MoS$_2$: a Choice Substrate for Accessing and Tuning the Electronic Properties of Graphene

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Research into the electronic properties of graphene and its viability for device applications has fueled an ongoing quest for substrate materials that are minimally invasive. While graphite was found to be perfectly suited for shielding graphene from external perturbations, its metallic screening precludes control of the carrier density by gating, which renders it unsuitable for device applications. Another candidate, hBN, which is atomically flat, chemically inert, and allows gating, can cause significant bandstructure reconstruction in graphene due to the close match of their atomic structures. Here we report on the suitability of MoS$_2$ substrates as measured by scanning tunneling microscopy and Landau level spectroscopy in a device configuration which allows tuning the carrier density of graphene by gating. We find that, similarly to hBN, graphene on MoS$_2$ is ultra-flat producing long mean free paths and sharp Landau levels down to magnetic fields of 2T, while completely avoiding the band structure reconstruction caused by hBN. Importantly, we find that the screening properties of the MoS$_2$ substrate can be tuned with relatively low gate voltages from insulating to metallic leading to a substantial increase in the scattering length. The use of MoS$_2$ substrates thus provides unique opportunities to access the intrinsic electronic properties of graphene and to study in situ the effects of screening on electron-electron interactions and transport.
The vulnerability of atomically thin layers such as graphene\textsuperscript{1-3} to environmental disturbances has prompted an ongoing search for substrates that can support the material without perturbing its electronic structure. Graphite substrates were found to be by far the least invasive, making it possible to observe the intrinsic low energy spectrum of graphene by using scanning tunneling microscopy (STM), spectroscopy (STS)\textsuperscript{4-7}, and cyclotron resonance (CR)\textsuperscript{8} measurements. Landau level spectroscopy showed that on graphite substrates the quasiparticle lifetime in graphene is intrinsic, originating from electron-electron interactions, with the only source of external scattering being the sample boundaries\textsuperscript{5}. In this sense graphite substrates are ideally suited for accessing the low energy spectrum of graphene. However the strong metallic screening of bulk graphite, which precludes control of the carrier density by gating and masks the electron-electron interactions, imposes severe limitations for both applications and fundamental studies. The alternative is to use insulating substrates, but the versatility gained comes at the price of enhanced sensitivity to surface corrugations\textsuperscript{9-11} and impurities\textsuperscript{12-16}, which create electron-hole puddles that obscure the low energy electronic properties at the Dirac point\textsuperscript{17}. These perturbations can be mitigated by the use of atomically flat\textsuperscript{18} and chemically inert substrates such as hexagonal boron nitride (hBN)\textsuperscript{19-22}. However the close match between the lattice structure of graphene and the substrate leads to a spatial modulation which significantly perturbs the electronic spectrum by producing Van-Hove singularities\textsuperscript{23, 24}, band gaps\textsuperscript{25} and new sets of Dirac cones\textsuperscript{26-30}. Here we show that atomically flat MoS\textsubscript{2} substrates provide access to the intrinsic band structure of graphene while at the same time allow tuning via a gate voltage both the carrier density and the strength of screening.

MoS\textsubscript{2} is a semiconductor in the layered transition metal dichalcogenite family consisting of covalently bonded S-Mo-S sheets held together by the van der Waals
force. Its weak interlayer coupling facilitates the extraction of ultra-thin layers by exfoliation. Bulk MoS$_2$ has an indirect bandgap of 1.2~1.3eV$^{31}$ which, due to quantum confinement, crosses over to a direct bandgap of $\sim$1.9eV when the material is exfoliated down to a monolayer$^{32}$. Thin layers of MoS$_2$ are well suited to serve as the channel material in FET applications, exhibiting high room temperature mobility, almost ideal switching characteristics, and low standby power dissipation$^{33-36}$. The fact that the position of the Fermi energy can be promoted from the gap to the conduction band with relatively modest gate voltages, allows tuning the screening properties of MoS$_2$ films from insulating to metallic. Further, the absence of dangling bonds and of surface states renders its surface inert, clean and minimally invasive. The large lattice mismatch between MoS$_2$ and graphene, together with its chemical inertness and the tunable screening, renders MoS$_2$ ideally suited as a substrate material for studying graphene by STM and STS.

We employed thin MoS$_2$ flakes that were exfoliated from commercial 2H-MoS$_2$ crystals (SPI CAS # 1317-33-5) and deposited onto a 300nm chlorinated SiO$_2$ substrate$^{37}$ capping a degenerately p-doped Si gate. The flakes were identified by optical microscopy and their thickness was measured using atomic force microscopy (AFM) in ambient conditions. Subsequently a flake of graphene which was exfoliated from bulk HOPG and deposited on a thin PMMA film was optically aligned with the MoS$_2$ substrate and pressed onto it while heating the sample stage to $\sim$100 $^\circ$C$^{19}$. We employed e-beam lithography followed by electron-beam evaporation at a base pressure of $2\times10^{-7}$ Torr to prepare the Ti/Au (3nm/70nm) contacts. Similar methods have been used to prepare samples on hBN substrates. As for graphene on SiO$_2$, graphene was deposited directly without the special alignment process. The devices were baked for 3hrs in forming gas (90% Ar, 10% H$_2$) at 250 $^\circ$C prior to performing STM measurements in a home-built STM operating at temperatures down to 4K and
in magnetic fields up to 12T. Coarse X-Y motors were used to locate the micron sized sample. Figure 1(a) illustrates the measurement set up and electrode configuration for the gated STM/STS studies. The images were acquired in constant current mode with the bias voltage, \( V_b \), applied to the sample and using Pt-Ir tips mechanically cut from a polycrystalline wire. Differential conductance, \( dI/dV \) which is proportional to the local density of states (LDOS), was measured with lock-in detection at frequency \( f = 440 \text{Hz} \) with fixed tip to sample distance. The gate voltage, \( V_g \), was applied between the Si backgate and the sample. This measurement configuration which combines STS with gating capabilities makes it possible to study the effect of screening on the electronic properties of graphene.

Figures 1(b-e) show STM topography images, 80nm × 80nm in size, of graphene on several substrates: MoS\(_2\) (b), SiO\(_2\) (c) and hBN (d,e). In Figure 1(f) we compare the height profile on these substrates taken along the lines indicated in the topography images. Since graphene tends to conform to the substrate its corrugation on atomically flat surfaces such as MoS\(_2\) or hBN is naturally much smaller than on amorphous surfaces such SiO\(_2\). Indeed we find that the average surface corrugation of graphene on hBN (0.1nm), as shown in Figure 1(d), is one order of magnitude smaller than on SiO\(_2\) (0.9 nm), consistent with earlier reports\(^9,^{20,21}\). This is in marked contrast to the case shown in Figure 1(e) where in spite of the atomically flat hBN substrate the surface exhibits a large periodic corrugation with an apparent height of ≈0.4nm. The stark difference between the images in Figures 1(d) and 1(e), both showing the topography of graphene on hBN, is due to different relative twists between the lattice orientations of graphene and hBN. The relative twist angle, \( \phi \), together with the lattice mismatch, \( \delta = \frac{a_{BN}}{a} \sim 1.8\% \), between graphene and hBN gives rise to a moire superstructure of period\(^{20}\) \[ \lambda = a \frac{(1 - \delta)}{\sqrt{2(1 - \delta)(1 - \cos \phi) + \delta^2}} \] where \( a_{BN} \) and \( a \) are the
lattice constants of hBN and graphene respectively. The superstructure in Figure 1(e) is due to the small twist angle, \( \sim 0.1^\circ \), which gives rise to the large periodic modulation in topography and in the LDOS. In contrast, the twist angle in Fig. 1(d) is too large (>20\(^\circ\)) to produce a measurable superstructure resulting in the much smoother appearance. Thus, substrates with lattice structures closely matched to that of graphene (small \( \delta \)) such as hBN \(^4\) or a second layer of graphene \(^23\), can produce a large disturbance in the band structure, even when they are atomically flat. In contrast, for substrates with large mismatch such as MoS\(_2\) the disturbance is minimal.

Figure 2 shows the evolution of the dI/dV spectra with gate voltage for graphene deposited on a \(~30\)nm thick MoS\(_2\) substrate. All energy measurements are referred to the Fermi energy (\( E_F \)), which is the zero of energy. Determining the position of the DP from the zero field LDOS of graphene on an insulating substrate is a challenging task \(^7\) because the inevitable presence of electron-hole puddles smears out the minimum at the DP. Furthermore, in the absence of screening the zero-bias anomaly produces a pronounced minimum which can overshadow the minimum at the DP \(^7\)-\(^40\).

The arrows in Fig. 2(a) at the center of the broad minimum are a rough estimate of the DP position. This choice was guided by the finite field data (Figure 4) where the position of the DP is much less ambiguous. This is because in a magnetic field the center of the N=0 Landau level (LL) coincides with the DP and the position of \( E_F \) coincides with its zero field value for \( V_g \) corresponding to a half filled LL \(^7\). Plotting the gate voltage dependence of \( E_D \) in Fig.2(b) we find that for \( V_g < -10V \) the data qualitatively follows the massless Dirac fermion spectrum expected for graphene: 

\[
E_D = \hbar v_F \sqrt{\pi \alpha |V_G - V_0|}.
\]

Here \( V_0 \sim -4.5V \) represents the voltage to compensate the unintentional doping, \( \alpha \approx 6.6 \times 10^{10} \) cm\(^2\)V\(^{-1}\) is the carrier density per volt of gate voltage and \( v_F = 1.21 \pm 0.02 \times 10^6 \) m/s is the Fermi velocity. The values of \( \alpha \) and \( v_F \) were obtained from the LL spectra as discussed below. We note that the for \( V_g > \)
−10V the gate dependence of $E_D$ is significantly slower, indicating that most of the
gate induced charge is taken up by the MoS$_2$ substrate. Indeed from the finite field
data we find that in this regime only ~25% of the gate induced charge goes the
graphene layer, the rest being absorbed by the MoS$_2$ substrate. This suggest that $E_F$
has entered the conduction band (CB) of MoS$_2$ at which point the gate induced shift
in the position of $E_D$ is determined by the LDOS of the combined graphene/MoS$_2$
substrate, as illustrated in the inset of Figure 2(b). Since the LDOS in the CB of MoS$_2$ is
larger than that of graphene most of the charge is absorbed by the former. For
comparison we show in Figure 2(b) the gate dependence of $E_D$ for graphene deposited
on chlorinated SiO$_2$ which remains insulating for all values of the applied $V_g$. In this
case the gate induced charge populates only states in graphene resulting in the
expected square-root gate dependence of $E_D$ for the entire range of applied $V_g$. For the
chlorinated SiO$_2$ substrate we find $\alpha \approx 7.3 \times 10^{10}$ cm$^{-2}$V$^{-1}$, $V_0 \sim 12$V and $v_F$
=1.1±0.02×10$^6$ m/s.

In the presence of a perpendicular magnetic field the dI/dV spectrum breaks up into a sequence of LL peaks. The evolution of the LLs with magnetic field for
graphene on MoS$_2$ and on chlorinated SiO$_2$ at $V_g=10$V is shown in Figures 3(a) and 3(b). In both cases the LL sequence follows the field and level index (N) dependence
characteristic of massless Dirac fermions as expected for single-layer graphene$^2$:

$$E_N = E_D + \text{sgn}(N)\sqrt{2e\hbar v_F^2|N|B} \quad N = 0, \pm 1, \pm 2,... \quad (1)$$

Here $e$ is the magnitude of the electron charge and $N > 0$ ($N < 0$) corresponds to
electron (hole) levels. Fitting the measured sequence of energy levels to this
expression we obtain $v_F =1.21\pm0.02 \times10^6$ m/s and $v_F =1.1\pm0.02 \times10^6$ m/s for
graphene on MoS$_2$ and chlorinated SiO$_2$ respectively. One of the prerequisites for
observing well developed LLs is for the random potential to be smooth on the length
scale of the cyclotron orbit, $l_c(B) = \frac{\hbar}{\sqrt{eB}} = \frac{25.64\text{nm}}{\sqrt{B}}$. Therefore the field at which LLs become resolved signals that the cyclotron orbit is sufficiently small to “fit” within the characteristic puddle size of a particular sample. For graphene on MoS$_2$, Figure 3(a), the LLs are already well resolved at 2T indicating that the characteristic puddle size exceeds $l_c(2T) \sim 18\text{nm}$. For the case of graphene on chlorinated SiO$_2$, Figure 3(a), LLs become distinguishable at 6T, indicating smaller puddles bounded by $l_c(6T) \sim 10\text{nm}$. The electron-hole puddles can be directly imaged through dI/dV maps representing the spatial dependence the local doping. Figures 3(c) and (d) show the maps of the $N = -1$ LL energy at 10T for graphene on the MoS$_2$ and chlorinated SiO$_2$ substrates respectively. The spatial fluctuations in the map reflect local substrate induced hole (blue) doping for negative energy shifts and electron (red) doping for positive energy shifts. For the MoS$_2$ substrate the average puddle size obtained from the color maps ~ 30nm, slightly larger than the values reported for graphene on hBN, suggests that LL would remain well resolved down to magnetic fields of 0.5T. The average puddle size for the chlorinated SiO$_2$ substrate, ~10nm, is in good agreement with that obtained from the LL spectra.

To study the effect of doping on the LLs we measured the gate dependence of the dI/dV spectra at fixed field. The results for $B = 8\text{T}$ and 10T (Supplementary material S2) are summarized in the map shown in Fig4(a). Each vertical line corresponds to the spectrum taken at a particular gate voltage. The pronounced staircase features reflect the high degeneracy of the LLs each of which can accommodate a carrier density of $D = 4 \frac{B}{\phi_0} = 10^{11}\text{B[T] states/cm}^2$, where $\phi_0 = 4.14 \times 10^{-11}\text{Tcm}^2$, is the fundamental unit of flux. In the process of gating, each LL pins the Fermi energy as it is filled causing the plateau features. The width of a plateau, $\Delta V_g = D/\alpha$, reflects the gate voltage required to supply D carriers per unit area to the
graphene layer. The bias-voltage dependent shifts in the step position appearing as diagonal lines on the map are due to tip induced gating.

For the data in Fig 4(a) in the regime where the MoS$_2$ substrate is insulating, $V_g < -10V$, we find $\Delta V_g = 11.8V$ which gives $\alpha \approx 6.6 \times 10^{10}$ cm$^{-2}$V$^{-1}$. For $V_g > -10V$, the plateaus become much wider with $\Delta V_g \sim 50V$ and $\alpha \approx 1.5 \times 10^{10}$ cm$^{-2}$V$^{-1}$ indicating that $E_F$ has entered the CB of MoS$_2$. At this point $\sim 75\%$ of the carriers introduced by the gate are taken up by the MoS$_2$ substrate which can now provide better screening of the random potential (Supplementary material S2).

In Figure 4(b) we present the LL spectra for several values of $V_g$. Fitting in Figure 4(c) the energies of the LLs obtained from these spectra with Eq. (1), we find $v_F \sim (1.21 \pm 0.5) \times 10^6$ m/s. Furthermore, as shown in the inset, we find no systematic gate dependence of $v_F$. Since $v_F$, is inversely proportional to the dielectric constant$^{41}$ this implies that, in spite of the increased screening accompanying the entry of $E_F$ into the conduction band, the dielectric constant of MoS$_2$ does not depend on doping for the range of $V_g$ employed here, consistent with recent theoretical work$^{42}$. This value of $v_F$ is comparable to that obtained on the chlorinated SiO$_2$ substrate whose dielectric constant $\sim 4$ is close to that of MoS$_2$.

To illustrate the effect of screening we compare in Figure 4(d) the linewidth, $\Delta E$, of the N=0 LL in the unscreened ($V_g = -30V$) and screened regimes ($V_g = +25V$). Using a Gaussian fit we find $\Delta E \sim 54$mV for the unscreened case, which corresponds to a quasiparticle lifetime of $\tau \approx h/\Delta E = 12$fs and to a scattering length of $l_{mfp} \sim v_F \tau \sim 15$nm. In the screened regime we find a much narrower linewidth, $\Delta E \sim 28$mV, indicating a significant reduction in scattering with correspondingly longer quasiparticle lifetimes $\sim 23$fs and a mean free path of $l_{mfp} \sim 28$nm. Interestingly the mean free path obtained from the N=0 LL linewidth is comparable to the average puddle size, in Figure 3(c), indicating that the electron-hole puddles are the main
scattering source in graphene. A similar analysis of the N=0 LL on chlorinated SiO₂ (Figure 3b) gives a quasiparticle lifetime of τ ~ 10fs and l_{mfp} ~ 11nm comparable to the puddle sizes in this system, so that here too electron-hole puddles are the main source of scattering.

In summary, the quality of MoS₂ substrates as measured by the quasiparticle mean free path is remarkably good: in the unscreened regime it is comparable to that in the best insulating substrates, hBN and chlorinated SiO₂, while in the screened regime it is larger still. The results presented here demonstrate that MoS₂ substrates are perfectly suited for accessing the low energy electronic properties of graphene while at the same time providing great flexibility through controllable carrier densities and tunable screening.

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**Figure 1.** (a) Schematic of graphene on multilayer MoS$_2$ substrate with gating capabilities. The sample bias $V_b$ is applied between the STM tip and the sample contacted by a Ti/Au electrode. The edge of the graphene flake is marked by the dashed line. The back gate voltage $V_g$ is applied between the Si substrate and the top electrode. (b)(c) Constant current STM topography image of graphene on MoS$_2$ and on chlorinated SiO$_2$ respectively. The area of both images is (80nm×80nm) (d)(e) Constant current STM topography image of graphene on BN(80nm×80nm) with and without moire pattern, respectively. (f) Profile line of Section view through (b),(c),(d) and (e) indicating the corrugation of graphene on MoS$_2$ (black), graphene on SiO$_2$ (red) and graphene on BN (blue) and graphene on BN with moire pattern (green). The tunneling conditions were: $I_{\text{set}}=20\text{pA}$ and $V_b=0.4\text{V}$. The Insets in (b-d) represent zoom-in images to atomic resolution with scale bar of 0.3nm.
**Figure 2.** (a) dI/dV measurements of graphene on MoS$_2$ taken at the same position for different gate voltages. Curves are vertically displaced for clarity. Arrows indicate the position of the Dirac point as discussed in the text. Measurement parameters: set point current $I = 20\,\text{pA}$ at $V_b = 0.35\,\text{V}$, AC modulation $5\,\text{mV}_{\text{rms}}$. (b) The Dirac point as function of gate voltage for graphene on MoS$_2$ (blue squares) and graphene on SiO$_2$ (red squares). The solid lines represent the simulated gate dependence of the Dirac point in the regime where the substrate is insulating. The top inset represents the density of states of graphene on an insulating substrate. The bottom inset shows the combined density of states of graphene (red) and the MoS$_2$ substrate (teal) together with the resulting gate dependence of the Dirac point energy as described in the text.
Figure 3. Magnetic field dependence of STS $dI/dV$ spectra. (a),(b) Landau level spectra for several magnetic fields and $V_g= 10V$ for graphene on MoS$_2$ and on SiO$_2$, respectively. The LL indices $N = 0, \pm 1, \pm 2.....$ are marked. STS parameters: set point $I=20 \text{ pA}$, $V_b=0.35V$, AC modulation $2mV_{\text{rms}}$. The lower panels are histogram of the height distribution measured by AFM of MoS$_2$, graphene on MoS$_2$, SiO$_2$ and graphene on SiO$_2$ as marked. (c),(d) Spatial variation of the $N= -1$ LL peak position in $B=10T$ obtained from a $dI/dV$ map at $V_g =0V$ representing the doping inhomogeneity in graphene. STS parameters: set point $I= 20\text{ pA}$, $V_b= 0.35V$, AC modulation $2mV_{\text{rms}}$.
Figure 4. (a) Gate map of the $dI/dV$ spectra at 8 T. Each vertical line in the map corresponds to a LL spectrum at a particular gate voltage. White stripes correspond to the LL peaks energies as indicated by $N = 0, \pm 1, \pm 2, \ldots$. STS parameters: set point current $I = 20$ pA, $V_b = 0.4$ V, AC modulation $5 mV_{\text{rms}}$. (b) LLs at $V_g = -28$ V, $-14$ V, 20 V and 12 V. (v) Solid dots are data points and the line represents a fitting for LLs of graphene on MoS$_2$ in B = 8 T at $V_g = -28$ V, $-14$ V, 20 V and 12 V. Inset: Gate dependence of Fermi velocity at $V_g = -30$ to $-25$ V. (d) The Solid squares are data points and the line represents a fitting for LLs $N = 0$ with Gaussian at $V_g = -30$ V and 25 V. The curves are offset for clarity.
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