Probing defect states in few-layer MoS₂ by conductance fluctuation spectroscopy

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Despite the concerted effort of several research groups, a detailed experimental account of defect dynamics in high-quality single- and few-layer transition-metal dichalcogenides remains elusive. In this paper we report an experimental study of the temperature dependence of conductance and conductance fluctuations on few-layer MoS₂ exfoliated on hexagonal boron nitride and covered by a capping layer of high-κ dielectric HfO₂. The presence of the high-κ dielectric made the device extremely stable against environmental degradation as well as resistant to changes in device characteristics upon repeated thermal cycling, enabling us to obtain reproducible data on the same device over a timescale of more than 1 year. Our device architecture helped bring down the conductance fluctuations of the MoS₂ channel by orders of magnitude compared to previous reports. The extremely low noise levels in our devices made it possible to detect the generation-recombination noise arising from charge fluctuation between the sulfur-vacancy levels in the band gap and energy levels at the conductance band edge. Our work establishes conduction fluctuation spectroscopy as a viable route to quantitatively probe in-gap defect levels in low-dimensional semiconductors.

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I. INTRODUCTION

Following the discovery of graphene [1], the exploration of the basic physics and technological implications of two-dimensional (2D) materials has gained tremendous importance. Although graphene is a system rich in novel physics, the lack of a band gap limits its applications in transistor technology. Transition-metal dichalcogenides (TMDs) like MoS₂ and MoSe₂, on the other hand, have band gaps of the order of eV in the few-layer limit [2]. On the flip side, the reported mobilities of these TMD-based field-effect transistor (FET) devices are very low [6], and the quoted values vary widely between samples. It is now understood that defect levels (primarily arising from chalcogenide vacancies) adversely affect the mobility and optical properties of these TMD-based devices [7–10].

Despite extensive research, there is no clear understanding of the underlying defect dynamics in this system. Traditional transport measurements like current-voltage characteristics and the temperature dependence of the resistance, while providing indications of the existence of defect states, cannot directly probe their energetics [9,11]. Photoluminescence measurements report the appearance, at low temperatures, of an additional peak in the spectrum which is tentatively attributed to transitions from a “defect” level [12,13], but no direct evidence of this level has been found from optical studies. Transmission electron microscopy (TEM) [7,14–17] and scanning tunneling microscopy (STM) [18–23] have shown that the primary point defects are S vacancies, although other types of defects like interstitials, dislocations, dopants, and grain boundaries were also seen. These two techniques come with their own sets of limitations. While TEM imaging is believed to induce additional defects in MoS₂ [24,25], atomic-resolution imaging of few-layer TMDs using STM has proved challenging [11,26–28]. Thus, although theoretical studies predict the presence of prominent defect levels in these materials [29–33], probing them experimentally has proved to be challenging.

In this paper, we present conductance fluctuation spectroscopy [34] as a viable technique to identify these defect states and their characteristic energy levels. Conductance fluctuations (noise) in TMD-based devices has been studied by several groups [35–39]. In different studies, the observed conductance fluctuations have been variously attributed to charge-carrier number density fluctuations due to trapping at the interface [26], to mobility fluctuations [37,38], or to contact noise [39]. In the high-doping regime, the carrier number density fluctuation model could explain the measured noise behavior, while in the low-doping regime mobility fluctuation models seemed to better fit the experimental observations [40]. Thus, there is a lack of consensus in the community as to the origin of the observed large conductance fluctuations in this system. The problem is aggravated by the fact that ultrathin layers of TMDs degrade extremely fast.
when exposed to the ambient [39,41–43]. This makes repeated, reliable measurements on the same device challenging while at the same time severely limiting the scope of practical applications.

We have performed detailed measurements of the temperature \( T \) dependence of conductance and conductance fluctuations on several few-layer MoS\(_2\) exfoliated on hexagonal boron nitride (hBN) and covered by a film of high-\( k \) dielectric HfO\(_2\). We find that over a large range of \( T \), the noise in the system is dominated by generation-recombination processes caused by random charge fluctuations via transitions between the \( S \)-vacancy impurity band and the conduction band of MoS\(_2\). The presence of the HfO\(_2\) capping layer makes it extremely stable against degradation upon exposure to the atmosphere and to repeated thermal cycling. The presence of the crystalline hBN below screens the device from charge fluctuations in the SiO\(_2\) substrate, resulting in the noise levels in our device being orders of magnitude smaller than previous reports of on-substrate devices. This enabled us to detect charge fluctuations between the \( S \)-vacancy levels and the conduction-band edge.

### II. DEVICE FABRICATION AND MEASUREMENT DETAILS

Samples were prepared in the FET configuration by the conventional polydimethylsiloxane (PDMS)-assisted dry-transfer method [44]. We studied two classes of devices. In the first class, a few-layer hBN flake (\( \sim \)20 nm thick) was transferred on a Si\(^{++}/\)SiO\(_2\) substrate followed by the transfer of a few-layer MoS\(_2\) on top. The transfers were made using a custom-built setup based on a motorized XYZ stage (Thorlabs model B51x) using a long-working-distance 50× objective under an optical microscope. Electrical contacts were defined by standard electron-beam lithography followed by thermal deposition of 5 nm of Cr and 25 nm of Au. This was followed by an electron-beam-assisted evaporation of 30 nm of HfO\(_2\) covering the entire surface of the device. The HfO\(_2\) thin film was deposited directly on MoS\(_2\) without any buffer layer or surface treatment; the details of the HfO\(_2\) film growth are discussed elsewhere [45,46]. Several such devices were tested. In this paper we concentrate on the results obtained on one such device, labeled D1. For comparison, we also studied a second class of devices; they were few-layer MoS\(_2\) devices fabricated directly on the Si\(^{++}/\)SiO\(_2\) substrate without the top encapsulation layer (labeled D2). The thickness of the SiO\(_2\) in all cases was 295 nm. In all cases, the gate bias voltage \( V_g \) is applied from underneath the Si\(^{++}/\)SiO\(_2\) substrate.

### III. TEMPERATURE AND \( V_g \) DEPENDENCE OF RESISTANCE

Electrical transport measurements were performed in a two-probe configuration using a low-frequency lock-in technique. The bias voltage across the device was set to \( V_d = 5 \) mV. The current \( I_{ds} \), flowing through the device was amplified by a low-noise current amplifier (Ithaco 1211) and measured by a digital dual-channel lock-in amplifier (LIA). The gate voltage \( V_g \) was controlled by a Keithley-2400 source meter.

An optical image of device D1 is shown in Fig. 1(a); the few-layer MoS\(_2\) (encapsulated between hBN and HfO\(_2\)) is outlined by a black dashed line. Figure 1(b) shows a plot of the sheet resistance \( R \equiv V_{ds}/I_{ds} \) of device D1 versus \( V_g \) measured over the temperature range 115–300 K. The gate response of the device establishes it to be an \( n \)-type semiconductor, which is typically what is observed in naturally occurring MoS\(_2\). The large on-off ratio (\( \sim 10^5 \)), low on-state resistance (\( \sim 30 \) K\( \Omega \)), and very low off-state current (\( \sim 10 \) pA) attest to the high quality of the device. From the inset of Fig. 1(b) it can be seen that the threshold voltage \( V_{th} \) decreases sharply with increasing temperature going to negative \( V_g \) near room temperature. On the other hand, \( V_{th} \) for D2 at room temperature was \( \sim 15 \) V.

In Fig. 2(a) we plot the sheet resistance \( R \) of device D1 in a semilogarithmic scale versus inverse temperature for a few representative values of \( V_g \). The linearity of the plots indicates that, at least in the high-\( T \) limit, electrical transport is dominated by thermal activation of the charge carriers. More specifically, as we go higher in the high-\( T \) limit, electrical transport is dominated by thermal activation of the charge carriers. A plot of the temperature dependence of the mobility is shown in Fig. 2(d). The activation energy \( \epsilon \) extracted from the slope of the ln(\( R \)) versus \( 1/T \) plots is plotted in Fig. 2(b). One can see that \( \epsilon \) increases as one decreases the gate bias, and it varies from 20 meV at high \( V_g \) to an order of magnitude higher, \( \sim 200 \) meV, close to the off state of the device. The activation energy for device D2, extracted in a similar fashion, is, as expected, higher than that of D1 at all values of \( V_g \).

The field-effect mobility \( \mu \) of the devices can be obtained from the relation \( \mu = \frac{dI_{ds}}{dV_g} \frac{L}{wV_{th}} \). Here \( L \) is the length of the channel, \( w \) is its width, and \( C \) is the gate capacitance per unit area. In Fig. 2(c) we show plots of \( I_{ds} \) versus \( V_g \); the slope of this curve gives the mobility of the device. A plot of the \( T \) dependence of the mobility is shown in Fig. 2(d). We find that \( \mu \) for device D1 is \( \sim 20 \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) at 100 K. With increasing \( T \), \( \mu \) increases monotonically until about 225 K, beyond which it begins to fall with increasing \( T \). To understand the measured \( T \) dependence of \( \mu \) we note that in 2D semiconductors, the mobility of the charge carriers is affected by Coulomb scattering, acoustic and optical phonon
scattering, scattering by the interface phonon, and roughness due to the surface [47]. At high $T$, scattering due to phonons is dominant, which causes the mobility to have a $T^{-3/2}$ dependence [48,49]. On the other hand, scattering from charge impurities located randomly in the sample is the dominant factor limiting $\mu$ at low temperatures, causing the mobility to depend on temperature as $T^{3/2}$ [8,50]. Following Matthiessen’s rule,

$$\frac{1}{\mu} = \frac{1}{M_p T^{-3/2}} + \frac{1}{M_i T^{3/2}}, \tag{1}$$

where $M_p$ and $M_i$ represent the relative contributions of the phonon-scattering and impurity-scattering mechanisms, respectively. These coefficients are not independent but are related by $(M_p/M_i)^{1/3} = T_{\text{max}}$, where $T_{\text{max}}$ is the temperature at which $\mu$ has a maximum. In Fig. 2(d) we show a fit of the $T$ dependence of the mobility of D1 to Eq. (1). The mobility of D2, on the other hand, monotonically increases with $T$.

![Fig. 2](image)

**FIG. 2.** (a) Scatterplot of resistance $R$ of device D1 plotted on a semilogarithmic scale versus $1/T$ at several representative values of $V_g$ from 10 to 90 V in steps of 5 V. The solid lines are the linear fits of $1/T$ vs $\ln(R)$. (b) Plots of activation energy $\epsilon$ versus $V_g$ extracted from the $\ln(R)$ versus $1/T$ plots for the two devices, D1 (red open circles) and D2 (green open squares). The lines are guides to the eye. (c) Plots of $I_{ds}$ versus $V_g$ at different $T$ ranging from 115 to 300 K for device D1. (d) Plots of mobility $\mu$ versus $T$ for the two devices, D1 (red open circles) and D2 (green open squares). The blue line is a fit to the data for D1 using Eq. (1).

showing that over the range of $T$ studied, impurity scattering dominates the transport in on-SiO$_2$ substrate devices.

**IV. CONDUCTANCE FLUCTUATION SPECTROSCOPY**

The presence of both bulk- and surface-transport channels complicates the charge transport in these systems. To understand the charge-carrier dynamics arising from the surface and bulk states in this system, we studied the low-frequency conductance fluctuations over the temperature range 70–300 K using a two-probe ac digital-signal-processing technique [51]. As established in several previous reports, $1/f$ noise is an excellent parameter to probe interband scattering of charge carriers in systems with multiple conduction channels [52–54]. We used an SR830 dual-channel digital LIA to voltage bias the sample at a carrier frequency of $f_0 \sim 228$ Hz. The current $I_{ds}$ through the device was amplified by the low-noise current preamplifier and detected by the LIA. The data were acquired at every $T$ and $V_g$ for 32 min at a sampling rate of 2048 points/s using a fast 16-bit data acquisition card. This time series of current fluctuations $I_{ds}(t)$ was digitally antialias filtered and decimated. The power spectral density (PSD) of current fluctuations $S_t(f)$ was calculated from this filtered time series using the method of the Welch periodogram [51,55]. The system was calibrated by measuring the thermal (Johnson-Nyquist) noise of standard resistors. The time series of $I_{ds}$ measured for device D1 at a few representative temperatures at $V_g = 90$ V are shown in Fig. 3. We find that over the $T$ range of $\sim 140$–190 K, the measured $I_{ds}(t)$ [and, consequently, the conductance $g(t) = I_{ds}(t)/V_{ds}$] for D1 fluctuates between two well-defined levels [56,57]. This “random telegraphic noise” (RTN) [58] usually signifies that the system has access to two (or more) different states separated by an energy barrier. We come back later in this paper to a discussion of the detailed statistics of the RTN and the physical origin of these states.

![Fig. 3](image)

**FIG. 3.** Plots of source-drain current $I_{ds}$ versus time at a few representative temperatures from 105 to 245 K for device D1. The data were taken for $V_g = 90$ V.
components: with increasing temperatures for device D1. The data were measured for \( V_g = 90 \) V. On the other hand, D1 had a lower threshold voltage than D2. Taking both devices (MoS2 encapsulated between hBN and HfO2); we find that the activation energy scales in all of them lie in the range of 370 meV. In Fig. 5, we show data for another device, D1b, for which we obtain \( E_a = 353 \) meV. We come back to the physical implications of this energy scale later.

The time series \( \delta(t) \) for device D2, on the other hand, did not have a RTN component [Fig. 6(a)], and the PSD had a \( 1/f^\alpha \) (with \( 0.9 < \alpha < 1.1 \)) dependence on \( f \) over the entire \( T \) and \( V_g \) range studied [Fig. 6(b)]. The \( I_d(t) \) data were obtained for device D2 at 72 V. We have attempted to compare the data in the two sets of devices at similar values of number densities. Due to the presence of the hBN layer, the effective thickness of the dielectric layer in D1 was higher than that of D2, requiring a higher gate voltage for D1 than that for D2 to achieve a similar carrier number density. On the other hand, D1 had a lower threshold voltage than D2. Taking both these factors into account, we have estimated the \( V_g \) at which the induced number densities are similar for both D1 and D2. Thus, for D1, the data are presented for \( V_g = 90 \) V, while for device D2, the data are presented for \( V_g = 72 \) V.

\[ S_f(f) = \frac{A_1}{f} + \frac{A_2 f_c}{f^2 + f_c^2}. \]
In Fig. 7(a) we present the $V_{ds}$ dependence of the quantity $fS_I(f)$ measured at $T = 175$ K and $V_g = 90$ V for device D1. We see that the form of the PSD is independent of $V_{ds}$. To make this observation quantitative, we plot in Fig. 7(b) the dependence of $f_c$ on $V_{ds}$ extracted from these plots using Eq. (2). The fact that $f_c$ is independent of $V_{ds}$ within experimental uncertainties shows that this timescale is intrinsic to the sample [59].

The PSD $S_I(f)$ can be integrated over the frequency bandwidth of the measurement to obtain the relative variance of conductance fluctuations $G_{\text{var}}$ at fixed $T$ and $V_g$:

$$G_{\text{var}} \equiv \langle \delta g^2 \rangle / \langle g \rangle^2 = \langle \delta I_{ds}^2 \rangle / \langle I_{ds} \rangle^2 \int_{0.03125}^{28} S_I(f) df.$$  

The relative variance of conductance fluctuations $G_{\text{var}}$ was found to be independent of $V_{ds}$ at all $T$ and $V_g$, confirming that the noise arises from conductance fluctuations in the MoS$_2$ channel and not from the contacts [for representative data, see Fig. 7(c)].

We measured the noise as a function of gate bias voltage $V_g$; the results obtained at $T = 170$ K for device D1 are plotted in Fig. 8(a). We find $f_c$ to be independent of $V_g$ [Fig. 8(b)] within experimental uncertainties. In Fig. 8(c) we plot $G_{\text{var}}$ as a function of $V_g$. The total noise has been separated into its $1/f$ component and the RTN component. At low values of $V_g-V_{th}$, the $1/f$-component noise contribution is comparable to that of the RTN component, while at higher $V_g-V_{th}$, the RTN component dominates the measured conductance fluctuations. This motivated us to perform our noise measurements at high $V_g$ (90 V), so that the RTN component of the noise is easily resolvable.

In Fig. 9 we show a plot of $G_{\text{var}}$ versus $T$ for the two devices. The noise data for device D1 (plotted by green open circles) has a prominent hump over the $T$ range ($\sim 140–190$ K) coinciding with the regime where we observed RTN. To appreciate this, we plot on the same graph the relative variance of conductance fluctuations arising from the $1/f$ component (red solid circles) as well as the Lorentzian component (blue open circles). It can be seen that the increase in noise over the 140–190 K temperature range is entirely due to two-level conductance fluctuations in the system. For comparison, we also add a plot of $G_{\text{var}}$ versus $T$ for the unencapsulated
device prepared on the SiO2 substrate, D2. The noise on SiO2 substrate devices is more than two orders of magnitude larger than that of D1 and matches previous reports of measured noise in MoS2 by various groups [37,39]. Our work thus shows that encapsulation helps to significantly improve the signal-to-noise ratio.

V. DISCUSSION

A careful study of Fig. 9 provides clues to the origin of the observed noise in this system. The temperature dependence of the relative variance of conductance fluctuations $\tilde{G}_{\text{var}}(T)$ measured for the on-SiO2 substrate device D2 closely resembles the T dependence of the $1/f$ component of $\tilde{G}_{\text{var}}$ measured on D1. This indicates that these two noises have similar origins. The primary source of the T dependence of noise in many semiconductor devices is generation-recombination noise due to trapping and detrapping of charges at the gate dielectric-channel interfaces. This process can be quantified by the McWhorter model [40,60,61]:

$$N_{im} = fS_I(f)|R|^2\frac{WLC^2}{e^2k_B} \frac{1}{T},$$

where $N_{im}$ is the areal density of trapped charges per unit energy, $W$ and $L$ are, respectively, the width and the length of the device channel, $C$ is the gate capacitance per unit area, $k_B$ is the Boltzmann constant, and $e$ is the charge of the electron. Equation (4) predicts the linear dependence of $fS_I(f)$ on the temperature. Figure 10 shows a plot of $fS_I(f)$ versus $T$ for both D1 and D2. The plots are linear to within experimental uncertainties. From the slopes of these plots, the value of $N_{im}$ for device D2 was extracted to be $3.5 \times 10^{12} \text{cm}^{-2} \text{eV}^{-1}$, which agrees with previously reported values for MoS2 devices prepared on SiO2 substrates [62]. On the other hand, for the HfO2-covered, on-hBN device D1, $N_{im} = 1.8 \times 10^{10} \text{cm}^{-2} \text{eV}^{-1}$, more than two orders of magnitude lower than that in the on-SiO2 substrate device D2.

The non-$1/f$ seen only in the encapsulated device has a different origin. The presence of RTN in the time series of conductance fluctuations and the associated Lorentzian component in the PSD indicates that the noise originates from random charge fluctuations via transitions between two well-defined energy states separated by an energy barrier. We propose that in this case, these two levels correspond to the $S$-vacancy impurity band and the conduction band. This is supported by the fact that the value of the activation energy, $E_a = 370 \text{meV}$, extracted from the temperature dependence of the corner frequency $f_c$ of the Lorentzian component of the current fluctuations matches closely with the estimated position of the $S$-vacancy impurity band with respect to the conduction-band edge [63]. Note that it was possible for us to detect this fluctuation component only because of the two
orders of noise reduction made possible by the introduction of hBN between the MoS2 and SiO2 substrate.

The HfO2 layer has a twofold effect on the noise. First, being a high-κ dielectric with a dielectric constant value of about 25, its presence screens the device from Coulomb scattering and reduces the 1/f noise by orders of magnitude, enabling us to detect the RTN. Second, it acts as a capping layer that shields the MoS2 from the ambient. We believe enabling us to detect the RTN. Second, it acts as a capping adsorbates, thus preserving the RTN. With the current data, we cannot distinguish between these two effects. Preliminary results obtained on devices fabricated on hBN without the HfO2 capping layer had higher on-off ratios, higher mobilities, and lower noise levels compared to MoS2 devices fabricated on SiO2 without the HfO2 capping layer; however, we did not find any RTN in these devices. From these results, one can tentatively conclude that both the top and bottom layers are necessary to preserve the RTN. This issue is currently under detailed investigation.

Finally, coming to the question of stability of the devices, we have compared the R versus T, R versus Vg, and noise measurements on device D1 immediately after fabrication and after a gap of several months. The sample was thermally cycled several times during this period between 300 and 77 K. As shown in Fig. 11, the temperature and Vg dependence of the resistance of the device were quite reproducible. This is in sharp contrast to unencapsulated on-SiO2 devices like D2, in which after a few days the channel and contacts both degrade drastically, making further measurements impossible [39]. Similarly, thermal cycling alters the characteristics of such devices and makes the channel resistance unstable. The stability of the resistance of D1 over a time period of months confirms that encapsulation between hBN and HfO2 makes the device robust to thermal cycling and against degradation with time.

VI. CONCLUSION

To conclude, in this paper we reported on detailed conduction fluctuation spectroscopy of high-quality MoS2 devices encapsulated between hBN and HfO2. The presence of the high-κ dielectric made the device extremely stable against environmental degradation, enabling us to obtain reproducible data on the same device for over 1 year. The hBN substrate helped bring down the conductance fluctuations by over two orders of magnitude compared to similar devices on bare SiO2 substrates. The low noise levels in our devices made it possible to detect the generation-recombination noise arising from charge fluctuation between the S-vacancy levels in the MoS2 band gap and states at its conductance-band edge. Our work establishes conduction fluctuation spectroscopy as a viable route to detect in-gap defect levels in low-dimensional semiconductors.

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