Transport Properties of Monolayer MoS$_2$ Grown by Chemical Vapor Deposition

Hennrik Schmidt,‡,§ Shunfeng Wang,‡,§ Leiqiang Chu,‡,§ Minglin Toh,‡,§ Rajeev Kumar,‡,§ Weijie Zhao,‡,§ A. H. Castro Neto,‡,§ Jens Martin,‡,§ Shaffique Adam,‡,§ Barbaros Özyilmaz,‡,§ and Goki Eda,‡,§,8

$^\dagger$Graphene Research Centre, National University of Singapore, 6 Science Drive 2, Singapore 117546
$^\ddagger$Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117551
$^\spadesuit$Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543
$^\spadesuit$Yale-NUS College, 6 College Avenue East, Singapore, 138614

Supporting Information

ABSTRACT: Recent success in the growth of monolayer MoS$_2$, via chemical vapor deposition (CVD) has opened up prospects for the implementation of these materials into thin film electronic and optoelectronic devices. Here, we investigate the electronic transport properties of individual crystallites of high quality CVD-grown monolayer MoS$_2$. The devices show low temperature mobilities up to 500 cm$^2$ V$^{-1}$ s$^{-1}$ and a clear signature of metallic conduction at high doping densities. These characteristics are comparable to the electronic properties of the best mechanically exfoliated monolayers in literature, verifying the high electronic quality of the CVD-grown materials. We analyze the different scattering mechanisms and show that the short-range scattering plays a dominant role in the highly conducting regime at low temperatures. Additionally, the influence of optical phonons as a limiting factor is discussed.

KEYWORDS: Molybdenum disulphite, chemical vapor deposition, electronic transport, two-dimensional crystal

Two-dimensional (2D) crystals of transition metal dichalcogenides (TMD) have received significant interest due to their potential in a wide range of novel applications as well as in basic research.1–3 Especially monolayers of semiconducting TMDs such as MoS$_2$ hold significant promise in electronics and optoelectronics due to their unusual electrostatic coupling,4 large carrier mobility,5 high current carrying capacity,6 and strong absorption in the visible frequencies.7 on top of their chemical and mechanical robustness. Strong spin–orbit coupling and the unique crystal symmetry of these materials lead to the coupling of spin and valley degrees of freedom, which can be exploited for the development of novel valleytronics devices.8

While monolayers of MoS$_2$ can be readily obtained by micromechanical cleavage of synthetic or natural bulk crystals,9 large area, high quality, and continuous thin films are needed for practical devices. To this end, several groups have recently succeeded in the growth of monolayer thin films of TMDs via chemical vapor deposition (CVD).9–13 The formation of monolayers during the CVD process occurs through nucleation and growth, resulting in a film that consists of misoriented grains stitched together by lines of 8- and 4-membered rings.10,11 Initial studies have suggested that the grain boundaries have minor effects on the charge transport properties.10 The reported room-temperature carrier mobility of these thin films, which is often used as a measure of the electronic quality, is found to be between 0.1 and 10 cm$^2$ V$^{-1}$ s$^{-1}$ for unencapsulated devices.9–11 While some improvement can be achieved with dielectric encapsulation of the channel,12 these values are distinctly lower than the theoretical prediction.15

While recent transport studies suggest that charged impurities16–18 and localized states19,20 play a crucial role in mechanically exfoliated samples, the dominant scattering processes that limit the carrier mobility remains elusive. Detailed studies on CVD-grown MoS$_2$ suggest that the contact resistance due to Schottky barriers needs to be carefully taken into account in order to properly evaluate carrier mobility.21,22 Similarly, high density of localized states prohibits access to the band transport regime.23 In highly doped samples, however, bandlike transport has been observed.5,6 In this regime, the contact resistance is roughly independent of gate bias and temperature, allowing the study the band transport mobility with less complication.5

In this article, we report on the electronic transport properties of CVD-grown crystallites of monolayer MoS$_2$ in...
the highly conducting regime and demonstrate that their electronic quality is comparable to that of mechanically exfoliated materials. In back-gated device geometry without encapsulation, our CVD MoS$_2$ monolayers exhibit room and low-temperature field effect mobilities of up to 45 and 500 cm$^2$V$^{-1}$s$^{-1}$, respectively. We also report the observation of crossover from insulating to metallic conduction as a function of carrier density and temperature. This phenomenon, previously referred to as metal-insulator-transition (MIT),$^{16}$ allows us to focus on the transport regime where the effect of band edge disorder can be neglected. Our analysis shows that low-temperature carrier mobility in the high charge carrier density regime is largely limited by structural defects.

Our CVD MoS$_2$ thin films were grown on silicon substrates covered with 300 nm of silicon dioxide using a method reported by other groups.$^{9,10}$ Near the edge of the continuous MoS$_2$ film, numerous large (>10 $\mu$m) crystallites of monolayer MoS$_2$ are found (Figure 1a). The triangular shape of most crystallites reflects the 3-fold symmetry of MoS$_2$ suggesting they are single-crystalline. Uniform Raman and photoluminescence signals (Figure 1b,c) from most individual crystallites further verify that they consist of a single crystal domain with no internal grain boundaries.$^{10}$ We note that some triangular crystallites consisting of multiple domains were occasionally found in different batches (see Supporting Information for details). The sharp spectral features indicate evidence of no substantial disorder in the sample (Figure 1d,e). In fact, the band gap photoluminescence peak from the CVD samples is distinctly sharper compared to that from mechanically exfoliated counterparts, suggesting their high electronic quality.

In the following, we discuss the transport properties of CVD-grown MoS$_2$ based on devices fabricated from individual crystallites (see methods for details of the device fabrication). Several devices in both two terminal (Figure 1g) and multiterminal geometry (Figure 1f) were studied.

After growth, the CVD films were transferred to a fresh silicon substrate with thermally grown oxide, which was used as the backgate dielectric. Selected devices were then contacted using standard electron beam lithography (Figure 2a). The output characteristic of a typical two-terminal device (Figure 2b) indicates good ohmic contact with the gold electrodes at large positive gate biases even at low temperatures.$^{4,18}$ In the highly conducting regime, the contact resistance plays a minor role and the 2-probe and 4-probe measurements yield similar results.$^{5}$ The activating behavior observed at lower gate biases indicates the insulating regime of the MoS$_2$ and the non-negligible effects of contact resistance due to Schottky barriers. In order to achieve optimal device performance, we employed a two-step annealing process: first at 200 °C for 2 h in N$_2$ and subsequently in vacuum at 120 °C for 4–10 h. Transport measurements were performed immediately after the second annealing step without exposing the device to ambient. This second annealing had a significant effect on the doping level as evidenced by the large shift in the transfer curve toward the negative gate bias, making the device more strongly n-type (Figure 2c). The shift is reversed upon exposure of the sample.

Figure 2. (a) Sketch of the field effect device. A monolayer of MoS$_2$ is contacted with gold electrodes on a Si/SiO$_2$ substrate on which a backgate voltage $V_{BG}$ is applied to tune the Fermi energy of the sample. (b) $I$–$V$ curves of two terminal measurements before in situ annealing at different gate voltages of 25, 45, 65, and 85 V (black) and a temperature of 5 K. (c) Gate dependence of the conductance before (red) and after (black) in situ annealing, measured at 10 K. (d) Differential conductivity in units of the gate capacitance, equivalent to the field effect mobility before and after annealing.
to the ambient (see Supporting Information). This indicates that annealing causes the removal of adsorbents such as O₂ or H₂O, which are known to deplete negative charge carriers and the resulting shift of the Fermi level toward the conduction band. It is worth noting that the threshold shift due to vacuum annealing can be as large as 100 V, which corresponds to increase in the carrier concentration by \(7 \times 10^{12} \text{ cm}^{-2}\). As discussed below, this allows us to readily access the metallic conduction regime with relatively small backgate voltages without the use of ionic or high-\(\kappa\) dielectric topgate. The channel resistivity at large positive gate bias was found to be below 10 kΩ, which is among the lowest values reported to date for monolayer MoS₂. At large negative gate biases, the insulating regime is achieved yielding on/off ratios of \(>10^5\) at low temperatures.

In backgated devices with no dielectric encapsulation, field-effect mobility \(\mu_{\text{fe}}\) can be obtained by \(\mu_{\text{fe}} = (d\sigma/dV_{\text{bg}})C_{\text{ox}}^{-1}\) where \(C_{\text{ox}} = 11.5 \text{ nF}\) is the gate oxide capacitance, \(\sigma\) is the channel conductivity, and \(V_{\text{bg}}\) is the backgate bias. Figure 2d shows the gate bias dependence of the field-effect mobility of a two-probe device at 10 K before and after the vacuum annealing step. The maximum \(\mu_{\text{fe}}\) of 200 cm² V⁻¹ s⁻¹ remains almost unchanged but the saturation of mobility, which corresponds to the linear regime of the conductivity, is observed only after the second annealing step. It may be noted that both 2- and 4-probe field effect mobilities were found to be in a range between 100–500 cm² V⁻¹ s⁻¹ (see Supporting Information) and the discrepancies between the two were only evident near the insulating regime (where \(R > 10 \text{ MΩ}\)) where the contact resistance becomes significant. Because of large uncertainties in the Hall mobilities and the large range in resistances studied, we focus the following discussions on field effect mobilities, which are obtained from DC two-terminal measurements.

Figure 3a shows the conductance of a device as a function of backgate voltage and temperature. For positive gate voltages, the conductance decreases with increasing temperature, indicating metallic behavior, whereas for negative biases the temperature dependence is reversed, showing the characteristic of an insulator. This crossover from insulating to metallic conduction is shown in more detail in Figure 3b,c. The transfer curves show a gradually shifting crossover point around \(V_{\text{bg}} = 0\) V above and below which the temperature dependence is opposite. The crossover point occurs at the channel conductivity on the order of \(e^2/h\) similar to the previous reports by Radisavljevic and Kis16 and Baugher et al., suggesting that they originate from the same physical phenomenon. In most of our devices, the crossover point occurs at low gate voltages, allowing the analysis of charge carrier transport in the fully metallic regime where band edge disorder plays a minor role. The resistance decreases with temperature in the insulating regime, suggesting phonon-assisted hopping conduction and thermal activation of carriers.

The low-temperature field effect mobility of our devices is among the highest reported to date, however, it falls significantly below the acoustic-phonon-limited mobility of \(\sim 10^8\) cm² V⁻¹ s⁻¹ predicted by theory. This strongly suggests that the mobility is limited by extrinsic factors at low temperatures. The gate-dependent field effect mobilities shown for different devices in Figure 4a,b can be used to distinguish three different transport regimes. For large negative gate voltages, transport is dominated by variable range hopping (see Supporting Information for details), as reported previously. On the other hand, at gate biases around zero, the field effect mobility increases with gate voltage. This behavior corresponds to \(\sigma \sim n^\alpha\) with \(1 < \alpha < 2\), which is indicative of charged impurity scattering in a two-dimensional system with parabolic dispersion and \(T > T_{\text{Fermi}}\). Because the material is strongly doped by electron donors, the presence of ionized donors or Coulomb impurities is expected. For high positive voltages, the system is in the metallic regime and reveals an upper limit of mobility, which becomes density-independent at low temperatures (\(<40\) K) as also shown in Figure 4b. This saturation of mobility with temperature as well as with charge carrier density is a signature of short-range scattering limiting the device performance. It is worth noting that a similar behavior was observed for topgated devices with high-\(\kappa\) dielectric16 where high charge carrier densities were reached.

As the temperature increases, scattering due to acoustic and polar optical phonons is expected to play a dominant role in decreasing mobility in the metallic regime. In the presence of more than one scattering mechanism, Matthiessen’s rule can be used to describe the contributions from the various scatterers

\[\frac{1}{\mu_{\text{total}}} = \frac{1}{\mu_{\text{ph}}} + \frac{1}{\mu_{\text{sr}}} + \frac{1}{\mu_{\text{lr}}}\]

where \(\mu_{\text{ph}}, \mu_{\text{sr}},\) and \(\mu_{\text{lr}}\) represent the mobilities limited by phonons, short-range, and long-range scatterers. Here we assume other contributions such as electron–electron scattering to be minor. At low temperatures, \(\mu_{\text{ph}}\) can be neglected in our system because the other scattering mechanisms dominate.
Figure 4. (a) Mobility as a function of gate voltage. Temperatures are 10, 20, 30, 40, 100, and 150 K. The regions limited by short and long-range scatterers as well as the phonon influence (red arrow points toward higher temperatures) can be clearly distinguished. (b) Temperature dependence of the measured mobility at different gate voltages from 67.5 to 87.5 V in double logarithmic scaling. The black line follows $T^{-0.7}$ as guide to the eyes. (c) Mobilities for the phonon dominated part at temperatures above 100 K. The as-measured mobilities $\mu_{\text{meas}}$ for three devices are shown as well as the values of $\mu'$. The black line indicates the theoretical prediction for the mobility limited by phonon scattering obtained from ref 15. (d) The mobility $\mu'$ as a function of temperature for several gate voltages with the according power-law fits. Each curve has been averaged over multiple gate voltages ($\pm 1$ V) before fitting. The plot shows that the $\gamma'$ values strongly depend on the gate bias (see Supporting Information for details).

We also neglect $\mu_0$ in the high-voltage regime because the mobility becomes density independent and $\mu_0 \ll \mu_\text{eff}$. As shown in Figure 4a,b, we extract $\mu_\text{eff}$ to be of the order 200 cm$^2$ V$^{-1}$ s$^{-1}$ for this sample.

In the metallic conduction regime, the phonon contribution leads to mobility damping with a power law dependence on temperature $\mu_{\text{ph}} \sim T^{-\gamma}$. The theoretical analysis by Kaasbjerg et al. predicts $\gamma$ to vary from 1 (at 100 K) to 1.7 (at room temperature). At low temperatures when only acoustic phonons are the limiting factor, $\gamma$ approaches 1, but above ~100 K optical phonons play a dominant role and a higher $\gamma$ is expected. At very low temperatures, the Bloch Grueneisen regime may be reached, in which large values of $\gamma$ are predicted. The reported damping factor $\gamma$ obtained from transport experiments on monolayer MoS$_2$ varies between 0.62 and 1.75 for unencapsulated devices and shows distinctly lower values of 0.3−0.78 for devices with high-κ top-gate dielectric. While some variations in the apparent phonon damping factor may be explained by charged impurity scattering and homopolar phonon quenching, the origin of the observed variations is unclear. We show below that the multiple factors affect the apparent phonon damping factor and extraction of true phonon contribution requires careful analysis.

The common feature of the previously reported results is that the low-temperature mobility is saturated around 100−200 cm$^2$ V$^{-1}$ s$^{-1}$ independent of the presence of high-κ top-gate dielectric. Although most of these measurements do not reach the linear conductivity regime at high charge carrier densities, the saturation of mobility with temperature suggests that the mobility is predominantly limited by short-range scatterers as we observe in our samples. Once multiple scattering mechanisms are present, the damping factor can appear to be strongly suppressed from its intrinsic value.

We found that the power-law fit of the as-measured mobilities below 170 K yields apparently low $\gamma$ values of ~0.7 (Figure 4b). Correct analysis of the intrinsic damping factor requires that contributions to scattering due to phonons be separated from those due to other scattering mechanisms. Because $\mu_0$ is known and temperature independent, we can subtract this contribution from the measured mobility to obtain $\mu' = (1/\mu_{\text{meas}} - 1/\mu_0)^{-1}$. Figure 4c shows the as-measured mobilities $\mu_{\text{meas}}$ and calculated mobilities $\mu'$ at high gate voltage for three different devices on a double logarithmic plot. While both $\mu_{\text{meas}}$ and $\mu'$ can be fitted reasonably well with power law dependence, the damping factor is significantly higher for $\mu'$. We can apply the same analysis to the previously reported results in the highly conductive regime and achieve similar increase in the $\gamma$ values (see Supporting Information for details). Applying the calculation to our high-temperature data results in an only slight increase of room temperature mobilities (e.g., $\mu_{\text{meas}} = 45$ cm$^2$ V$^{-1}$ s$^{-1}$ to $\mu' = 58$ cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature), which is in agreement with the fact that in this temperature range phonon scattering is dominant over short-range scattering.

Figure 4d shows the temperature damping of $\mu'$ for several gate voltages with the according fits. The curves follow the expected $\sim T^{-\gamma'}$ very well in this temperature regime and the extracted values for the new damping factor $\gamma'$ vary with backgate voltage between 1 and 2.6. This points toward the collective role of multiple scattering mechanisms besides phonons in the metallic regime influencing the transport. Large damping factors approaching that of the bulk (2.6) observed in our analysis suggest that the effects of optical phonons may be dominant even at low temperatures and indicate that the deformation potentials for the acoustic and optical phonons in monolayer MoS$_2$ are considerably different from the values expected theoretically. Another possibility is that at low temperatures and high charge carrier density, the Bloch Grueneisen regime is approached resulting in a significant increase in $\gamma$ as predicted theoretically by Kaasbjerg et al.

In summary, we demonstrate that the electronic transport properties of CVD-grown monolayer MoS$_2$ are comparable to those of mechanically exfoliated counterparts. Despite the common perception that CVD-grown thin films are structurally defective due to thermal stresses caused during the growth process, large field effect mobility was achieved. Our observation of the crossover from the insulating to metallic conduction verifies the high electronic quality and inherent n-type doping of the material. We further show that short-range scatterers limit the mobility at high carrier densities and at low temperatures and discuss the collective role of multiple scattering mechanisms. Our results provide positive prospects for further improvements of the device performance and device implementation of CVD MoS$_2$ thin films.

**ASSOCIATED CONTENT**

§ **Supporting Information**

Additional information on sample fabrication, additional data from optical and transport experiments, and additional analysis of the insulating and metallic regime and temperature dumping.
This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors
*Email: (H.S.) physche@nus.edu.sg.
*Email: (G.E.) g.eda@nus.edu.sg.

Notes

The authors declare no competing financial interest.

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