

Intrinsic Electronic Transport Properties of High-Quality Monolayer and Bilayer MoS₂

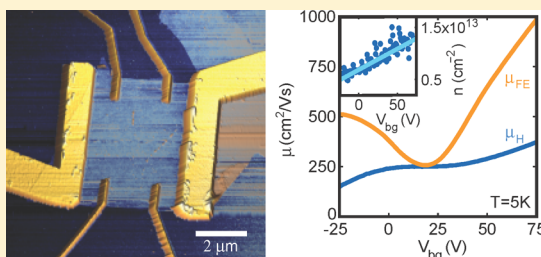
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S Supporting Information

ABSTRACT: We report electronic transport measurements of devices based on monolayers and bilayers of the transition-metal dichalcogenide MoS₂. Through a combination of in situ vacuum annealing and electrostatic gating we obtained ohmic contact to the MoS₂ down to 4 K at high carrier densities. At lower carrier densities, low-temperature four probe transport measurements show a metal–insulator transition in both monolayer and bilayer samples. In the metallic regime, the high-temperature behavior of the mobility showed strong temperature dependence consistent with phonon-dominated transport. At low temperature, intrinsic field-effect mobilities approaching 1000 cm²/(V·s) were observed for both monolayer and bilayer devices. Mobilities extracted from Hall effect measurements were several times lower and showed a strong dependence on density, likely caused by screening of charged impurity scattering at higher densities.

KEYWORDS: Molybdenum disulfide (MoS₂), transition metal dichalcogenides (TMD), two-dimensional (2D) electronics, layered semiconductor, contact, mobility



Molybdenum disulfide (MoS₂), a layered transition-metal dichalcogenide (TMD) semiconductor, is attracting increasing interest for its novel nanoelectronic and optoelectronic properties.¹ Bulk MoS₂ is a stack of atomic trilayers composed of a single atomic layer of molybdenum between two layers of sulfur (Figure 1a). Strong intralayer covalent bonds lead to high mechanical strength in plane,² while weak van der Waals bonds between layers render the material chemically inert with robust electrical properties.³ As with graphite, this weak interlayer coupling also allows individual layers to be isolated and studied.⁴ Monolayer MoS₂ (one S–Mo–S unit) is of particular interest as a large (1.8 eV), direct-gap semiconductor⁵ with strong spin–orbit interaction leading to a spin- and valley-split valence band.^{6,7} These qualities could lead to novel physics such as an unconventional quantum Hall effect, combined spin Hall and valley Hall effects,⁸ and new devices such as high-performance, ultralow power transistors,⁹ and devices integrating spin- and valley-tronics.¹⁰ Further, MoS₂ is compatible with standard semiconductor manufacturing,¹ can be grown in large-scale by chemical vapor deposition,^{11–13} and integrated with other two-dimensional, flexible, and transparent materials.¹⁰

Few-layer MoS₂-based devices in field-effect transistor geometries have demonstrated the promise of these materials.^{1,14–18} However, in a two-terminal contact configuration mobilities are underestimated by including contact resistance. This point is illustrated by measurements of multiterminal devices based on thick MoS₂ with mobilities up to ~500 cm²/(V·s), whereas two-terminal measurements showed mobilities

on the order of 10–50 cm²/(V·s).^{3,19–22} Encapsulating monolayer MoS₂ in high-*k* dielectric or a polymer electrolyte improved device performance in several ways: increasing mobilities for monolayer devices from ~15 cm²/(V·s) up to ~160 cm²/(V·s),^{10,14,23–26} increasing the on/off current ratio to 10⁸ (ref 9), and enabling observation of a metal–insulator transition.²⁶ Nevertheless, investigation of the novel quantum transport phenomena expected for TMDs will require further improvements in device quality. Here we report multiterminal devices based on monolayer and bilayer MoS₂ with sufficiently transparent contacts at high density to enable access to the intrinsic mobility of MoS₂ at low temperatures. These measurements highlight the potential for observing novel quantum transport phenomena in TMDs.

Devices based on monolayer and bilayer MoS₂ were fabricated from bulk MoS₂ (SPI Supplies) that was exfoliated on highly doped silicon substrates with 285 nm of thermal oxide using the micromechanical cleavage process standard for graphene.²⁷ Monolayer and bilayer flakes were identified by optical contrast²⁸ and confirmed with AFM measurements (Supporting Information). We present data from two monolayer and two bilayer devices, denoted M1, M2, B1, and B2. Device contacts were patterned using PMMA masks and e-beam lithography. To optimize fabrication procedures, we investigated a number of process variations. Titanium/gold

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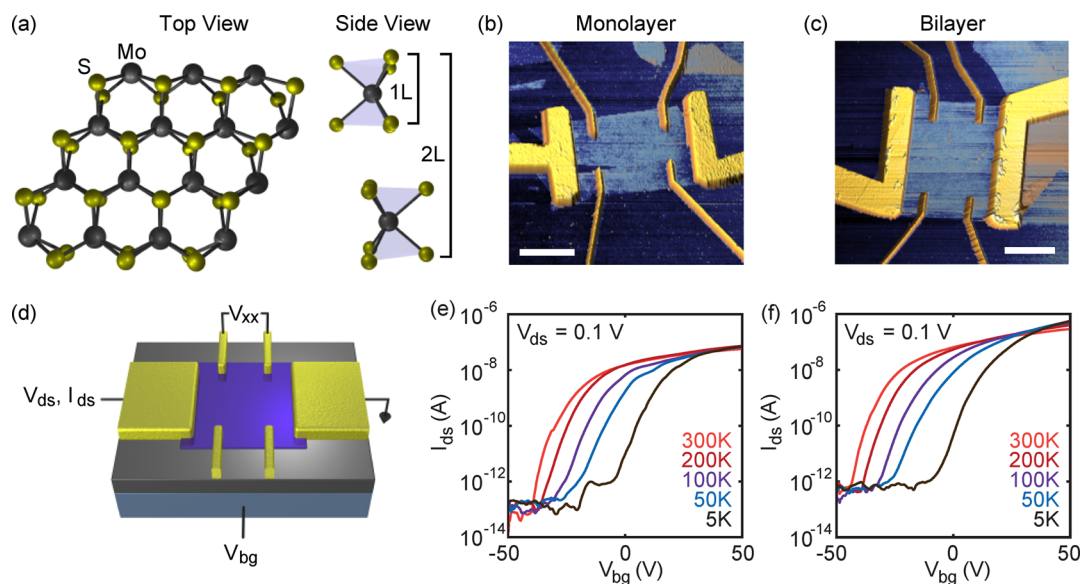


Figure 1. MoS₂ device schematics, images, and two-terminal transport measurements. (a) Structure of a single sheet of MoS₂ from both a top and side view, showing the locations of molybdenum (black) and sulfur (yellow) atoms. (b,c) Color-enhanced AFM height images of six-terminal monolayer (M1) and bilayer (B1) devices. Scale bars are 2 μm . (d) Device schematic and measurement setup. (e) Two-terminal drain-source current, I_{ds} , of monolayer MoS₂ as a function of back-gate voltage, V_{bg} . Temperatures from 300 to 5 K are denoted with traces colored from red to black in (e) and (f). (f) I_{ds} of bilayer MoS₂ as a function of V_{bg} . The dc drain-source voltage, V_{ds} , was 0.1 V for both (e) and (f). Data in (e) and (f) from devices M1 and B1.

contact metal was evaporated in thicknesses of 0.3–4 nm for Ti and 50–100 nm for Au. Some devices were annealed in an Ar/H₂ atmosphere at 350 $^{\circ}\text{C}$ for 3 hours, both before and after contacting. All of the devices were annealed in situ at high temperatures (~ 120 $^{\circ}\text{C}$) for up to 20 h in vacuum ($\sim 10^{-6}$ mbar) before measurement. Variations in contact metal thickness and whether devices were annealed in Ar/H₂ were not found to have a substantial effect on mobility or contact resistance. In contrast, vacuum annealing caused a substantial drop in two-terminal resistivity (Supporting Information) and the nearly complete elimination of Schottky behavior in the contacts, even at 4 K (Figure 2).

Vacuum annealing substantially doped the sample with n-type carriers, shifting the threshold gate-voltage for conductance by as much as 100 V toward negative values. The formation of S vacancy donors would cause n-doping,²⁹ but this scenario is unlikely given the thermal stability of MoS₂ up to 1000 $^{\circ}\text{C}$ in vacuum.³⁰ We speculate that this effect points to intrinsic doping of mined, natural MoS₂.³¹ The result is a large increase in carrier density and conductivity, and a significant decrease in contact resistance. After vacuum annealing, both monolayer and bilayer devices displayed stable, smooth field-effect transistor characteristics with on/off current ratios up to 10^6 (Figure 1). Two-terminal measurements such as these reiterate the viability of MoS₂ as a transistor material, but contact resistance ultimately obscures the intrinsic material properties.

To investigate the intrinsic properties of MoS₂, we further annealed our devices to reduce contact resistance, allowing us to use standard voltage-biased lockin techniques (17.78 Hz and 100 mV excitation) to measure four-probe resistivity for a second set of monolayer and bilayer devices. Without vacuum annealing, two-terminal I – V measurements showed evidence of large Schottky barriers. After sufficient annealing, two-terminal I – V measurements remain nearly linear at small drain-source bias, low back-gate voltage, and low temperature with a clear

positive slope across zero bias at 5 K and 0 V_{bg} (insets to Figure 2a,b). Nonlinearities indicating small residual Schottky barriers begin to appear at 0 V_{bg} but are small enough to allow reliable four-terminal measurements of resistivity in the regimes studied here.

To measure the contact resistance, the devices were connected as shown in Figure 1 with the outer contacts serving as the current drain and source and two inner contacts as voltage probes. These measurements, combined with the two-probe measurements like those shown in Figure 1, allowed for the separation of the MoS₂ resistivity and the device contact resistance (both shown in Figure 2). Contact resistance was calculated from the resistivity as $R_{\text{c}} = V_{\text{ds}}/I_{\text{ds}} - \rho(l/w)$, where l and w are the full sample length and width, respectively, and $\rho = (V_{\text{xx}}/I_{\text{ds}}) \cdot (l_{\text{in}}/w)$, with l_{in} the length between the inner contacts. Even after annealing, contact resistance makes up a significant portion of the total device resistance. Contact resistances of 5–50 k Ω could be reliably achieved at higher densities, though R_{c} increases to greater than 1 M Ω at low temperature and low density (Figure 2).

The temperature dependence of the resistivity provides useful information such as whether a sample is metallic or insulating and provides a means of distinguishing mobility-limiting scattering mechanisms. At high gate voltages, ρ monotonically decreases with decreasing temperature, showing a consistent metallic state for both monolayer and bilayer MoS₂ (Figure 2). In an intermediate range, ρ is nonmonotonic but ultimately increases at low temperature. At the lowest gate voltages, ρ monotonically increases with temperature, characteristic of insulating behavior. These observations indicate the presence of a metal–insulator transition in the samples with critical resistivities $\rho = 0.8 h/e^2$ for the monolayer sample and $0.3 h/e^2$ for the bilayer, consistent with previous observations for monolayer MoS₂²⁶ and theoretical expectations.³² Other monolayer and bilayer samples we measured also showed critical resistivities of order h/e^2 (Supporting Information).

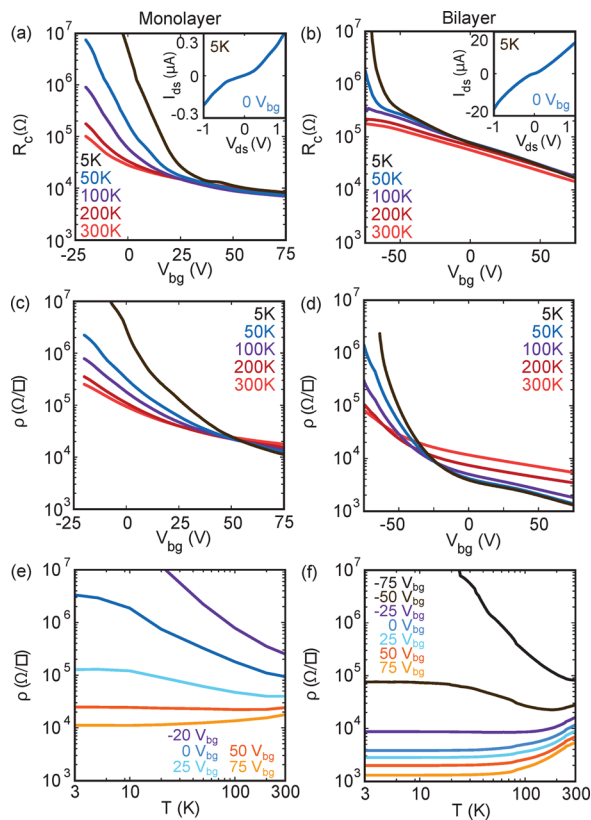


Figure 2. Contact resistance and four-terminal resistivity of monolayer and bilayer MoS₂. (a) Contact resistance, R_c , to monolayer MoS₂ as a function of V_{bg} . Curves colored from red to black show measurements at 300, 200, 100, 50, and 5 K, respectively, across panels (a–d). Inset: Two-terminal I_{ds} vs V_{ds} at 5 K and $V_{bg} = 0$ V for the monolayer. (b) Contact resistance, R_c , to bilayer MoS₂ as a function of V_{bg} . Inset: Two-terminal I_{ds} vs V_{ds} at 5 K and $V_{bg} = 0$ V for the bilayer. (c) Four-terminal resistivity of a monolayer device as a function of V_{bg} . (d) Four-terminal resistivity of a bilayer device as a function of V_{bg} . (e) Resistivity of a monolayer device as a function of temperature. The curves, from purple to yellow, correspond to $V_{bg} = -20, 0, 25, 50$, and 75 V. (f) Resistivity of a bilayer device as a function of temperature. The curves, from black to yellow, correspond to $V_{bg} = -75, -50, -25, 0, 25, 50$, and 75 V. Data from devices M2 and B2.

Hall effect measurements were used to determine carrier density, n , as a function of V_{bg} . The Hall coefficient, $R_H = 1/ne$, was calculated by fitting the slope of the transverse resistance, R_{xy} , as a function of magnetic field up to 1 T (Supporting Information). We note here that for the full gate voltage and temperature ranges of the Hall measurements, contact resistances of both the monolayer, M1, (with further annealing relative to data shown in Figure 1) and bilayer, B2, devices remained below 500 k/ Ω . The nearly linear dependence of n on V_{bg} corresponds to a capacitance per unit area of $c = 10 \pm 2$ nF/cm² for the monolayer and 13 ± 1 nF/cm² for the bilayer sample (Figure 3a, b, insets). These values are in rough agreement with the capacitance expected for a parallel plate geometry, 12 nF/cm², which we expect to underestimate the true capacitance by about 10% due to finite size effects for an MoS₂ flake only a few times wider than the oxide thickness due to the contribution from fringing fields.^{33,34} At fixed V_{bg} , the density varied with temperature significantly for the monolayer, though not for the bilayer. The monolayer density decreased by a factor of 1.5 from 300 to 5 K, whereas the density change in the bilayer was negligible (Supporting Information). A

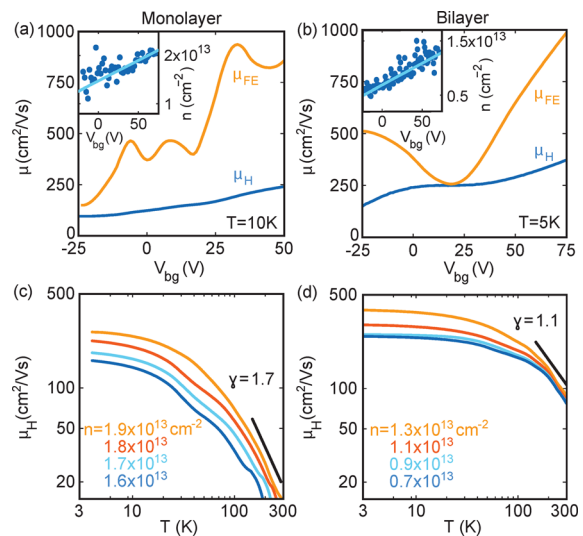


Figure 3. Field-effect and Hall mobilities as a function of back-gate voltage and temperature for monolayer and bilayer MoS₂. (a) Field-effect mobility, μ_{FE} (yellow) and Hall mobility, μ_H (blue) of a monolayer device as a function of back-gate voltage, V_{bg} , at 10 K. Inset: Density of a monolayer device as a function of V_{bg} at 10 K. Solid lines in the insets to (a) and (b) are fits to $n = mV_{bg} + b$, where the slope, m , and the intercept, b , are free parameters. (b) μ_{FE} (yellow) and μ_H (blue) of a bilayer device as a function of V_{bg} at 5 K. Inset: Density of a bilayer device as a function of V_{bg} at 5 K. (c) μ_H as a function of temperature for a monolayer device. The curves, from blue to yellow, correspond to $n = 1.6, 1.7, 1.8$, and 1.9×10^{13} cm⁻². The black line is a power law fit, $\mu_H \propto T^{-\gamma}$, with $\gamma = 1.7$ for the high density data from 150 to 300 K. (d) μ_H as a function of temperature for a bilayer device. The curves, from blue to yellow, correspond to $n = 0.7, 0.9, 1.1$, and 1.3×10^{13} cm⁻². The black line is a power law fit, $\mu_H \propto T^{-\gamma}$, with $\gamma = 1.1$ for the high density data from 150 to 300 K. Data from devices M1 and B2.

reduction in density is expected in inhomogeneous samples due to localization of charge carriers at low temperatures. Inhomogeneities in electric potential from different sources such as the substrate, charged impurities, or defects will trap more charge carriers as the device cools and the ability of carriers to be thermally excited out of these potential wells decreases.

Combining the measurements of n and ρ (M1's ρ can be found in the Supporting Information), we extract Hall mobility $\mu_H = \sigma/ne$ as a function of n , where $\sigma = 1/\rho$ is the conductivity and e is the electron charge (Figure 3a,b). The Hall mobilities increased with density, reaching 250 cm²/(V·s) for the monolayer and 375 cm²/(V·s) for the bilayer at high n . Another method commonly used to estimate carrier mobility is to calculate the field-effect mobility $\mu_{FE} = d\sigma/dV_{bg}(1/c)$, where $c = \epsilon_r\epsilon_0/d$ is the gate capacitance per unit area (12 nF/cm² for 285 nm of SiO₂). The large carrier density of these highly doped samples leads to very high field effect mobilities. Both devices show $\mu_{FE} \approx 1000$ cm²/(V·s) (Figure 3a,b), the highest field-effect mobilities reported to date for either monolayer or bilayer MoS₂. Encapsulating MoS₂ in a high- k dielectric has shown substantial mobility improvements.^{10,14,23–26} The devices reported here are not in a high- k environment, however, suggesting the possibility of further mobility improvement in future devices.

The discrepancy between μ_H and μ_{FE} evident in Figure 3a,b can be explained by the density dependence of the Hall mobility. Substituting $\sigma = ne\mu_H$ and $ne = cV_{bg}$ into the field

effect mobility formula, we find $\mu_{FE} = (d/dn)(\mu_H n) = \mu_H + n d\mu_H/dn$. Thus, the field effect mobility can differ significantly from the Hall mobility if the Hall mobility changes with density. Within this model a linear trend of μ_H with density would lead to a field effect mobility trend with twice the slope (Supporting Information). Conversely, when $d\mu_H/dn$ approaches zero, the two mobility values should nearly match. These two behaviors roughly match the data: in the gate range where μ_H is nearly independent of density, μ_{FE} approaches μ_H (Figure 3b). Also, where μ_H increases with density, μ_{FE} does so at about twice the rate. Additionally, we note that the devices were not operated in a regime of saturated current with drain-source bias, a situation which would lead to a similar overestimation in the calculation of μ_{FE} .

For high densities in the metallic regime, Hall mobilities at constant density increase monotonically from 300 to 5 K for both the monolayer and the bilayer samples (Figure 3c,d). At high temperatures (above ~ 100 K), μ_H approximately follows a power law in temperature, $\mu_H \propto T^{-\gamma}$ with $\gamma = 1.7$ for the monolayer device and 1.1 for the bilayer. It is expected that MoS₂ devices with mobilities limited by homopolar, optical phonons should follow this form in this temperature range, with $\gamma = 1.69$ for monolayer³⁵ and $\gamma = 2.6$ for bulk MoS₂.³⁶ The monolayer value agrees well with the prediction, though we note that the fit was obtained over a limited temperature range. The power law for the bilayer sample is significantly lower than the prediction. This is similar to a previously reported value where a suppressed $\gamma = 1.4$ was attributed to phonon quenching by a top-gate dielectric.²⁶ Such quenching, however, is not expected in our case.

The monolayer and bilayer mobilities begin to saturate below 100 K, a temperature by which scattering from optical phonons is expected to become negligible.³⁵ At lower temperatures, scattering from phonons should be dominated by acoustic modes with a linear dependence of mobility on temperature,³⁶ in contrast with the near saturation we observe (Figure 3c,d). Another candidate explanation is mobility limited by long-range Coulomb scattering. This picture is consistent with our observation of μ_H being roughly linear with carrier density,³⁷ which is not expected for phonon scattering.³⁵ Whether the temperature dependence we observed can be mostly described by long-range Coulomb scattering awaits further experimental and theoretical study.

In conclusion, we have demonstrated high quality MoS₂ devices that may open opportunities for measuring novel quantum transport phenomena at low temperature. We showed that in situ vacuum annealing can dope devices and significantly reduce Schottky barriers and contact resistance, allowing for ohmic contact to MoS₂ down to 4 K at high densities. A clear metal–insulator transition was evident in both monolayer and bilayer samples at $\rho \sim h/e^2$, showing that high density MoS₂ devices remain conducting at low temperature. Additionally, the field-effect mobilities were quite high, indicating good sample quality. Finally, Hall mobilities calculated from density measurements gave relatively high values, though the field effect equivalents are still several times larger due to the density dependence of the Hall mobility. On the basis of the temperature and density dependence of the mobilities, we infer a crossover from a regime limited by optical phonon scattering at high temperature to one likely limited by long-range Coulomb scattering below 100 K.

■ ASSOCIATED CONTENT

Supporting Information

Supporting text and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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