Microwave Near-Field Imaging of Two-Dimensional Semiconductors

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Supporting Information

ABSTRACT: Optimizing new generations of two-dimensional devices based on van der Waals materials will require techniques capable of measuring variations in electronic properties in situ and with nanometer spatial resolution. We perform scanning microwave microscopy (SMM) imaging of single layers of MoS2 and n- and p-doped WSe2. By controlling the sample charge carrier concentration through the applied tip bias, we are able to reversibly control and optimize the SMM contrast to image variations in electronic structure and the localized effects of surface contaminants. By further performing tip bias-dependent point spectroscopy together with finite element simulations, we distinguish the effects of the quantum capacitance and determine the local dominant charge carrier species and dopant concentration. These results underscore the capability of SMM for the study of 2D materials to image, identify, and study electronic defects.

KEYWORDS: Transition metal dichalcogenide, MoS2, microwave, near-field, quantum capacitance, atomic force microscope

Two-dimensional (2D) materials have emerged as a source of novel fundamental physics1,2 and are expected to form building blocks for hybrid materials with stacking-dependent tunable properties. While the palette of suitable materials is rapidly expanding, the semiconducting transition metal dichalcogenides (TMDs) have emerged as promising materials for applications ranging from catalysis4 to electronic devices.5 In particular, TMD-based van der Waals heterostructure analogues of traditional semiconductor devices are rapidly being demonstrated and improved.6, 7 However, with device fabrication still imprecise, resulting performance is often highly variable due to sample-dependent differences in electronic properties that arise from doping and associated spatial inhomogeneities such as structural defects.

In order to understand variations between devices as they relate to their performance, techniques to identify and study the electronic inhomogeneities in 2D semiconductor materials in situ and on their characteristic nanometer length scales are highly desirable. While electron-based techniques such as transmission electron microscopy are well suited to study the structural defects that underlie many electronic discontinuities, they are time-consuming and require specialized sample preparation. In contrast, scanning probe techniques can obtain simultaneous topographic and electronic information with nanometer spatial resolution, are nondestructive, and can operate under ambient conditions with little sample preparation. However, some common scanning probe implementations such as scanning gate microscopy13 require fabricated electrodes to achieve a transistor-like geometry, which often alters material properties. While scanning capacitance microscopy14 does not require electrodes, material information is lost as it typically measures only the imaginary (capacitive) portion of the complex-valued sample impedance, and the overall signal strength is reduced due to the lower (typically on the order of MHz) frequencies used.

In scanning microwave microscopy (SMM),15 a gigahertz (GHz) signal applied to a scanning probe tip measures the complete complex-valued tip–sample admittance $\tilde{Y}$ resulting from the local electronic properties. Contact electrodes are not required and insulating or electrically isolated samples can readily be measured. While SMM is capable of quantitative capacitance determination in dedicated sample architectures,16 applications to solid-state systems typically yield qualitative conductivity measurements,17 and studies of 2D materials have largely focused on graphene.18–21 SMM imaging of the prototypical TMD MoS2 was able to resolve the presence of growth defects and grain boundaries via conductivity changes but the single TMD layer itself showed only weak contrast and the electronic origin of these effects was not established.19

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Here we demonstrate a new approach to SMM imaging of 2D materials, which we illustrate with the TMDs MoS₂ and WSe₂. By controlling the TMD conductivity via the tip bias-dependent charge carrier concentration, we significantly improve the otherwise poor contrast from single-layer crystals and identify spatial inhomogeneities in electronic structure. For single-layer systems, we further perform tip bias-dependent point spectroscopy, which we combine with finite element simulations and simple band structure approximations to extract doping concentrations and the associated quantum capacitance, which is in good agreement with expected values. Within thicker crystals, large variations in electronic properties are seen, revealing a complex behavior resulting from thickness dependent doping, the band structure, and possible interactions between layers of different thicknesses. While we use TMDs as model systems, this method is in principle applicable to all semiconducting van der Waals materials and heterostructures.

MoS₂ samples were obtained commercially (SPI supplies) while stochiometric WSe₂ (n-doped) and W₁₋ₓNbₓSe₂ (x ≈ 0.01, heavily p-doped) were grown by chemical vapor transport. Substrates were prepared by growing 260 nm of thermal oxide on p+2-doped Si for optimal visibility of TMDs, followed by solvent cleaning and O₂ plasma ash to remove residual organics. TMD crystals were prepared by conventional micromechanical exfoliation. Few-layer regions were identified by optical microscopy and studied under ambient conditions. Figure 1a shows an optical image of a MoS₂ sheet with superimposed contact mode atomic force microscope (AFM) topography confirming single-layer thickness of ~0.7 nm.

The SMM is based on a commercial AFM (Agilent 5400) operating in SMM mode as illustrated in Figure 1b. The microwave signal delivered to the tip is sourced from a vector network analyzer, which also detects the reflected signal, Ŝ₁₁. A dc bias Vₚ and low-frequency signal Vₓ, with a combined maximum of ~± 15 V are summed with the microwave signal at the tip. By modulating Vₓ at a frequency ν = 15 kHz and Vₚ = 2 V, together with a dopant profiling measurement module (DPMM) and lock-in detection, we measure the differential signal dŠ₁₁/dV = Ŝ₁₁ concurrently with Ŝ₁₁. Raster-scanned images are acquired with a lock-in time constant τ = 10 ms, while Ŝ₁₁-voltage sweeps use larger acquisition times τ ≥ 100 ms for improved sensitivity.

In order to maintain electrical contact to the TMD sheets and minimize adverse effects on experimental sensitivity from the stray admittance Ţₓₓ, as shown in Figure 1c we use 80 µm tall platinum cantilevers (Rocky Mountain Nanotechnology) in contact mode feedback. However, we find the Ŝ₁₁ signal to be highly sensitive to ambient effects and as a result use the robust Ŝ₁₁ signal (see Supporting Information).

Shown in Figure 2a is the contact mode AFM topography of an exfoliated WSe₂ patch with single and three-layer regions as indicated. The large center portion of the patch has a terraced structure with varying thickness, as well as a large region near the top with poor substrate adhesion. The Ŝ₁₁ signal is acquired simultaneously with the topography at a frequency of 2.39 GHz and after correcting for the stray admittance gives Ř₁₁, as shown in Figure 1c we use 80 µm tall platinum cantilevers (Rocky Mountain Nanotechnology) in contact mode feedback. However, we find the Ŝ₁₁ signal to be highly sensitive to ambient effects and as a result use the robust Ŝ₁₁ signal (see Supporting Information). Also shown in Figure 2 are S₁₁ = Re(Š₁₁) (b) and S₁₁′ = Im(Š₁₁) (c), the resistive and capacitive signal components, respectively. While neither signal component shows any visible contrast from the WSe₂ patch at zero tip bias, S₁₁ increases strongly with tip bias while a smaller increase is seen in S₁₁′. Overall the contrast is stronger over the bulklike thicker regions with changes in contrast between layers mostly seen in S₁₁′. Compared to the thicker regions, contrast from the three-layer region emerges only at higher bias and the single-layer remains without discernible contrast during imaging.

We find that all TMD materials studied here follow a qualitatively similar tip bias dependence of the signal. Shown in Figure 3 are AFM topography (i) and SMM images (ii–v) acquired from single and bilayer W₁₋ₓNbₓSe₂ (a) and single-layer MoS₂ (b). Both materials show little or no signal under neutral bias, but it increases at positive biases for W₁₋ₓNbₓSe₂ and negative biases for MoS₂, notably improving visibility of sheets. Little or no contrast is seen in S₁₁′ in all cases as further discussed below. Furthermore, no signal is seen at negative bias.
for both species of WSe₂ and for positive bias for MoS₂ with the same trend observed in $S_{ii}$ (not shown). For all materials, signal variations are seen within single sheets both over distances of several microns, as well as locally due to surface defects, with examples illustrated by dashed circles.

Some line-to-line signal variations are seen. This arises from increases in the tip-sample resistance due to, for example, residual soft matter from exfoliation adsorbing onto the tip and is often seen from large surface defects. However, signal levels quickly return to expected values and scans are highly reproducible (see Supporting Information), suggesting that the tip-sample contact is robust and that adsorbates do not accumulate and are rapidly removed during scanning due to the tip-sample friction.

In order to understand the origin of the observed contrast we model our system using finite-element solving software (COMSOL 4.2). Shown in Figure 4a is the model axisymmetric geometry with a single-layer TMD shown in white. The TMD thickness of 0.65 nm is based on accepted values to maximize the accuracy of our simulations. The left and right panels show the spatial distribution of the quasistatic potential for two different TMD sheet conductivities as indicated. (b) Conductivity-dependent admittance for TMD geometry with thick- and sheet diameter as indicated. Contact resistance is 50 Ω unless otherwise noted.

Figure 3. AFM topography (i) and SMM images (ii–v) of few layer W₁−ₓNbₓSe₂ (a) and single-layer MoS₂ (b) with tip bias $V_b$ as indicated. Note decreased pixel density in (b,ii) and (b,iv).

Figure 4. (a) Geometry used for finite element simulations. Left and right panels show spatial distribution of the calculated quasistatic potential for two different TMD sheet conductivities as indicated. (b) Conductivity-dependent admittance for TMD geometry with thickness and sheet diameter as indicated. Contact resistance is 50 Ω unless otherwise noted.
the GHz range, and it appears in series with the geometric capacitance as shown in the inset of Figure 5b. It is directly related to the voltage-dependent two-dimensional charge density \( Q \) by \( C_Q = \frac{dQ}{dV} \). We estimate \( Q \) and thus the quantum capacitance, from the bias-dependent conductivity obtained from the simulation fit and assuming ambient room temperature mobilities of \( \mu = 10 \text{ cm}^2/\text{V} \cdot \text{s} \). Shown in Figure 5b is the calculated \( \text{Im}(Y(V_b)) \) without quantum capacitance (solid lines) and with calculated quantum capacitance (dashed and dotted) by \( C_Q \). The dashed and dotted lines assume a constant area with radii of 0.25 and 0.1 \( \mu \text{m} \) contributing to the quantum capacitance, respectively. Although the spatial extent of the effective area contributing to the capacitance is bias-dependent, an estimate based on the full width at half maximum of the spatial distribution of the simulated quasi-static potential suggests that this area is smaller than a disk of 0.25 \( \mu \text{m} \) for all values of the conductivity considered here. With \( C_Q \) for large values of the conductivity, the series capacitance is determined by the smaller value and does not increase as calculated from the simulations alone. As a consequence, good agreement is seen with \( S_C \) and \( S_R \) for the case of WSe\(_2\) and W\(_{1-x}\)Nb\(_x\)Se\(_2\), although the increase in \( S_C \) seen for MoS\(_2\) suggests the influence of additional capacitive effects not accounted for here, including charges at the \( \text{SiO}_2\)–MoS\(_2\) interface.

The fit parameters \( E_0 \) and \( a \) directly relate to material electronic properties. For the scaling parameter \( a \) we find \( a \approx 1.1 \) for both WSe\(_2\) species and \( a \approx 2 \) for pristine MoS\(_2\). This corresponds to the steeper increase in the calculated band edge integrated DOS for electrons than holes expected for TMDs and supports our approximation.

\( E_0 \) is found to change with material according to doping levels and carrier type and for \( V_b = 0 \) can be used to estimate the charge carrier density via the corresponding values of \( \sigma \). For the case of pristine MoS\(_2\) and W\(_{1-x}\)Nb\(_x\)Se\(_2\) with \( E_0 = 2 \text{ V} \) and \( E_0 = -4.5 \text{ V} \), we estimate carrier concentrations of \( n_e = 5 \times 10^{16} \text{ cm}^{-2} \) and \( n_p = 5 \times 10^{17} \text{ cm}^{-3} \), respectively, which is in good agreement with expected values. For the case of WSe\(_2\), the value \( E_0 = 2 \text{ V} \) reflects the expected negative doping of the material, which requires carrier inversion in order for appreciable SMM signal to be obtained. Similarly, for the case of the MoS\(_2\) defect, the value of \( E_0 = -2 \text{ V} \) indicates modification of the local electronic structure via hole-doping, although the poor agreement for \( S_C \) suggests additional electronic effects.

These results underscore the applicability of SMM for nondestructive characterization of 2D materials. Similar to previous results, in the absence of a tip bias our imaging shows little or no signal from single-layer as well as thicker TMD sheets. However, by applying a tip bias to modify the sample conductivity and carrier type we can control and optimize the sample contrast in order to readily identify spatial variations in the \( S \) signal arising from electronic inhomogeneities as well as localized electronic defects. Using \( S \)-voltage point spectroscopy we obtain excellent agreement between the measured and simulated tip bias-dependent signal for the real (resistive) data which we use to semiquantitatively determine carrier concentration and type. We further account for the quantum capacitance via the bias-dependent charge carrier concentration obtained form the simulation fit, which significantly improves agreement for the imaginary (capacitive) data. Although our calculated quantum capacitance on the order of 100 nF/cm\(^2\) is significantly smaller than typical values for 2D materials of 1–10 \( \mu \text{F/cm}^2\), its value is highly dependent on the sample geometry. In particular, with quantum capacitances typically measured in a transistor geometry through a gate oxide with typical thickness \( <5 \text{ nm} \), our measured quantum capacitance is expected to be significantly smaller with the tip bias referenced against the Si ground through a 260 nm oxide layer. Although the quantum capacitance provides good agreement in \( S_C \) for the WSe\(_2\) species, differences for MoS\(_2\) remain, likely arising due to interfacial charging and effects that will be the subject of future investigations.

Of particular interest is the nature of the tip–sample interaction, as there has been significant debate regarding the electronic nature of metal-TMD contacts. We find that our signal is dominated by the resistive signal component, which strongly suggests a noncapacitive junction. Furthermore, a capacitively coupled MIS junction would be expected to yield \( S \)-voltage curves based on intrinsic doping, characterized by contrast at opposite bias values for n- and p-doped WSe\(_2\) (see Supporting Information), as observed in previous SMM studies. We therefore conclude that our tip-TMD interaction results in a largely resistive junction. Our reproducible signal levels strongly suggest a low-resistance contact, which is consistent with reports that such contacts to TMDs are routinely established using high work function metals. This underscores a unique advantage of 2D materials: unlike conventional semiconductors with dangling surface bonds, 2D material surfaces do not react under ambient conditions to form insulating oxide layers. As the tip–sample junction readily allows charge to flow to the sample, we have assumed a uniform conductivity across the TMD sheet in response to the dc tip bias. For small values of the conductivity, however, high associated sheet resistances \( \geq 1 \text{ G}\Omega \) may prevent effective charge equilibration. As our signal onset is typically around \( \sigma \approx 100 \text{ S/m} \), we do not expect that resulting conductivity variations affect our measurements.
Simulations of conductivity variations in the immediate vicinity of the tip suggest that the primary influence of such effects would be changes in our estimate of the zero-bias conductivity and doping (see Supporting Information).

While much of the interest in TMDs and van der Waals materials in general have focused on single-layer systems, multilayer systems also hold promise for technological applications. For the single-layer $S$-voltage sweeps shown here, the behavior is largely consistent among several single-layer regions studied, although some inhomogeneity is observed both within and between crystals. Unlike single layers, crystals thicker than two or three layers exhibit widely varying $S^-$-voltage behavior as seen in Figure 2b. While the origin of this behavior is unclear, it likely originates from thickness-dependent doping, together with the complexity of the DOS structure not accounted for by the quadratic approximation used. These results caution that device applications based on multilayer TMD materials require uniform film thicknesses.

As optimal device performance of 2D materials necessitates uniform structural and electronic properties over a large region, the capability for in situ characterization of devices and sheets is highly desirable. Even within single sheets of TMD materials, a large degree of electronic inhomogeneity can be observed and locally measured. The measured electronic effects of the MoS$_2$ surface defect with the region influenced by the defect significantly larger than its physical size suggest this defect strongly p-dopes its immediate vicinity.

We have demonstrated that microwave near-field microscopy together with tip bias-dependent control of carrier concentration and associated spectroscopy can be used to optimize sample contrast as well as extract local doping values of both pristine sheets and defects. In this respect, SMM is a highly attractive technique, capable of studying the local electronic structure and its spatial variations with nanometer resolution without the need for electrode deposition or device modification. While providing useful information on its own, this technique should not be viewed as a stand-alone method. Rather, SMM is compatible with and can yield complementary information to other electrostatic and electrodynamic scanning probe techniques. Although demonstrated for the specific case of TMD materials, this technique is in principle applicable to any 2D semiconductor system. Of particular interest are van der Waals heterojunctions where the tunability of material properties via interlayer interactions combined with expected spatial variations in material properties will necessitate the spatially resolved determination of electronic structure.

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**REFERENCES**

(29) This is in contrast to the conventional assumption for 3D semiconductors, where the band-edge DOS is expected to follow a $\sqrt{E}$-dependence over the narrow energy range at the band edge where the energy-momentum dispersion relation can be approximated as parabolic.