ag. However, further reduction of contact resistance by an order of magnitude is necessary for sub-10-nm scale transistors.

Improving contact resistance to 2D materials requires better understanding of the metal-2D interface, which remains limited in its scope today. Previous studies used X-ray photoelectron spectroscopy (XPS) and cross-section transmission electron microscopy (TEM) to show that reactions between metals and multilayer MoS2 can occur.
However, it is unclear how many layers deep the reactions penetrate the 2D material, which is important for contacts to monolayer versus multilayer materials. A previous study points to the lack of interfacial reaction as a requirement for epitaxy of metals on 2D materials,21 and Ag, Au, Pb, Pd, Pt, Al, Cu, and Zn films were found (by TEM) to grow epitaxially on MoS2, indicating that these metals do not react with MoS2.22 Other studies have reported large strain effects from thin (1−3 nm) evaporated metals on MoS2 using Raman spectroscopy.23−26 However, Raman analysis provides only an indirect measurement of strain by assuming shifts in MoS2 Raman peaks are solely due to strain, so quantification using a direct lattice constant measurement technique, such as X-ray diffraction (XRD), remains necessary.

Here we conduct a comprehensive study of contact interfaces between several metals and monolayer MoS2 using Raman spectroscopy, XPS, grazing incidence XRD, TEM, and electrical characterization. We deposit thin metal films (Y, Sc, Ag, Al, Ti, Au, and Ni) using high-vacuum e-beam evaporation (∼10−7 Torr) onto monolayer MoS2 (additional details in Methods). Raman spectroscopy is used to characterize the metal-coated MoS2 samples and provide insight on changes in its reactions,27 carrier concentration,28 defects,29 and strain.30 Compared to other techniques, Raman spectroscopy can be done quickly, nondestructively, and with submicron spatial resolution, which makes it easy to distinguish between MoS2 monolayers and bilayers, for example. Various techniques are then used to further refine the observations from Raman characterization: (1) XPS reveals details about chemical bonding.
and reactions, (2) XRD measures lattice spacings and, therefore, provides direct strain information, and (3) TEM displays the metal morphology on the 2D material. Finally, (4) we build transistor test structures allowing us to correlate the observations from these analytical techniques with changes in electrical transport characteristics (e.g., mobility and doping) of the MoS$_2$ beneath the metal film.

RESULTS AND DISCUSSION

Figure 1a displays the schematic for the Raman measurement of metal-coated monolayer MoS$_2$. The MoS$_2$ was grown by chemical vapor deposition (CVD) directly on a 90 nm SiO$_2$/Si substrate. The nominal deposited metal thickness (∼1.5 nm) is transparent to the Raman laser, allowing straightforward measurement of the underlying MoS$_2$ Raman signatures. Figure 1b shows the Raman spectra of monolayer MoS$_2$ bare and coated with the ultrathin metal. The inset displays a zoomed in view of changes in the plane atomic vibrations, and intensities are normalized by the Si peak. The Ti oxidation states between the TiO$_2$ and metallic Ti peaks, thus could have lower Schottky barrier for electron injection than the bare one. Figure 1b reveals red-shifting of the A$_1$$_{1}$D peak from contacts with the top layer of MoS$_2$ (Figure S1). This is also an efficient MoS$_2$ conduction band. Similar oxidation and reactions with MoS$_2$ occur for Y and Sc, but none of the other metals in this study (Al, Ag, Ni, or Au) show evidence of reactions with MoS$_2$. XPS data for all samples are shown in Supporting Information section 2, where the ultrathin Al and Ni are found to oxidize after exposure to air, while Au and Ag remain unreactive with MoS$_2$ and oxygen. However, the Ag-coated MoS$_2$ sample shows a broadened S 2p spectrum compared to bare MoS$_2$. Since the Mo 3d spectrum remains unaffected, this suggests that Ag is tarnishing in air (and not reacting with MoS$_2$). To validate this, we performed X-ray photoelectron spectroscopy (XPS) on the Ag-coated MoS$_2$ sample, which confirms the presence of MoS$_2$, polycrystalline Ag, and Ag$_2$S (see Supporting Information section 3 for SAED data and Methods for SAED sample preparation). Table 1 shows a summary of reactions for each sample studied.

The observed reactions between metals and MoS$_2$ mostly match expectations based on thermodynamic enthalpies of formation (ΔH) for each metal sulfide and oxide (values reported in Supporting Information section 4). For example, Y, Sc, and Ti sulfides have ΔH (per mole of solid S) that are much more negative than MoS$_2$, meaning the sulfur atoms in MoS$_2$ prefer to bond with Y, Sc, and Ti rather than Mo, assuming small entropies of formation and no kinetic limitations. Ag, Au, and Ni have less negative ΔH with sulfur and were not experimentally found to react with MoS$_2$. Indeed, a previous report has predicted Au to be in thermodynamic equilibrium with MoS$_2$ while ternary phases in the Ag–Mo–S and Ni–Mo–S systems are reported without corresponding thermodynamic data. The only exception is Al, which has ΔH favoring reaction with sulfur but is not experimentally found to react with MoS$_2$. This has also been observed in previous studies and can be explained by a larger kinetic barrier for reaction with sulfur, or by Al oxidation since Al$_2$O$_3$ also has a very negative ΔH (see Supporting Information section 4).

Doping. Figure 1b reveals red-shifting of the A$_1$$_{1}$D peak in Al-coated MoS$_2$, which has been shown to correlate with increased electron concentration (4.5 ± 0.5 × 10$^{12}$ electrons/cm$^2$) peak shift$^{25,42}$. Ultrathin Al oxidizes into substoichiometric AlO$_x$ which is known to behave as an electron charge transfer doping layer for MoS$_2$.

Similar oxidation and reactions with MoS$_2$ occur for Y and Sc, but none of the other metals in this study (Al, Ag, Ni, or Au) show evidence of reactions with MoS$_2$. XPS data for all samples are shown in Supporting Information section 2, where the ultrathin Al and Ni are found to oxidize after exposure to air, while Au and Ag remain unreactive with MoS$_2$ and oxygen. However, the Ag-coated MoS$_2$ sample shows a broadened S 2p spectrum compared to bare MoS$_2$. Since the Mo 3d spectrum remains unaffected, this suggests that Ag is tarnishing in air (and not reacting with MoS$_2$). To validate this, we performed selective area electron diffraction (SAED) on the Ag-coated MoS$_2$ sample, which confirms the presence of MoS$_2$, polycrystalline Ag, and Ag$_2$S (see Supporting Information section 3 for SAED data and Methods for SAED sample preparation). Table 1 shows a summary of reactions for each sample studied.

The observed reactions between metals and MoS$_2$ mostly match expectations based on thermodynamic enthalpies of formation (ΔH) for each metal sulfide and oxide (values reported in Supporting Information section 4). For example, Y, Sc, and Ti sulfides have ΔH (per mole of solid S) that are much more negative than MoS$_2$, meaning the sulfur atoms in MoS$_2$ prefer to bond with Y, Sc, and Ti rather than Mo, assuming small entropies of formation and no kinetic limitations. Ag, Au, and Ni have less negative ΔH with sulfur and were not experimentally found to react with MoS$_2$. Indeed, a previous report has predicted Au to be in thermodynamic equilibrium with MoS$_2$ while ternary phases in the Ag–Mo–S and Ni–Mo–S systems are reported without corresponding thermodynamic data. The only exception is Al, which has ΔH favoring reaction with sulfur but is not experimentally found to react with MoS$_2$. This has also been observed in previous studies and can be explained by a larger kinetic barrier for reaction with sulfur, or by Al oxidation since Al$_2$O$_3$ also has a very negative ΔH (see Supporting Information section 4).

Doping. Figure 1b reveals red-shifting of the A$_1$$_{1}$D peak in Al-coated MoS$_2$, which has been shown to correlate with increased electron concentration (4.5 ± 0.5 × 10$^{12}$ electrons/cm$^2$) peak shift$^{25,42}$. Ultrathin Al oxidizes into substoichiometric AlO$_x$ which is known to behave as an electron charge transfer doping layer for MoS$_2$.

Similar oxidation and reactions with MoS$_2$ occur for Y and Sc, but none of the other metals in this study (Al, Ag, Ni, or Au) show evidence of reactions with MoS$_2$. XPS data for all samples are shown in Supporting Information section 2, where the ultrathin Al and Ni are found to oxidize after exposure to air, while Au and Ag remain unreactive with MoS$_2$ and oxygen. However, the Ag-coated MoS$_2$ sample shows a broadened S 2p spectrum compared to bare MoS$_2$. Since the Mo 3d spectrum remains unaffected, this suggests that Ag is tarnishing in air (and not reacting with MoS$_2$). To validate this, we performed selective area electron diffraction (SAED) on the Ag-coated MoS$_2$ sample, which confirms the presence of MoS$_2$, polycrystalline Ag, and Ag$_2$S (see Supporting Information section 3 for SAED data and Methods for SAED sample preparation). Table 1 shows a summary of reactions for each sample studied.

The observed reactions between metals and MoS$_2$ mostly match expectations based on thermodynamic enthalpies of formation (ΔH) for each metal sulfide and oxide (values reported in Supporting Information section 4). For example, Y, Sc, and Ti sulfides have ΔH (per mole of solid S) that are much more negative than MoS$_2$, meaning the sulfur atoms in MoS$_2$ prefer to bond with Y, Sc, and Ti rather than Mo, assuming small entropies of formation and no kinetic limitations. Ag, Au, and Ni have less negative ΔH with sulfur and were not experimentally found to react with MoS$_2$. Indeed, a previous report has predicted Au to be in thermodynamic equilibrium with MoS$_2$ while ternary phases in the Ag–Mo–S and Ni–Mo–S systems are reported without corresponding thermodynamic data. The only exception is Al, which has ΔH favoring reaction with sulfur but is not experimentally found to react with MoS$_2$. This has also been observed in previous studies and can be explained by a larger kinetic barrier for reaction with sulfur, or by Al oxidation since Al$_2$O$_3$ also has a very negative ΔH (see Supporting Information section 4).

Doping. Figure 1b reveals red-shifting of the A$_1$$_{1}$D peak in Al-coated MoS$_2$, which has been shown to correlate with increased electron concentration (4.5 ± 0.5 × 10$^{12}$ electrons/cm$^2$) peak shift$^{25,42}$. Ultrathin Al oxidizes into substoichiometric AlO$_x$ which is known to behave as an electron charge transfer doping layer for MoS$_2$.
Based on the observed \(A_1'\) peak shift, the \(\sim 1.5\) nm oxidized Al contributes \(4.8 \pm 2.7 \times 10^{12}\) electrons/cm\(^2\) doping of MoS\(_2\), where the uncertainty comes from variation in \(A_1'\) peak position for bare versus Al-coated MoS\(_2\). Electron doping pushes the Fermi level near the conduction band, which can cause optical phonons to interact with the continuum of electronic states. This is evidenced in the MoS\(_2\) Raman spectrum, where an asymmetric Fano line shape can be fit to the Al-coated MoS\(_2\) E\(^\prime\) Raman peak. This Fano line shape has also been reported as evidence of doping for other semiconductors, such as Si, Ge, and carbon nanotubes.\(^{47−50}\) See Table 1 for positions of the \(A_1'\) peak for each metal on MoS\(_2\) and Supporting Information section 1 for further discussion of the Fano fits for each metal on MoS\(_2\).

To verify the doping effect inferred from Raman analysis, we also fabricated MoS\(_2\) transistors, with SiO\(_2\)/Si back-gates and Au contacts, then deposited the same ultrathin \(\sim 1.5\) nm of metals on the device channels (Figure 3a). The metals are discontinuous, not shorting the source and drain, and preserving an MoS\(_2\) transistor on/off ratio > 10\(^3\) for the nonreactive metals, as shown in Figures 3b and 4a. Our MoS\(_2\) transistors remain strongly n-type (even with ultrathin NiO\(_x\) islands which could be p-type), while control structures using the same ultrathin metals on SiO\(_2\) without the MoS\(_2\) show no measurable conduction. Figures 3c and 4b display plan view TEM images of the thin, discontinuous Al- and Au-coated MoS\(_2\), using the same TEM grids from the SAED analysis. These images further confirm that the MoS\(_2\) device source and drain are not shorted by the thin metal. Figure S5 shows additional plan view TEM images of metal-coated MoS\(_2\) samples, including Ag and Ni.

Figure 3b displays measured drain current versus back-gate voltage of the monolayer MoS\(_2\) transistors before and after depositing Al, revealing an average threshold voltage shift \(\Delta V_T\).
reactions are observed between Ag and MoS₂, which agrees with our Raman, XPS, and SAED measurements, as well as with previous reports of cross-sectional TEM of Ag on multilayer MoS₂.⁵³

There are potential trade-offs of inducing damage to semiconductor contact regions. We have shown that increasing defects in MoS₂ lowers its effective mobility, so the sheet resistance under the contacts will be higher than in the channel.⁶⁴ However, defects can also improve the contact resistance between the metal and MoS₂ as conductive atomic force microscopy (C-AFM) has shown that charge injection can be higher at MoS₂ defect sites.⁶⁵ Other experiments have found up to a 50% decrease in contact resistance when an Ar ion beam was used to induce defects in multilayer MoS₂ before Ni contact deposition.⁶⁶ Similarly, etching holes into graphene at the contact regions was found to create improved edge current injection.⁶⁷ While the defect density is most likely determined by the metal deposition instrument and parameters, it is interesting to note that some of the best contacts to MoS₂ have been obtained with evaporated Ag,¹³,⁶⁶ Au,¹²,¹⁴,⁴⁵ or Ni,⁶⁹ suggesting these may be good contacts in part because their deposition creates “just enough” defects in MoS₂, while Au and Ag do not oxidize. In contrast, “defect-free” contacts (e.g., with h-BN depinning layers,⁴¹ transfer-stamped Au,¹⁰ or In deposition²⁰) suffer from additional van der Waals tunneling resistance. Thus, defect engineering may play an important role in improving contacts to 2D materials.

**Strain in As-Grown MoS₂.** Strain in 2D materials is often characterized using Raman spectroscopy, by correlating observed peak shifting to strain.³⁰,⁷¹–⁷⁴ However, many other factors can affect the phonon modes of 2D materials, causing shifts in Raman peaks. Therefore, it is important to confirm Raman-based strain estimates with a direct lattice constant measurement technique. Here, we report a direct measurement of strain in monolayer MoS₂ using grazing incidence XRD at a synchrotron radiation light source. By measuring a large polycrystalline MoS₂ film in grazing incidence with high-energy X-rays, we measure the strain of monolayer MoS₂, which is compared with Raman-based strain analysis.

We first measure the built-in strain of our as-grown monolayer MoS₂. Because of the larger MoS₂ thermal coefficient of expansion compared to SiO₂, the high-temperature (850 °C) CVD growth process results in tensile-strained MoS₂. This causes an E’ Raman peak red-shift, consistent with previous observations.⁷⁵ Comparing the E’ Raman peak position of CVD-grown versus transferred MoS₂ (where transferring is assumed to relax built-in strain), we estimate that our as-grown MoS₂ is biaxially tensile strained ~0.4 to 0.5%, depending on the growth. This is based on a calibration of 4.5 cm⁻¹ E’ peak shift per percent of biaxial strain, as reported by Li et al.⁷⁶ We then used grazing incidence XRD to analyze the monolayer MoS₂ in-plane (10) peak before and after MoS₂ transfer, which verified that the strain values measured from Raman peak shifting were accurate within ~0.02% strain (Supporting Information section 6). The 0.02% mismatch is within the distribution of strains of CVD-grown MoS₂ calculated using a Williamson–Hall analysis of several monolayer MoS₂ growths (see Supporting Information section 6). These Raman and XRD results also confirm the ~4.5 cm⁻¹ MoS₂ E’ Raman peak red-shift per percent of biaxial tensile strain.⁷³ Based on these measurements, we find that Raman analysis can be useful to determine built-in strain in bare as…
grown 2D materials, which has been previously used for WSe$_2$. However, we will show in the next section that in more complicated systems, such as MoS$_2$ coated with metals, Raman analysis of MoS$_2$ strain is not accurate.

Strain in Metal-Covered MoS$_2$. As strain can affect the metal-2D semiconductor band alignment, it is important to understand and accurately represent strain in the semiconductor contact regions. The Raman spectra of as-grown MoS$_2$ after metal deposition (Figure 1b) reveal red-shifting of the E' peak position, which is typically attributed to strain. The largest E' peak shift (7.6 cm$^{-1}$) from the already shifted as-grown bare MoS$_2$ is seen in the Ag-coated sample, which would suggest that the MoS$_2$ is biaxially tensile strained by $\sim$1.7% from the thin metal, in addition to the $\sim$0.5% built-in MoS$_2$ strain from CVD growth. Similar claims of MoS$_2$ strain due to thin (1$-$3 nm) Au and Ag based on Raman analysis have been previously reported, but until now, this remains unconstrained using a direct strain measurement technique.

Here, we perform grazing incidence XRD to directly measure the CVD-grown monolayer MoS$_2$ lattice constant with and without thin deposited Ni, Al, Au, and Ag. Testing three samples for each metal, we found that none of the metals appreciably strain the underlying MoS$_2$. Figure 5a shows one set of samples displaying that the MoS$_2$ (10) peak is conserved across all bare and metal-coated MoS$_2$ samples (see Supporting Information section 6), which reveals that there is also no change of MoS$_2$ strain distribution due to contact metals.

We recall that most thin metals (especially Au, see Figure 4c) form incomplete coverage on MoS$_2$. To test if metal continuity affects the strain measurements, we deposit 1.5, 3, 5, and 7 nm of Au on monolayer MoS$_2$ and compare the Raman and grazing incidence XRD data. In Figure 5c, the Raman spectra of MoS$_2$ with thicker Au show that the shifted E’ peak (from regions of MoS$_2$ covered by Au) becomes more prominent as Au coverage on MoS$_2$ increases. However, grazing incidence XRD measurements on the same samples, in Figure 5d, indicate that increasing the metal thickness and coverage still does not strain the underlying MoS$_2$. Therefore, based on the XRD results presented here, we conclude that using Raman peak shifts alone is likely to lead to an overestimate of strain in MoS$_2$ under thin metals.

The discrepancy between the Raman and XRD measurements of strain is due to the nature of the experimental techniques. XRD measures the constructive scattering of ordered lattice spacings, which is a direct measurement of the material strain. On the other hand, Raman-based estimates rely on calibrating shifts of phonon modes to strain, assuming that strain is the only factor affecting the phonon modes. However, shifts of the MoS$_2$ E’ peak can arise from other effects, such as increased disorder (defect density), or decreased domain size of MoS$_2$. It has also been shown that Au and Ag-coated MoS$_2$ which exhibit the largest E’ peak shifts, induce plasmon coupling with MoS$_2$ excitons. This
causes a coupling of phonons to the MoS2 electronic continuum, which likely contributes to E' peak red-shifting.

Discussion. While these experiments were performed with monolayer MoS2, the methodologies and results from this work can be used to draw hypotheses about contacts to other 2D materials. For example, in this study, most contact metal–MoS2 reactions follow what is expected based on thermodynamics. Therefore, thermodynamic analysis can be carried out for projections of expected metal reactions with selenides and tellurides, and indeed, a recent experimental report of metal epitaxy and reactivity with few-layer WSe2 was consistent with calculated isothermal phase diagrams.15 Defect sites may also enhance a 2D material’s reactivity18,79 which is an important consideration as selenides and tellurides tend to be more defective than sulfides, and CVD-grown 2D materials tend to be more defective than exfoliated 2D materials.55 Additionally, since the bond energy is weaker for Mo–Te and Mo–Se than Mo–S55,80, it is reasonable to expect that they would be even more susceptible to metal evaporation-induced damage and reactions at their contacts.71 As 2D monolayers represent the ultimate channel thinness limit for all semiconductors, the lessons gleaned here could also benefit other semiconductors in this extreme limit.

Finally, we briefly discuss our vision to improve contact resistance to 2D semiconductors based on the findings in this study and lessons from past generations of contact engineering. First, Schottky barrier widths must be decreased by doping the source and drain regions. Few results, including those shown in this work with AlOx, have demonstrated such doping through charge transfer from nonstoichiometric oxide capping layers to MoS2.44,45,68 Second, reacting the contact metal with the 2D semiconductor may be used to create a more intimate contact interface, as is well-known from silicid contact interfaces for Si devices.59 This intimate contact interface may also be achieved by defect engineering (tuning defect density in the contact region, e.g., by adjusting deposition techniques and parameters). However, we have shown that defects and reactions can destroy a monolayer 2D material, but do not completely destroy a bilayer material. Therefore, thicker 2D material at the contacts should be explored (e.g., by regrowth), not unlike “raised source/drain” of Si devices,61 where only the top one or two layers react with the metal and the bottom layers remain unharmed. Third, the contact metal band alignment with the 2D semiconductor may be tuned by Fermi level depinning.11 or alloying and strain, as was previously achieved by alloying Ge into Si source/drain regions to improve p-type contacts.62 Further efforts in each of these areas are critical to reduce contact resistance below 100 Ω·μm for 2D semiconductors.

CONCLUSIONS

In summary, we deposited thin films of Y, Sc, Ag, Al, Ti, Au, and Ni on monolayer MoS2 and studied the contact interface by Raman spectroscopy, XPS, XRD, TEM, and electrical characterization. We found through Raman spectroscopy and XPS that low work function metals (Y, Sc, and Ti, often used as adhesion layers) oxidize and react with the underlying monolayer MoS2, which negatively impacts the contact resistance. We also showed through Raman spectroscopy and electrical characterization that ultrathin Al oxidizes and dopes MoS2, while Ag, Au, and Ni show varying levels of damage to MoS2. Lastly, we analyzed the strain effects of metals on MoS2 using Raman spectroscopy and XRD, noting discrepancies between the two techniques, and we conclude that the thin evaporated metals studied do not strain MoS2, contrary to previous reports. The findings in this work, as well as the implications discussed for other 2D materials, are crucial for understanding and improving metal contacts to 2D semiconductor devices.

METHODS

Sample Preparation. Monolayer MoS2 (in the 2H semiconducting phase) is grown directly onto 90 nm SiO2/Si substrates by CVD using solid sulfur and MoO3 precursors, and perylene-3,4,9,10 tetracarboxylic acid tetrapotassium salt (PTAS) as a seeding layer. MoS2 growths take place at 760 Torr and 850 °C, with an Ar flow rate of 30 sccm. The growth results in large (~30–80 μm) MoS2 triangles near the edges of the chip which converge into a continuous film in the center of the chip. The MoS2 is a primarily monolayer film with sparse (<10%) regions of bilayer MoS2.55 Additional details on the MoS2 growth can be found in Smith et al.35,36 Thin metals (~1.5 nm, measured by crystal monitor) were deposited using the Kurt. J. Lesker PVD 75 e-beam evaporation system in high vacuum (~10−7 Torr) at a rate of ~0.5 Å/s. Each metal was deposited on 3 separate MoS2 growths to ensure repeatability of results.

Raman Measurements. All Raman measurements were taken using the Horiba Labram HR Evolution Raman System in the Stanford Nanofabrication Shared Facility. A green laser source of wavelength 532 nm was used with 2.5% incident laser power (0.12 mW) to avoid heating effects, and the spot size is less than 1 μm. An 1800 grooves/mm grating was used, resulting in a spectral resolution of ~0.3 cm−1. Peak fitting details are described in Supporting Information section 1.

XPS Measurements. All XPS measurements were taken in the Stanford Nanofabrication Shared Facility using a PHI VersaProbe III scanning XPS microprobe. The XPS instrument uses a monochromatized Al(Ka) radiation (1486 eV) as source of incident X-rays. We performed all measurements at a chamber pressure <10−7 Torr. The X-ray spot size was ~100 μm with 100 W incident power (high power). Additionally, we performed auto sample neutralization to overcome sample charging effects. The XPS analysis and peak fitting was performed in CasaXPS.

TEM Measurements. MoS2 was grown onto SPI 20 nm SiO2 TEM grids, and subsequent metal evaporation was performed as described above. The MoS2 growth process was the same as described in the Sample Preparation section, however, instead of using the PTAS seeding layer directly on the growth substrate, a separate chip covered in PTAS was placed directly upstream from the growth substrate. This different growth geometry was due to the small size of the TEM grid substrates. Plan view TEM and SAED examination were performed using a FEI Talos F200X in the Materials Characterization Laboratory at The Pennsylvania State University. All samples were analyzed using an accelerating voltage of 80 kV to limit e-beam damage of the MoS2. The imaging data was performed all measurements at a chamber pressure <10−12 Torr where the polycrystalline nature of the CVD-grown MoS2 samples enabled the diffraction conditions necessary to obtain MoS2 signal. The imaging data provided insight concerning the size of metal nuclei on the MoS2 surface as well as their continuity. Electron diffraction patterns provided information concerning whether the metal nuclei were epitaxial or randomly oriented on the MoS2 surface.

XRD Measurements. All XRD measurements were taken at the Stanford Synchrotron Radiation Lightsource beamline 7–2, where the diffraction geometry is illustrated in Figure S11. The polycrystalline nature of the CVD-grown MoS2 samples enabled the diffraction conditions necessary to obtain MoS2 signal. The sample was attached to a six-circle diffractometer with the sample plane vertical during the measurements. The sample was covered with a Kapton dome and purged with helium gas to improve signal-to-noise ratio by reducing air scattering. The 14 keV (0.885 Å) incident beam was set to grazing incidence (0.1°) relative to the sample surface and the scattered radiation was collimated to 1 mm by Soller slits and collected by a Vertex point detector. The sample was rocked during the measurement to remove potential beam damage, and each measurement was averaged over 3 exposures to further reduce noise. Based on the grazing incidence angle and sample rocking, the effective sample...
measurement area is \( \sim 2.8 \) mm wide by the whole length of the sample \((\sim 7-12 \text{ mm})\). Therefore, like the XPS measurements, sparse (<10%) bilayer MoS\(_2\) regions are included in the XRD signal. The experimental setup was calibrated using a lanthanum hexaboride standard.

**Device Fabrication and Measurement.** All device fabrication was performed in the Stanford Nanofabrication Facility. Optical lithography is used to define probe pads, electrical contacts, and channels in three separate steps. O\(_2\) plasma (10 W) is used to etch the MoS\(_2\) for channel definition.\(^{36}\) Au is evaporated using e-beam evaporation as a planar contact to the MoS\(_2\). Finally, the substrate is loaded into a Janis vacuum probe station \((\sim 10^{-3} \text{ Torr})\) for measurements using a Keithley 4200-SCS. After measurements, devices were coated with a thin layer \((\sim 1.5 \text{ nm})\) of metals using the e-beam evaporation parameters outlined above, then remeasured using the same Janis setup. At least 10 transistors were measured for each sample, before and after coating with metal, to ensure consistency of results.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c03515.

Additional details on Raman measurements and analysis, XPS measurements, SAED measurements, thermodynamic analysis, Fano line fits, plan view TEM measurements, TLM mobility extraction, electrical characterization of low work function metals on MoS\(_2\), strain measurements of as-grown monolayer MoS\(_2\), and X-ray diffraction measurements (PDF)

**AUTHOR INFORMATION**

Corresponding Author

Eric Pop — Department of Electrical Engineering, Department of Materials Science and Engineering, and Precourt Institute for Energy, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0003-4036-8534; Email: epop@stanford.edu

**Authors**

Kirstin Schauble — Department of Electrical Engineering, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0002-1430-9818

Dante Zakhidov — Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0003-3107-104X

Eilam Yalon — Department of Electrical Engineering, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0001-7965-459X

Sanchit Deshmukh — Department of Electrical Engineering, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0003-1848-2127

Ryan W. Grady — Department of Electrical Engineering, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0002-0457-5026

Kayla A. Cooley — Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States; orcid.org/0000-0002-6598-4296

Connor J. McClellan — Department of Electrical Engineering, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0002-8733-9968

**ACKNOWLEDGMENTS**

This work was supported in part by ASCENT, one of six centers in JUMP, a Semiconductor Research Corporation (SRC) program sponsored by DARPA. It is also supported by the National Science Foundation (NSF) EFRI 2-DARE, the Air Force Grant FA9550-14-1-0251, and the Stanford SystemX Alliance. Work was performed in part at the Stanford Nanofabrication Facility and the Stanford Nano Shared Facilities, which are supported by the NSF as part of the National Nanotechnology Coordinated Infrastructure under Award ECCS-1542152. Use of the Stanford Synchrotron Radiation Lightsource at SLAC National Accelerator Laboratory was supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Contract DE-AC02-76SF00515. Plan view TEM was supported by NSF through DMR 1410334. We thank Adedapo Oni for cross section TEM measurements and support and Intel Corporation for funding. K.S. thanks the NSF Graduate Research Fellowship Program (GRFP), under Grant DGE-1656518, and the Stanford Graduate Fellowships for support. D.Z. and R.W.G. also acknowledge support by the NSF GRFP under Grant DGE-1656518, and K.A.C. thanks the NSF GRFP Grant No. DGE-1255832 for support. The Knut and Alice Wallenberg Foundation partially supported S.V. through a postdoctoral fellowship. A.K.S. thanks Department of Science and Technology, India, for Year of Science Professorship which funded the travel to facilitate the collaboration.

**REFERENCES**


Supporting Information

Uncovering the Effects of Metal Contacts on Monolayer MoS$_2$

Kirstin Schauble,1 Dante Zakhidov,2 Eilam Yalon,1,3 Sanchit Deshmukh,1 Ryan W. Grady,1 Kayla A. Cooley,4 Connor J. McClellan,1 Sam Vaziri,1 Donata Passarello,5 Suzanne E. Mohney,4 Michael F. Toney,5 A. K. Sood,6 Alberto Salleo,2 and Eric Pop1,2,7,*

1Department of Electrical Engineering, Stanford Univ., Stanford, CA 94305, USA. *epop@stanford.edu
2Department of Materials Science and Engineering, Stanford Univ., Stanford, CA 94305, USA
3Present address: Andrew and Erna Viterbi Department of Electrical Engineering, Technion, Haifa, 3200003, Israel
4Department of Materials Science and Engineering, The Pennsylvania State Univ., University Park, PA 16802, USA
5Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA
6Department of Physics, India Institute of Science, Bangalore 560012, India
7Precourt Institute for Energy, Stanford Univ., Stanford, CA 94305, USA

1. Raman Analysis Details

For Raman analysis (data shown in main text Figure 1b), we fit the MoS$_2$ $A_1'$ peaks with a Lorentzian. The MoS$_2$ E' peaks are fit as follows: for bare MoS$_2$, a Lorentzian is fit. For monolayer MoS$_2$ covered by Ti, Sc, and Y, the MoS$_2$ peaks disappear (Figure S1). For MoS$_2$ covered by ultrathin Al and Ni, an asymmetric Fano line shape is fit due to observed doping and damage effects (Figure S2). For MoS$_2$ covered by Au and Ag, two separate Lorentzian peaks are fit because these metals grow in islands on MoS$_2$ (see Figures S2d and S5), where one peak is from the MoS$_2$ not contacted by metal, and the other red-shifted peak is from the MoS$_2$ directly contacted by metal. For these metals, the position and full width at half maximum (FWHM) of the shifted peak (MoS$_2$ contacted by metal) are listed in Table 1 and Figure 4b of the main text.

Figure S1: (a) Raman spectra of monolayer (1L, solid lines) and bilayer (2L, dashed lines) MoS$_2$ bare (blue) and coated with 1.5 nm Y (green), on our SiO$_2$/Si substrates. The inset shows zoomed in regions of the E' and A$_1'$ MoS$_2$ peaks (E$_g$ and A$_{1g}$ in bilayer, respectively), where the Raman signal is present for Y on 2L MoS$_2$ but not 1L, suggesting Y reacts with the top layer but not fully with the bottom layer of 2L MoS$_2$. Si peaks remain present after Y deposition, which rules out laser reflection from the metal as the cause of the MoS$_2$ signal disappearance. These data are representative of ~1.5 nm (b) Ti and (c) Sc on MoS$_2$. 
The Fano profile in Figure S2 is defined by \( \alpha(\omega) = \alpha_0(q + x^2)/(1 + x^2) \) where \( \alpha_0 \) is the prefactor, \( x = 2(\omega - \omega_p)/\gamma \), \( \omega \) is frequency, \( \omega_p \) is bare phonon frequency, \( \gamma \) is linewidth, and \( q \) is the symmetry parameter which depends on electron-phonon coupling strength.\(^1\) A smaller absolute value \( |q| \) means more asymmetry and heavier doping. Heavy \( n \)-type doping shifts the Fermi level near the conduction band, causing interactions between the continuum of electronic states and optical phonons, and thus asymmetry in the Raman peak.

The \( E' \) peak of bare MoS\(_2\) has a large \( |q| \) showing the most symmetry, as expected. Al-coated MoS\(_2\) has a small \( |q| \) and thus large asymmetry, implying heavy doping. In addition, because the mobility under the Al-coated samples remains unchanged but a large negative \( V_I \) shift is observed vs. the bare samples (see main text Figure 3b), we can ascribe the observed line asymmetry to \( n \)-type doping and not MoS\(_2\) damage.

Ni-coated MoS\(_2\) has even lower \( |q| \) than Al, which would imply heavier MoS\(_2\) doping based on the Fano fit. However, Ni-coated transistors also show the lowest mobility (see main text Figure 4) which suggests MoS\(_2\) sustained the most damage during the evaporation of ultrathin Ni. Because \( E' \) peak broadening and asymmetry can be caused by damage (leading to phonon confinement and contribution of dispersive TO modes)\(^2,3\) we conclude that the asymmetric \( E' \) peak of Ni-coated MoS\(_2\) is most likely due to damage.

Finally, the \( E' \) Raman peak of Au-coated MoS\(_2\) (Figure S2d) shows a poor Fano fit and is better fit by two separate Lorentzian peaks, as explained above. These two Lorentzians (dashed gray lines) roughly correspond to the LO and TO phonon branches (partly activated by disorder)\(^2,3\) although a quantitative analysis of their asymmetry and the defect density induced is left to be pursued in future work.

**Figure S2:** Fano line fits for the \( E' \) Raman peak of (a) bare MoS\(_2\), (b) Al, (c) Ni, and (d) Au on MoS\(_2\). The raw data are colored, the Fano fits are solid black lines, the Lorentzian fits in (d) are dashed gray lines.

**2. XPS Analysis Details**

All XPS spectra are normalized in binding energy (B.E.) by the sp\(^3\) C 1s spectra at 284.8 eV, and normalized in height by the tallest peak in the spectral window. The bare MoS\(_2\) XPS spectra (blue) are shown on the
bottom of Figure S3, and the metal-coated MoS$_2$ spectra are listed in order of increasing metal work function. The spectra are color-coded based on the observed reactions, described below. We note that the XPS spot size (~100 μm) is much larger than the Raman spot size (<1 μm), so the sparse (~10%) bilayer overgrowth regions of MoS$_2$ inevitably contribute signal to these data (additional details in Methods), and trace amounts of MoO$_x$ precursor from the growth process may appear in the XPS signal, which will vary depending on the area measured.

First, the bare MoS$_2$ spectra (plotted in blue) are used as a reference, where the Mo 3d and S 2p spectra are from MoS$_2$, and the O 1s spectrum shows an SiO$_2$ substrate peak. Second, Y, Sc, and Ti (plotted in green) react with MoS$_2$ and oxidize. For MoS$_2$ coated with these metals, a shift in the Mo 3d spectrum is seen, indicating sulfur-deficient MoS$_{2-x}$ and metallic Mo are left behind after the metals react with the sulfur from MoS$_2$ (detailed peak fitting of Ti on MoS$_2$ is provided in Figure 2 of the main text). These metals also induce broadening of the MoS$_2$ S 2p spectra, indicating metal-sulfide bonding. Note that the Y-coated MoS$_2$ S 2p spectrum is washed out by a large Y peak (Fig. S3d); however, the shifting of the S 2s signal on the low binding energy side of the Mo 3d spectrum supports the conclusion that Y reacts with the sulfur in MoS$_2$. We also see a shift in the O 1s spectra, which indicates signal from Ti, Sc, and Y oxides instead of the SiO$_2$ substrate. Third, Al and Ni (plotted in purple) oxidize but do not react with MoS$_2$. The Mo 3d and S 2p spectra remain relatively unchanged, indicating that MoS$_2$ is still present and no reactions with the metal take place. Note that the Ni-covered MoS$_2$ sample shows an increase in MoO$_x$ signal (at B.E. ≈ 236 eV), which is likely caused by the degradation of MoS$_2$ due to Ni deposition, as evidenced by broadening of the Raman peaks (main text Fig. 1b) and decreased electrical mobility (main text Fig. 4). The O 1s spectra are shifted, indicating that the signal is from Al and Ni oxides instead of the SiO$_2$ substrate. Lastly, Ag and Au (plotted in black) do not react with MoS$_2$ or oxidize. The Mo 3d, S 2p, and O 1s spectra remain relatively unchanged from the bare MoS$_2$ spectrum. The S 2p spectrum of Ag-capped MoS$_2$ shows broadening, suggesting sulfurization of Ag. However, since the MoS$_2$ Mo 3d peaks unaffected, and cross-section TEM images (Fig. 4d in main text) reveal a pristine interface, we conclude that the sulfurization of Ag is due to Ag tarnishing from sulfur-containing gases in ambient air instead of reactions with MoS$_2$.

Figure S3: (a) XPS Mo 3d spectra shows doublet Mo 3d5/2 and Mo 3d3/2 peaks. (b) XPS S 2p spectra shows doublet S 2p3/2 and S 2p1/2 peaks. (c) XPS O 1s spectra shows SiO$_2$ or oxidized metals. (d) XPS Y 3d spectrum shows overlap between large Y3d peak and weak S 2p peak.
3. SAED and TEM Data

Figure S4 shows selected area electron diffraction (SAED) patterns for MoS$_2$ coated with ultrathin Ag and Ni on TEM grids (see Methods for sample preparation). For Ag-coated MoS$_2$, in addition to polycrystalline MoS$_2$ and Ag, an additional crystalline phase is present and can be attributed to Ag$_2$S or Mo$_8$O$_{23}$. For the Ni-coated sample, there is no evidence of crystalline phases besides MoS$_2$, indicating that Ni is oxidizing into an amorphous phase. These results are consistent with XPS data in Figure S3.

<table>
<thead>
<tr>
<th>Measured Ring Radius [nm$^{-1}$]</th>
<th>MoS$_2$ Planes</th>
<th>Ag Planes</th>
<th>Ag$_2$S Planes</th>
<th>Mo$<em>8$O$</em>{23}$ Planes</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50</td>
<td>100</td>
<td>020</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.07</td>
<td>110</td>
<td>030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.23</td>
<td>002</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.63</td>
<td>010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>021</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.13</td>
<td>012</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.43</td>
<td>013</td>
<td>111</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.77</td>
<td>006</td>
<td>002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.93</td>
<td></td>
<td>022</td>
<td>504</td>
<td></td>
</tr>
<tr>
<td>5.10</td>
<td></td>
<td></td>
<td>058</td>
<td></td>
</tr>
<tr>
<td>5.40</td>
<td></td>
<td></td>
<td>212</td>
<td></td>
</tr>
<tr>
<td>5.77</td>
<td></td>
<td></td>
<td>220</td>
<td>528</td>
</tr>
<tr>
<td>6.30</td>
<td>110</td>
<td></td>
<td>123</td>
<td>800</td>
</tr>
<tr>
<td>6.53</td>
<td>112</td>
<td></td>
<td>123</td>
<td>820</td>
</tr>
<tr>
<td>6.80</td>
<td>022</td>
<td>104</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.07</td>
<td></td>
<td>004</td>
<td>00 12</td>
<td></td>
</tr>
<tr>
<td>7.30</td>
<td>018</td>
<td>141</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.60</td>
<td>023</td>
<td></td>
<td>321</td>
<td>02 12</td>
</tr>
</tbody>
</table>

(a) SAED pattern of (a) Ag-coated MoS$_2$ and (b) Ni-coated MoS$_2$. The table identifies SAED diffraction planes for each ring in the Ag/MoS$_2$ system. The interplanar spacing (not shown) for the given phases was determined from crystal structures on the Crystallography Open Database. Ring radii are colored according to the SAED diffraction plane identification (using the calculated interplanar spacing values): MoS$_2$ (yellow), Ag (green), Ag$_2$S (purple), and Mo$_8$O$_{23}$ (gray). Rows with two striped colors indicate that diffraction planes exist with the given ring radius for both materials.

Figure S5 shows additional plan view TEMs, revealing Au and Ag non-uniformly “ball up” when deposited on MoS$_2$ into ~10 to 20 nm size islands. Au (also in main text Figure 4c) shows slightly denser nucleation on SiO$_2$ than MoS$_2$, whereas it is difficult to see contrast of MoS$_2$ edges at this scale on the Ag sample due to high contrast between MoS$_2$ and Ag. Al and Ni also deposit as discontinuous films on MoS$_2$, where Ni was found to completely oxidize but some unoxidized Al signal was present in EDS. Ag and Au did not oxidize, consistent with XPS (Figure S3). Al on MoS$_2$ (also in main text Figure 3c) has the largest island size, as well as increased continuity on MoS$_2$ than SiO$_2$. Ni islands are very small (~2-3 nm), but upon careful examination we find that they are discontinuous and nucleate with similar density on MoS$_2$ and SiO$_2$. These results are consistent with predictions of Au, Ag, and Ni island growth morphology on MoS$_2$ based on the adhesion energies and diffusion barriers of metal monomers on MoS$_2$, where Ni was also predicted to form much smaller islands due to its larger diffusion barrier.
Figure S5: Plan view TEM of ultrathin (a) Au, (b) Ag, (c) Al, and (d) Ni on as-grown monolayer MoS$_2$.

4. Enthalpy of Formation Analysis

Table S1 displays enthalpy of formation of MoS$_2$, metal oxides, and metal sulfides, in kJ per mole of solid S for the sulfides and gaseous O$_2$ for the oxides (their most stable forms). Y, Sc, and Ti sulfides have enthalpies of formation that are more negative than MoS$_2$, meaning the sulfur atoms in MoS$_2$ prefer to bond with Y, Sc, and Ti rather than Mo, assuming small entropies of formation and no kinetic limitations. Ag, Au, and Ni have less negative enthalpies of formation with sulfur (or nonexistent in the case of Au), and thus their reactions with MoS$_2$ are thermodynamically unlikely (consistent with our XPS data).

Al is thermodynamically expected to react with MoS$_2$, but none of our results indicate a reaction between Al and MoS$_2$. This has also been observed in previous studies, and can be explained by a larger kinetic barrier for reaction with sulfur, or by Al oxidation since Al$_2$O$_3$ has a much more negative enthalpy of formation (Table S1). In addition, Al has the lowest melting temperature and requires the lowest power evaporation of all metals studied, so its deposition may induce fewer MoS$_2$ defects than other metals during evaporation, which could prevent a reaction with MoS$_2$ (assuming that defects mediate the reaction).

We note that full thermodynamic analysis would involve the Gibbs free energy, which includes the entropy of formation, and the construction of a phase diagram. However, many entropy values required for such an analysis are either unavailable or have large error bars, so we use enthalpy of formation for rapid but approximate insight. To make a fairer comparison, we report values per mole of solid S (sulfides) or gaseous O$_2$ (oxides), allowing the larger entropy term for gaseous O$_2$ to cancel in the comparison among oxides.

<table>
<thead>
<tr>
<th>Enthalpy of Formation (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S Result Ref.</td>
</tr>
<tr>
<td>Au --</td>
</tr>
<tr>
<td>Ag -32 Ag$_2$S [12]</td>
</tr>
<tr>
<td>Sc -774 Sc$_{0.8065}$S [13]</td>
</tr>
</tbody>
</table>

Table S1: Thermodynamic enthalpy of formation for sulfides and oxides of the metals studied at room temperature. Bolded values are the reactions seen experimentally in XPS data (from Figure S3).
5. Additional Electrical Measurements

Figure S6 shows an example pseudo-TLM mobility extraction (following Smithe et al.\textsuperscript{15}) for a bare MoS\textsubscript{2} channel, where the same analysis is done to calculate the mobility of the MoS\textsubscript{2} channel after depositing each non-reacting metal. The resulting mobility values for MoS\textsubscript{2} devices bare and coated with each non-reacting metal are reported in the main text Figure 4b, and are found to degrade drastically after deposition of Ni, Au, and Ag. Note that while the channel lengths here are too long to accurately extract contact resistance, mobility values can be estimated from the sheet resistance (slope of $R_{TOT}$ vs. $L$).

**Figure S6:** Example of pseudo-transfer length method (TLM)\textsuperscript{15} extraction of mobility for bare (uncapped) monolayer MoS\textsubscript{2} devices. (a) Measured drain current vs. back-gate voltage ($I_D$ vs. $V_{GS}$) at $V_{DS} = 1$ V for channel lengths 3 to 6 $\mu$m. Red dashed lines show linear extrapolation\textsuperscript{15} to find threshold voltage $V_T$. (b) Total device resistance $R_{TOT}$ vs. channel length ($L$) measured by TLM at various gate overdrives ($V_{GS} - V_T$). (c) Estimated effective mobility ($\mu$) vs. carrier density ($n$) based on $\mu = (qnR_{SH})^{-1}$, where sheet resistance $R_{SH}$ is the slope of $R_{TOT}$ vs. $L$ in (b). Figure 4c in the main text displays this mobility (for bare, Ag-, Au-, and Ni-coated samples) at $n \approx 7 \times 10^{12}$ cm\textsuperscript{-2}.

Figure S7 shows electrical measurements of MoS\textsubscript{2} capped with ultrathin Ti, Sc, and Y. These data are representative of several devices measured. Ti- and Y-coated MoS\textsubscript{2} devices lost nearly all gate dependence, and any conduction is due to byproducts of the reaction between the metal and MoS\textsubscript{2} (see Raman data in Figure S1 and XPS data in Figure S3). Sc-coated MoS\textsubscript{2} devices still show gate dependence, indicating some semiconducting behavior in the device channel, which must be due to either remaining MoS\textsubscript{2} (e.g. under bilayer regions) or byproducts of the Sc reaction with MoS\textsubscript{2} (ScS is an $n$-type conductor).\textsuperscript{16} Additionally, we note the device channels had gone through several rounds of photolithography prior to ultrathin metal evaporation, so any residual photoresist may hinder interfacial reactions.
**Figure S7:** Measured drain current vs. back-gate voltage ($I_D$ vs. $V_{GS}$) of monolayer MoS$_2$ devices coated with ultrathin films (~1.5 nm) of low work function metals (Y, Sc, and Ti). $L = 3$ μm, $V_{DS} = 1$ V. Small arrows show the sweep direction, revealing repeatable measurements with minimal hysteresis. These data are representative of 5-10 devices measured for each kind of ultrathin metal coverage.

### 6. XRD Analysis Details

In order to calculate the built-in strain of our monolayer MoS$_2$ grown by chemical vapor deposition (CVD), we transfer (with the process described by Vaziri et al.\textsuperscript{17}) the as-grown MoS$_2$ onto a fresh SiO$_2$/Si substrate and measure the strain before and after transferring (without any contact metals). This analysis assumes that transferring the MoS$_2$ releases its built-in strain. Figure S8 displays Raman and X-ray diffraction (XRD) data of as-grown and transferred MoS$_2$. Using Raman-based strain analysis, we find that the as-grown MoS$_2$ is tensile strained ~0.4 to 0.5%, based on a calibration of 4.5 cm$^{-1}$ E’ peak shift per % biaxial strain as reported by Li et al.\textsuperscript{18} XRD-based strain analysis uses Bragg’s law to calculate the spacing between (10) rows of MoS$_2$ atoms in the 2D layer, $d = n\lambda/[2\sin(\theta)]$, where the X-ray wavelength $\lambda = 0.886$ Å (14 keV) and $n$ is the order of reflection [here $n = 1$ for the MoS$_2$ (10) rows, $n = 2$ for MoS$_2$ (20) rows, etc.]. XRD analysis verifies that the Raman-based estimates of built-in MoS$_2$ tensile strain after CVD growth are accurate, as seen in Figure S8c. Raman and XRD analysis are in agreement for measuring built-in strain of bare MoS$_2$, however we show in the main text Figure 5 that Raman analysis is not predictive in determining strain of MoS$_2$ under contact metals, ostensibly due to the metal influence on the E’ peak shift.
The distribution of strains across the crystallites, i.e., affected by line defects, dislocations, stacking faults, or other disorder. We also estimate the average crystallite size, where $K$ is the Scherrer coefficient, and the slope gives the microstrain within the crystallites, as fit with dashed lines in Figure S9. We find that with $K = 1.05$, the average crystallite size is $61 \pm 4.2$ nm, which is smaller than the grain size of the MoS$_2$ film, as the estimated crystallite size is affected by line defects, dislocations, stacking faults, or other disorder. We also estimate the average microstrain in all four samples is $0.084 \pm 0.047\%$, i.e., the distribution of strains across the crystallites.

**Figure S8:** (a) Raman spectra of transferred vs. as-grown MoS$_2$, reveal E’ peak red shifts corresponding to ~0.4 to 0.5% tensile strain, depending on the particular growth. (b) Grazing incidence XRD of transferred vs. as-grown monolayer MoS$_2$ in-plane (10) peak. The XRD peak shift also reveals ~0.4 to 0.5% biaxial tensile strain in the as-grown MoS$_2$. Note Raman data are point spectra over < 1 $\mu$m$^2$ regions (the laser spot size) whereas XRD averages over an effective measurement area of 2.8 mm by the whole length of the sample (7-12 mm). (c) Table shows Raman-based MoS$_2$ strain calculated from change in E’ peak position after transfer, and XRD-based MoS$_2$ strain calculated from change in $d$ spacing after transfer ($\Delta d/d_0$). $d_0$ is $d$-spacing after transfer (assumed unstrained), $d$ is before transfer (tensile strained), and $\Delta d$ is the change.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta$Pos(E’) (cm$^{-1}$)</th>
<th>Strain (Raman)</th>
<th>$d_0$ (Å)</th>
<th>$d$ (Å)</th>
<th>$\Delta d$ (Å)</th>
<th>Strain (XRD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>2.3</td>
<td>0.51%</td>
<td>2.7327</td>
<td>2.7467</td>
<td>0.014</td>
<td>0.51%</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1.9</td>
<td>0.42%</td>
<td>2.7431</td>
<td>2.7453</td>
<td>0.011</td>
<td>0.40%</td>
</tr>
</tbody>
</table>

Figure S9 displays Williamson-Hall XRD analysis of bare CVD-grown MoS$_2$, a method where peak broadening due to crystallite size and microstrain is deconvoluted by considering the peak width (FWHM of “as-grown” MoS$_2$ peaks in Figure S8b) as a function of X-ray Bragg angle $\theta$. The Williamson-Hall formula (inset in Figure S9) shows a linear relationship between the (10), (20), and (30) peak FWHM ($= B_{sample}$) multiplied by $\cos(\theta)$ as a function of $\sin(\theta)$.$^{19}$ The $y$-intercept of this model gives information on the crystallite size, where $K$ is the Scherrer coefficient, and the slope gives the microstrain within the crystallites, as fit with dashed lines in Figure S9. We find that with $K = 1.05$, the average crystallite size is $61 \pm 4.2$ nm, which is smaller than the grain size of the MoS$_2$ film, as the estimated crystallite size is affected by line defects, dislocations, stacking faults, or other disorder. We also estimate the average microstrain in all four samples is $0.084 \pm 0.047\%$, i.e., the distribution of strains across the crystallites.
Figure S9: Williamson-Hall analysis of four different bare, as-grown monolayer MoS$_2$ growths (on our typical SiO$_2$/Si substrates) using grazing incidence XRD data, where each color represents a different growth. The dashed lines represent linear fits to the scattered data points.

Figure S10 shows the spacing $d$ between (10) rows of MoS$_2$ atoms measured by grazing incidence XRD (calculated from XRD 20 scans, in main text Figure 5a). Average strain is calculated based on change in lattice spacing relative to the as-grown monolayer MoS$_2$ ($\Delta d/d$), indicating no change in MoS$_2$ strain due to ultrathin metal capping. We note that in the case of contact metals on MoS$_2$, it was not possible to do a Williamson-Hall analysis due to poor signal-to-noise ratio of the (20) peak. As a result, the FWHMs reported in Figure S10 embody the microstrain in addition to other broadening effects such as crystallite size. Overall, the FWHM of the MoS$_2$ (10) XRD peak is similar between bare MoS$_2$ and MoS$_2$ capped with ultrathin metals, indicating no significant changes in MoS$_2$ strain distribution or crystallite size due to metals. However, from transport measurements (main text Figure 4b) we note that some metals, especially Ni, introduce point defects which reduce the electron mobility. (XRD is not sensitive to these point defects.)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d$ spacing ($\text{Å}$)</th>
<th>Strain based on $d$-spacing</th>
<th>FWHM ($^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare MoS$_2$</td>
<td>2.7429</td>
<td>--</td>
<td>0.12</td>
</tr>
<tr>
<td>Ag on MoS$_2$</td>
<td>2.7430</td>
<td>0.003%</td>
<td>0.12</td>
</tr>
<tr>
<td>Au on MoS$_2$</td>
<td>2.7432</td>
<td>0.012%</td>
<td>0.13</td>
</tr>
<tr>
<td>Al on MoS$_2$</td>
<td>2.7433</td>
<td>0.014%</td>
<td>0.12</td>
</tr>
<tr>
<td>Ni on MoS$_2$</td>
<td>2.7439</td>
<td>0.037%</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Figure S10: Table shows measured $d$-spacing between (10) rows of atoms, calculated strain, and MoS$_2$ (10) XRD peak FWHM values for bare as-grown MoS$_2$ and coated with each non-reacting metal. The strain listed is relative to the as-grown bare MoS$_2$ in the top row (itself ~0.4 to 0.5% tensile strained with respect to transferred MoS$_2$, see Figure S8). Figure (right) shows the physical distance $d = 3^{1/2}a/2$ measured by XRD, where $a = 3.167$ Å (for our tensile strained as-grown MoS$_2$). We note $a_0 = 3.15$ Å is the accepted (unstrained) lattice constant of bulk MoS$_2$.\textsuperscript{21,22}
For XRD measurements, the sample was attached to a six-circle diffractometer and rotated vertically in the $\chi$ direction (Figure S11). The sample was covered with a Kapton dome (not shown) and purged with helium gas to improve the signal-to-noise ratio by reducing air scattering and to reduce sample damage. The 14 keV (0.886 Å) incident beam was set to grazing incidence ($\omega = 0.1^\circ$) and the scattered radiation was collimated to 1 mrad by Soller slits and collected by a Vortex point detector. The sample was rocked up and down in the $z$ direction during the measurement to reduce potential beam damage, and each measurement was averaged over 3 exposures to reduce noise.

Figure S11: X-ray diffraction geometry at the Stanford Synchrotron Radiation Lightsource. The purple square represents the sample, with the small triangles symbolizing polycrystalline MoS$_2$ grains. The labels $x$, $y$, and $z$ define the 3D coordinate system, and labels $\eta$, $\phi$, $\chi$, $\gamma$, $\omega$, and $2\theta$ define rotational degrees of freedom. $2\theta$ sweeps the detector arm during measurement and $\omega$ sets the incidence angle. Note that $\eta$, $\phi$, $\chi$, and $\gamma$ are not used during measurement and, in this configuration, $\eta$ serves the same purpose as $\phi$.

7. Supplementary References