Low-Temperature Ohmic Contact to Monolayer MoS$_2$ by van der Waals Bonded Co/h-BN Electrodes

Xu Cui,†,¶ En-Min Shih,‡,§ Luis A. Jauregui,§ Sang Hoon Chae, ¶ Young Duck Kim,†,∥ Baichang Li,† Dongjea Seo,⊥ Kateryna Pistunova,§ Jun Yin,∥ Ji-Hoon Park,⊥ Heon-Jin Choi,⊥ Young Hee Lee,§,◆ Kenji Watanabe,◆ Takashi Taniguchi,◆ Philip Kim,§ Cory R. Dean,‡ and James C. Hone*†

†Department of Mechanical Engineering and ‡Department of Physics, Columbia University, New York, New York 10027, United States
§Department of Physics, Harvard University, Cambridge, Massachusetts 02138, United States
∥ Department of Physics and Center for Humanities and Sciences, Kyung Hee University, Seoul 02447, Republic of Korea
◆Department of Materials Science and Engineering, Yonsei University, 120-749 Seoul, Republic of Korea
⊥State Key Laboratory of Mechanics and Control of Mechanical Structures, Institute of Nanoscience, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China
◆Center for Integrated Nanostructure Physics, Institute for Basic Science (IBS), Suwon 16419, Republic of Korea
○Department of Energy Science, Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea
◆National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

Supporting Information

ABSTRACT: Monolayer MoS$_2$, among many other transition metal dichalcogenides, holds great promise for future applications in nanoelectronics and optoelectronics due to its ultrathin nature, flexibility, sizable band gap, and unique spin-valley coupled physics. However, careful study of these properties at low temperature has been hindered by an inability to achieve low-temperature Ohmic contacts to monolayer MoS$_2$, particularly at low carrier densities. In this work, we report a new contact scheme that utilizes cobalt (Co) with a monolayer of hexagonal boron nitride (h-BN) that has the following two functions: modifies the work function of Co and acts as a tunneling barrier. We measure a flat-band Schottky barrier of 16 meV, which makes thin tunnel barriers upon doping the channels, and thus achieve low-T contact resistance of 3 k$\Omega$ $\mu$m at a carrier density of $5.3 \times 10^{12}$/cm$^2$. This further allows us to observe Shubnikov–de Haas oscillations in monolayer MoS$_2$ at much lower carrier densities compared to previous work.

KEYWORDS: Work-function, tunneling contact, monolayer MoS$_2$, low temperature

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transition-metal dichalcogenides (TMDCs), which can be isolated as single monolayers either by exfoliation from bulk crystals or by direct synthesis, have attracted widespread recent interest due to their unique properties and potential for applications.$^{1-6}$ Among those, MoS$_2$ is the most widely studied. In the monolayer limit, it is a direct-gap semiconductor$^2$ and hosts fascinating physical behavior near the band edge at the K-point, including valley-spin coupled physics$^7$ that gives rise to a variety of phenomena including the valley Hall effect.$^3$ However, its large bandgap (2.15 eV measured by scanning tunneling spectroscopy) of monolayer MoS$_2$ (as well as that of similar materials such as MoSe$_2$, WS$_2$, and WSe$_2$) makes achieving Ohmic electrical contacts highly challenging, and in fact the contact problem has been highlighted as a central challenge for both applications and basic studies.$^9,10$ A great deal of recent experimental work has demonstrated progress toward improved contacts. This includes use of low-work function metals,$^{11,12}$ graphene,$^{13-15}$ or doped TMDCs$^{16}$ as electrodes, thermal annealing,$^{17}$ ionic-liquid doping of the contact regions,$^{18,19}$ phase-engineering,$^{20}$ selective etching,$^{21,22}$ and introduction of thin tunnel barriers.$^{23-25}$ However, this work has largely focused on few layer TMDCs and room-temperature behavior (see in Supporting Information S1). Low-temperature contact to monolayer TMDCs remains a significant challenge.

In this study, we focus on the challenge of obtaining low-resistance contacts to the conduction band of monolayer MoS$_2$ at low temperature. This is a critical prerequisite for detailed study of quantum transport,$^{26}$ valley-tronic properties,$^{27}$ and transport signatures of interlayer excitonic states.$^{28,29}$ We have previously demonstrated that few-layer graphene can achieve...
robust low-T contact to few-layer MoS2 at moderate carrier densities, but reliable contact to monolayer MoS2 is only achieved at high carrier densities ($\sim 1 \times 10^{13}$ cm$^{-2}$), making phenomena near the band edge inaccessible. Similar results have been seen for Au contacts, where low contact resistance is achieved only after aggressive thermal annealing, which can negatively affect the channel characteristics due to the creation of sulfur vacancies. Low work-function metals such as Sc and Al have also been explored and perform well at room temperature but show non-Ohmic contact behavior at low temperature (Supporting Information S2).

Recently, Farmanbar et al. proposed a new route to achieve stable low work function metal contacts to TMDs. In this scheme, a monolayer of graphene or h-BN is placed between a transition metal contact and the TMD. The monolayer spacer serves two advantageous purposes: it strongly interacts with the transition metal, reducing its work function by over 1 eV, and it breaks the metal–TMD interaction to eliminate the interface states that cause Fermi level pinning. Here, we experimentally validate this prediction. We use cobalt electrodes with monolayer h-BN to achieve substantially improved low-T contacts to monolayer MoS2 and verify the work function modification directly using X-ray photoemission spectroscopy. Multiterminal magneto-transport measurements show that Ohmic contacts are achieved at low carrier density of 3.5 × 10$^{12}$ cm$^{-2}$, allowing Hall mobility measurement and the observation of quantum oscillations to lower carrier densities than previously possible.

Figure 1a shows a schematic of the devices used in this study. MoS2 and h-BN were exfoliated from bulk crystals (MoS2 obtained from SPI Supplies) onto SiO2 (285 nm)/Si substrates and identified by optical microscopy with thickness verified by Raman spectroscopy, photoluminescence, and atomic force microscopy (Supporting Information S3). Next, following the previously described dry van der Waals transfer method, a polymer film was used pick up a stack of ~30 nm thick h-BN (top), 1L MoS2 (middle), and 1L h-BN (bottom). The polymer and stack were inverted and placed, polymer down, on a Si/SiO2 substrate, and then heated in vacuum at 250 C for 30 min to remove the supporting polymer (Supporting Information S4 for details). We verify below that this process does not introduce any extra doping. Subsequently, the stack was patterned into the desired shape by e-beam lithography followed by SF6/O2 plasma etching. Finally, 30 nm Co and 50 nm Au electrodes were patterned by a second e-beam lithography step, electron beam evaporation, and liftoff. For the devices described below (unless noted otherwise), we evaporated Co under ultrahigh vacuum (UHV) conditions (~10$^{-10}$ Torr) to minimize interfacial contamination and Co oxidation. We find that this method produces the lowest contact resistance and highest yield, as described below. We also found similar results using chemical vapor deposition (CVD)-grown monolayer h-BN on CVD monolayer MoS2 (Supporting Information S5), confirming the possibility of large-scale applications.

As a first demonstration, we examine the quality of the contacts by performing gate-dependent transport measurements on a short channel (200 nm) two-terminal device, at temperatures from 20 to 300 K (Figure 1b). Characteristic of an n-type FET, the two-terminal resistance decreases with increasing gate voltage. Above ~30 V, the resistance decreases with decreasing temperature, indicative of metallic conduction in the channel and barrier-free contacts, and falls below 2.7 kΩ·μm at $V_g = 80$ V and $T = 20$ K. Furthermore, at all temperatures the resistance is lower than 100 kΩ·μm for gate voltages larger than 10 V. This provides strong initial evidence that the proposed technique does indeed provide good contacts.

We next confirmed the low work-function of h-BN/Co using XPS on a large-area Co/h-BN film. This sample was created by evaporating 30 nm of Co onto CVD-grown h-BN transferred onto a Si/SiO2 wafer, then peeling the film from the substrate and inverting it. In this way, a pristine Co/h-BN interface could be studied without oxidation of the Co. The XPS spectrum was measured using a Thermo Scientific K-Alpha XPS system ($h\nu = 1486.6$ eV), using an applied stage bias of ~30 V, so the cutoff of the sample can be distinguished (cutoff energy = 1485.5 eV, as shown in Figure 1c). The spectrum width is determined by the difference between the cutoff energy and the Fermi edge (spectral width = 1483.3 eV). The Fermi edge position is determined by the center of the first rising slope, while the cutoff energy is determined by the change of slope (maximum of the second derivative, Supporting Information S6). The work function ($\Phi$) of the film is determined by subtracting the spectrum width from the Al Ka line (1486.6 eV), resulting in $\Phi = 3.3$ eV, which is 1.7 eV smaller than Co work-function of 5.0 eV. We also checked the work function of a thick Au film (after 5 min of in situ Ar ion milling to remove any contamination on the surface) and obtained $\Phi = 5.2$ eV, which is in good agreement with published values.

Having established that the Co/h-BN structure has a low work function and provides very good contacts to MoS2, we studied the properties of these contacts in more detail using multiterminal devices in a Hall bar geometry (Figure 2a), which allows independent determination of the channel resistance, contact resistance, and carrier density. First, we performed two-
contacts using MgO, TiO$_2$, Ta$_2$O$_5$, and h-BN as the insertion layer$^{13-25,35,36}$ which showed a decrease in Fermi level pinning but did not achieve Ohmic contact to monolayer TMDCs at cryogenic temperatures.

The barrier-free behavior for the h-BN/Co contacts is further confirmed by extracting the activation energy from the slope of an Arrhenius plot of ln(I/I$_{Vsd}$) versus $1000/T$ (Supporting Information S9). The derived activation energy is plotted as a function of gate voltage for devices with (Figure 2e) and without (Figure 2f) 1L h-BN. In these plots, the Schottky barrier height is the activation energy at the flat-band gate voltage, seen as the point where the activation energy ceases to decrease linearly with gate voltage;$^{10}$ this analysis technique has been used to measure barrier heights of 30–200 meV$^{11,24,25,36,37}$ for contacts to multilayer MoS$_2$ (see Supporting Information S9 for detailed discussion). Using the same technique, we obtain Schottky barrier heights of 16 meV for Co contact with 1L h-BN and 38 meV for Co direct contact to 1L MoS$_2$ (Figure 2f). We note two important limitations of this analysis. First, the measured value of 16 meV is close to the disorder limit of our sample (Supporting Information S10). Second, it does not account for the presence of the 1L h-BN tunnel barrier, which should act in series with the Schottky barrier.$^{38-40}$ Therefore, more detailed modeling will be required for precise quantification of the barrier height. Nevertheless, the above analysis clearly indicates both that the h-BN/Co is an improvement over both Co alone and previous reports.

Next, two-probe and four-probe resistance measurements were combined with Hall effect measurements to determine the channel resistivity and contact resistance as a function of carrier density. Measurements were performed using alternating current (ac) bias (100 nA) with simultaneous lock-in measurement of two-probe ($V_{2p}$) and four-probe voltage drops ($V_{4p}$) (Figure 3a inset). We calculated the channel resistivity as $\rho_{xx} = V_{4p}/I_{4p} \times W/L_{4p}$ and the contact resistance

![Figure 2](image1.png)

**Figure 2.** Hall bar geometry devices images, transfer curves, $I$–$V$ curves and Schottky barrier measurements. (a) Optical image of a Co/1L h-BN/1L MoS$_2$ contact device. Scale bar is 2 $\mu$m. (b) Two-terminal source-drain current, $I_{sd}$ of the Co/1L h-BN/1L MoS$_2$ contact device as a function of back-gate voltage, $V_{gb}$. Temperature from 300 to 1.7 K are denoted with traces colored from red to blue. The dc source-drain voltage, $V_{sd}$, was 10 mV. (c) Low-bias output characteristics of Co/1L h-BN contact showing linear $I_{sd}$–$V_{sd}$ behavior starts at the turn-on gate voltage (20 V), indicating the Ohmic nature even at 1.7 K. (d) Low-bias output characteristics of Co direct contact to 1L MoS$_2$ showing nonlinear $I_{sd}$–$V_{sd}$ behavior, indicating non-Ohmic behavior at 1.7 K. (e,f) Schottky barrier measurement with activation energy method. The activation energy, $\Phi_{fb}$, is extracted from the slope of an Arrhenius plot (Supporting Information S9). The Schottky barrier height is the activation energy at the flat-band gate voltage. For (e) 1L h-BN/Co contact the Schottky barrier is $\sim$16 meV, whereas for (f) Co direct contact it is $\sim$38 meV.

![Figure 3](image2.png)

**Figure 3.** Channel resistivity, contact resistance as a function of temperature, carrier density, and magnetic field. Four-probe resistivity (a), contact resistance (b), and Hall mobility (c) as a function of carrier density at temperatures of 300, 250, 200, 150, 100, 50, 10, and 1.7 K. (d) Shubnikov–de Haas oscillations of monolayer MoS$_2$ at different carrier densities of $3.5 \times 10^{12}/cm^2$, $4 \times 10^{12}/cm^2$, and $4.6 \times 10^{12}/cm^2$ at $T = 1.7$ K.
as \( R_c = \left( V_{xy}/I_d - (V_{xy}/I_s) \times L_{xy}/L_{sd} \right) \times W \), where \( I_d \) is the source-drain current, \( L_{xy} \) is the length between the source and drain contacts, \( L_{sd} \) is the length between the voltage contacts, and \( W \) is the channel width. The carrier density \( n \) was determined by measuring Hall voltage under an applied magnetic field (Supporting Information S11). We find that the conduction band edge \( (n = 0) \) is close to 0 V (±3 V), indicating that our samples are not heavily doped during the fabrication process, and that the carrier density obtained from Hall measurements agrees well with the predicted value from the gate capacitance.

Figure 3ab shows the derived channel resistivity and contact resistance for a typical device (all three measured devices show similar behavior), as a function of carrier density at temperatures from 300 to 1.7 K. Importantly, we find that the robust h-BN/Co contact allows us to reliably measure multiterminal the gate capacitance. Hall measurements agrees well with the predicted value from fabrication process, and that the carrier density obtained from indicating that our samples are not heavily doped during the fabrication process, and that the conduction band edge \( (n = 0) \) is close to 0 V (±3 V), indicating that our samples are not heavily doped during the fabrication process, and that the carrier density obtained from Hall measurements agrees well with the predicted value from the gate capacitance.

Figure 4 summarizes the performance of the h-BN/Co contacts in two different ways. Figure 4a shows contours in temperature and density for \( R_c = 100, 50, 10, 5, \) and \( 3.8 \, \text{k}\Omega\mu\text{m} \). Figure 4b shows the low-\( T \) contact resistance versus carrier density for the h-BN/Co contacts compared to other methods for monolayer MoS\(_2\). First, we note that the contact resistance is roughly 5 times larger when ordinary high vacuum (\( \sim 10^{-8} \) Torr) is used for Co evaporation (Supporting Information S13), which is consistent with improvements seen for UHV evaporation of Au contacts.\(^{46} \)

Elimination of the 1L h-BN (with UHV Co evaporation) also results in a poorer contact. The use of few-layer graphene can provide an adequate contact \((R_c \sim 10 \, \text{\kOmega\mu m})\) but only at large carrier densities, \( \sim 10^{12} \, \text{cm}^2/\text{cm}^2 \). Finally, the previously reported high quality contacts using Au only achieve low resistance for even higher densities, for example, above \( 2 \times 10^{13} / \text{cm}^2 \). Thus, we conclude that the h-BN/Co structure provides a superior contact to any other reported method and is particularly well suited to studies of properties at low temperature and low carrier density.

In conclusion, we have demonstrated a new contact scheme to the conduction band of monolayer MoS\(_2\) that is robust at low temperature and at low carrier density in which monolayer h-BN is inserted between Co and MoS\(_2\). This scheme provides the best contacts reported to date, \( 3.0 \, \text{\kOmega\mu m} \) at \( 5.3 \times 10^{12} \, \text{cm}^2 / \text{cm}^2 \) at 1.7 K. Finally, we present the observation of quantum oscillations at carrier density as low as \( 3.5 \times 10^{12} / \text{cm}^2 \). Further improvement of the quality of the material and channel encapsulation, combined with this contact scheme, will allow us to explore details of quantum transport behavior in the conduction band of large-gap TMDC semiconductors that have remained largely inaccessible. In addition, h-BN/transition contacts may prove useful for electron injection in a wide range of other systems.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b01536.

MoS$_2$ contact techniques summary; contacts with low work-function metals; Co/h-BN/MoS$_2$ device fabrication and characterization; device characterization of CVD h-BN and CVD MoS$_2$; XPS characterization of Co/h-BN; room-temperature and low-temperature output curve characterization; Schottky barrier extraction; disorder analysis; Hall measurement and Hall mobility; contacts deposited at different pressure (PDF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail: jh2228@columbia.edu. Phone (212) 854-6244 (J.C.H).
*E-mail: cd2478@columbia.edu. Phone (212) 854-3189 (C.R.D.).

ORCID®
Xu Cui: 0000-0001-8432-8756
Ji-Hoon Park: 0000-0003-4776-5206
Young Hee Lee: 0000-0001-7403-8157

Author Contributions
$^3$X.C. and E.-M.S. contributed equally to this work.

Notes
The authors declare no competing financial interest.

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