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Influences of water molecules on the electronic properties of atomically thin molybdenum disulfide

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Although it is well known that the performances of two-dimensional transition metal dichalcogenide (2D-TMD) based devices are strongly affected by humidity, the roles of water molecules in the electronic properties of 2D-TMDs are still unclear. In this work, the influence of water molecules on the electrical properties of monolayer molybdenum disulfide (MoS₂) is studied systematically using the dielectric force microscopy (DFM) technique. Taking the advantage of the DFM technique and other nondestructive characterization techniques, the electronic properties (surface potential, dielectrics, and carrier mobility) of atomically thin MoS₂ exposed to different levels of humidity are investigated. Furthermore, Raman spectroscopy manifested the correlation between the optical phonon and the mobility drop of MoS₂ flakes when subjected to humidity variations. Our results provide an in-depth understanding of the mechanism of water molecules interacting with MoS₂. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4996731>]

Two-dimensional transition metal dichalcogenides (2D-TMDs) such as molybdenum disulfide (MoS₂) have demonstrated great potential in electronic and optoelectronic applications.^{1–3} In many studies, ambient humidity has been shown to significantly alter their electrical performances.^{4–8} The mechanisms of water molecules interacting with 2D-TMDs and the influence of relative humidity (RH) on the electrical performance of 2D-TMDs are still under debate. In the work by Jonker *et al.*,⁴ monolayer MoS₂ flakes showed no electrical conductivity response to water molecules. However, in another work,⁵ a two-layer MoS₂ flake had its electrical conductivity largely decreased when subject to RH increases. Moreover, the effects of RH on the electrical transport of MoS₂ based field-effect transistors (FETs) were investigated by Liang *et al.*,⁸ and water molecule induced p-type doping was observed in both pristine and oxygen plasma treated MoS₂ flakes. It is noted that previous characterization studies were carried out on conventional MoS₂ FET devices, where the unpassivated metal surface and the metal/MoS₂ interface may absorb water molecules, which may change the work function of the metal electrodes and affect the contact properties between the metal and MoS₂ flakes.

In order to avoid uncertainties from the metal/MoS₂ contact and process induced contaminations, noncontact characterization studies are typically employed. The scanning probe microscopy technique is an ideal technique to perform noncontact and nondestructive characterization of 2D-TMD materials.^{9–11} However, there is still a lack of noncontact scanning probe characterization of the electrical conductivity of 2D-TMD materials without introducing metal electrodes. In this work, dielectric force microscopy (DFM),¹² which

was successfully applied to Single-Walled Carbon Nanotubes (SWCNTs) in previous studies,^{13–15} is used to investigate the influences of water molecules on the electrical properties of thermal CVD grown monolayer MoS₂ flakes. Compared to electrical characterization in the FET platform, the DFM technique has additional advantages of local characterization capability and dielectric constant measurements and thus provides insightful information on electrical property changes of the MoS₂ flakes by water molecules.

Figure 1 illustrates the DFM setup used in this study. As shown in Fig. 1(a), the DFM technique relies on a double-path technique to observe the electrostatic interaction between the probe and the samples.¹⁴ In the first path, a standard AC air mode (tapping mode) scan is performed to obtain the topographical profile. In the second path, the cantilever is lifted at a constant height over the topographical baseline obtained in the first path. During the second path, a dc + ac modulation voltage is applied to the probe so that the electrostatic responses from the sample will cause harmonic phase shifts of the probe oscillation which is recorded using lock-in amplifiers. The inset of Fig. 1 shows the obtained first order and second order phase images of a MoS₂ flake scanned at the RH of 40% and the dc voltage of 3 V.

As illustrated in Figs. 1(b)–1(d), by varying the dc bias to the probe, the local carrier type and density of the material under test could be modulated through its local band bending. For each dc bias to the probe, the local conductivity of the sample could be interpreted through the second harmonic phase shift of the probe oscillation.¹⁴

Thermal CVD grown MoS₂ flakes on the Si/SiO₂ substrate were used in this work.¹⁶ Most of the MoS₂ flakes were monolayers as manifested by the AFM measurement (supplementary material, Fig. S1). The MoS₂ flakes on the

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FIG. 1. Illustration of the DFM scanning setup (a). Illustration of the band bending and carrier density of a MoS₂ flake at negative (b), zero (c), and positive (d) dc bias. Inset: The first and second harmonic components of the phase image of the MoS₂ flake at a RH of 40% and a dc bias of 3 V.

Si/SiO₂ substrate were placed in a sealed AFM chamber connected to two valve-controlled gas inlets as shown in Fig. S2 in the [supplementary material](#). One of the gas inlets was connected to a pure N₂ gas line, while the other gas inlet was connected to a water molecule containing N₂ gas line. The RH inside the chamber was controlled by adjusting the flow ratio between the two gas inlets, and the resultant RH was monitored using the RH meter inside the chamber.

First, with the AFM chamber filled with pure N₂, the sample was baked at 105 °C for 20 min to remove water molecules adsorbed onto the MoS₂ flakes. After the baking process, around 100 mV drop in the contact potential difference (Δ CPD) between the MoS₂ flakes and the AFM probe was manifested by Scanning Kelvin Probe Microscopy (SKPM), probably due to the desorption of the adsorbed molecules on the MoS₂ flakes [refer to Fig. S3(a) in the [supplementary material](#)]. In addition, no further drop of Δ CPD was observed after the second baking cycle, implying the completion of the desorption process. The subsequent humidity dependent SKPM characterization [refer to Figs. S3(b) and S3(c) in the [supplementary material](#)] suggested that the monolayer MoS₂ flake had an ~ 2.5 mV drop in its Fermi level for every 1% increase in the RH, implying a p-type doping of water molecules to the MoS₂ flakes.¹⁷

DFM scanning was then performed at different RH levels to further investigate the electrical conductivity and dielectric properties of MoS₂ influenced by water molecules. The same MoS₂ flake was scanned with different dc bias voltages (from -6.5 V to 6.5 V at steps of 0.25 V) applied to the AFM probe. For each scan, a sinusoidal modulation voltage with a 3 V amplitude and 200 Hz was applied, and the corresponding first and second harmonic phase shifts were recorded.

Based on the parallel-plate capacitor assumption, the first-harmonic phase shift, $\Delta\phi_{\omega}$, of the probe should be linearly related to the dc voltage, V_{dc} , applied, while the second-harmonic phase shift, $\Delta\phi_{2\omega}$, should be a parabolic function of the ac voltage amplitude. All the AFM probes used in this work were calibrated based on the above relationships (see

Fig. S5 in the [supplementary material](#)). The slope of the $\Delta\phi_{\omega}$ versus V_{dc} plot is determined by the capacitance (i.e., dielectrics) of the samples under test. Figures 2(a) and 2(b) show the $\Delta\phi_{\omega}$ versus V_{dc} plots for the bare SiO₂ substrate and the monolayer MoS₂ flakes, respectively. It is noticed that the slope of the $\Delta\phi_{\omega}$ versus V_{dc} plot for the bare SiO₂ is almost unaffected by RH changes from 10% to 40% [Fig. 2(a)]. However, for the MoS₂ flake, the slope of its $\Delta\phi_{\omega}$ versus V_{dc} plot is significantly increased when RH is increased from 10% to 40%. Therefore, there must be an increase in the dielectric constant of the MoS₂ flake due to the adsorption of water molecules.

In order to extract the dielectric constant of the MoS₂ flakes, rigorous simulation must be performed.^{18,19} However, for the study of the influence of RH on the dielectric properties of the MoS₂ flakes, the absolute value of the dielectric constant is not necessary. In this work, the relative value of an effective dielectric of MoS₂ is calculated by assuming only the aperture capacitance and a strong screening of the MoS₂ flake (see Figs. S6 and S7 and Table S1 in the [supplementary material](#)).

Figure 2(c) shows the effective dielectric constant of ten monolayer MoS₂ flakes at different RH values. The dielectric constants of the monolayer MoS₂ flakes increase from ~ 7 to ~ 10 as RH increases from 10% to 40%. Statistically, there is an $\sim 26\%$ increase in the dielectric constant of monolayer MoS₂ flakes when RH is increased from 10% to 40% [Fig. 2(d)], implying a strong influence of the water molecules on the dielectric properties of monolayer MoS₂ flakes. It should be pointed out that adsorbed water molecules can also be polarized under the vertical electrical field.²⁰ Therefore, the above calculated dielectric constant of MoS₂ flakes is partially contributed from the polarization of the adsorbed water molecules. However, experimentally determining the influence of the polarization of these water molecules on the obtained dielectric constant of MoS₂ flakes is not well

FIG. 2. Plot of the first harmonic of the phase shift versus dc voltage applied to the probe for the SiO₂ substrate (a) and the MoS₂ flake (b) at RH = 10% and RH = 40%, respectively. (c) Calculated effective dielectric constant change of ten MoS₂ flakes at different RH values. (d) Statistical plot of the percentage increment in the effective dielectric constant of the MoS₂ flakes when RH increases from 10% to 40%.

established in this setup, and therefore, we are not able to discuss this in-depth.

The response of the second-harmonic phase shift of the probe versus the dc voltage applied on the probe at RH = 10% and RH = 40% is plotted in Fig. 3(a). The much stronger phase shift at positive probe voltages is attributed to the n-type conduction characteristic of the MoS₂ flake. However, the second-harmonic phase shift includes not only the local charge oscillation but also the contributions from the induced dipoles in the sample. The dipole contribution can be removed from the second-harmonic phase shift so as to obtain exclusively the local conductivity of the MoS₂ flakes as a function of the probe voltage (see Fig. S8 in the [supplementary material](#)). As shown in Fig. 3(b), the effective local conductivity of the MoS₂ flake (with an arbitrary unit) versus probe voltage plot is analogue to an I_D - V_G curve in conventional FET transistors. According to Fig. 3(b), the MoS₂ flake has a strong n-type FET characteristic at RH = 10%. However, at RH = 40%, the OFF state current at -6.5 V is increased, while the ON state current is dropped, implying a p-type doping to MoS₂ by water molecules. This result is consistent with theoretical calculations by Li *et al.*,²⁰ where 0.012e charge will be transferred from monolayer MoS₂ to the adsorbed H₂O molecule. This is also further consistent with our SKPM measurement (see Figs. S3 and S4 in the [supplementary material](#)), where a downshift of the MoS₂ Fermi level is observed when RH is increased from 10% to 40%.

Similar to the I_D - V_G curves for a conventional FET, the effective FET mobility (with an arbitrary unit) could also be calculated based on the effective conductivity versus probe voltage curve in Fig. 3(b).²¹ The mobility for ten different samples at different RH values is plotted in Fig. 3(c), and significant degradation of mobility can be observed as RH increases. The statistical plot in Fig. 3(d) shows around 78% drop in effective mobility as RH increases from 10% to 40%. This suggests that the electrical performance of MoS₂

based FETs will be largely degraded when tested in ambient conditions, especially in a high RH environment.

The strong electron-phonon interaction in MoS₂ flakes has been shown to significantly limit their electronic mobility, as well as their phonon frequencies and dispersion.²² Therefore, Raman spectroscopy was applied to investigate the phonon scattering influenced by water molecules. Raman scattering was performed on the MoS₂ flakes at RH = 10% and 40%. The MoS₂ samples on the Si/SiO₂ substrate were exposed to a pure N₂ environment and baked at 105 °C for 20 min to remove the molecule adsorbed in ambient conditions. The MoS₂ flakes were then exposed to 10% and 40% RH in N₂ and subsequently sealed below a fused quartz for the Raman spectroscopy measurement. Figure 4(a) shows a typical Raman shift comparison between RH = 10% and RH = 40% conditions. Clearly, a blue-shift of the A_{1g} peak and a red-shift of the E_{2g} peak can be observed at 40% RH. In addition, significant broadenings of both the A_{1g} and E_{2g} peaks at 40% RH were also observed.

The shift of the Raman A_{1g} peak is sensitive to the doping levels, while the full-width at half-maximum (FWHM) of the A_{1g} peak is sensitive to the phonon renormalization of the MoS₂ flakes.²² The blue-shift of the A_{1g} peak is consistent with the previously reported doping induced Raman shift of MoS₂ flakes.^{23–26} Figure 4(b) shows the correlation between the Δ CPD change and the Raman A_{1g} peak shifts for ten samples subject to the RH change. When RH is increased from 10% to 40%, an ~ 80 mV drop in the Δ CPD and an ~ 1 cm⁻¹ blue-shift of the Raman A_{1g} peaks are observed.

The broadening of the Raman A_{1g} peak suggests that the attached water molecules result in phonon renormalization in the MoS₂ flakes, which could largely affect the electron-phonon interactions.^{27,28} It has been shown through first principles that the carrier mobility of 2D MoS₂ flakes is largely limited by the short-range acoustic phonon scatterings.^{29,30} However, at temperatures above ~ 100 K, optical

FIG. 3. (a) Plot of the second harmonic of the phase shift versus dc voltage applied to the probe for the MoS₂ flake. (b) Calculated effective conductance of the MoS₂ flakes versus dc voltage applied to the probe. The inset shows the same plot on a log scale. (c) Calculated effective FET mobility of ten MoS₂ flakes at different RH values. (d) Statistical plot of the percentage drop in the effective FET mobility of the MoS₂ flakes when RH increases from 10% to 40%.

FIG. 4. Raman shift of the MoS₂ flake when RH is increased from 10% to 40% (a). Statistical plot of the Raman E_{2g} peak (b) and A_{1g} peak (c) positions and FWHMs at RH = 10% and RH = 40%, respectively.

phonons may play a dominant role in the mobility damping in 2D MoS₂ flakes.³¹ The effective carrier mobility versus FWHM of the Raman A_{1g} peaks of ten MoS₂ flakes is plotted in Fig. 4(c). Clearly, as RH increases from 10% to 40%, a significant mobility drop associated with the FWHM increase can be observed. Therefore, the perturbation of phonon scattering by water molecules is probably the origin of the significant mobility drop of the monolayer MoS₂ flakes.

In summary, adsorbed water molecules were shown to induce p-type doping to as-grown monolayer MoS₂ flakes, as manifested by both the SKPM and DFM characterization studies. In addition, the water molecules were found to significantly enhance the dielectric response, while severely degrading the carrier mobility of the monolayer MoS₂ flakes. Furthermore, Raman peak broadening caused by water molecule adsorption reveals the correlation between the optical-phonon scattering and the carrier mobility in the MoS₂ flakes. Our results reveal the influences of water molecules on the electronic properties of monolayer MoS₂ flakes and provide insightful information for studying MoS₂ related electronic devices in ambient conditions. In addition, this work also demonstrated that DFM could be an excellent non-contact characterization approach to determine the variations in local electronic properties of the 2D materials subjected to environmental condition changes.

See [supplementary material](#) for detailed data interpretation of SKPM and DFM techniques.

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- ¹A.-J. Cho, K. C. Park, and J.-Y. Kwon, *Nanoscale Res. Lett.* **10**, 115 (2015).
- ²X. Tong, E. Ashalley, F. Lin, H. Li, and Z. M. Wang, *Nano-Micro Lett.* **7**, 203 (2015).
- ³R. Ganatra and Q. Zhang, *ACS Nano* **8**, 4074 (2014).
- ⁴F. K. Perkins, A. L. Friedman, E. Cobas, P. M. Campbell, G. G. Jernigan, and B. T. Jonker, *Nano Lett.* **13**, 668 (2013).
- ⁵D. J. Late, Y.-K. Huang, B. Liu, J. Acharya, S. N. Shirodkar, J. Luo, A. Yan, D. Charles, U. V. Waghmare, V. P. Dravid, and C. N. R. Rao, *ACS Nano* **7**, 4879 (2013).
- ⁶H. Qiu, L. Pan, Z. Yao, J. Li, Y. Shi, and X. Wang, *Appl. Phys. Lett.* **100**, 123104 (2012).
- ⁷D. J. Late, B. Liu, H. S. S. R. Matte, V. P. Dravid, and C. N. R. Rao, *ACS Nano* **6**, 5635 (2012).
- ⁸M. Chen, S. Wi, H. Nam, G. Priessnitz, and X. Liang, *J. Vac. Sci. Technol., B* **32**, 06FF02 (2014).
- ⁹X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, and R. S. Ruoff, *Science* **324**, 1312 (2009).
- ¹⁰C.-P. Lu, G. Li, J. Mao, L.-M. Wang, and E. Y. Andrei, *Nano Lett.* **14**, 4628 (2014).
- ¹¹L. H. Li and Y. Chen, *J. Appl. Phys.* **116**, 213904 (2014).
- ¹²J. Zhang, W. Lu, Y. S. Li, J. Cai, and L. Chen, *Acc. Chem. Res.* **48**, 1788 (2015).
- ¹³Y. S. Li, J. Ge, J. Cai, J. Zhang, W. Lu, J. Liu, and L. Chen, *Nano Res.* **7**, 1623 (2014).
- ¹⁴K. Zhang, N. Marzari, and Q. Zhang, *J. Phys. Chem. C* **117**, 24570 (2013).
- ¹⁵W. Lu, J. Zhang, Y. S. Li, Q. Chen, X. Wang, A. Hassanien, and L. Chen, *J. Phys. Chem. C* **116**, 7158 (2012).
- ¹⁶S. Najmaei, Z. Liu, W. Zhou, X. Zou, G. Shi, S. Lei, B. I. Yakobson, J.-C. Idrobo, P. M. Ajayan, and J. Lou, *Nat. Mater.* **12**, 754 (2013).
- ¹⁷M. Nonnenmacher, M. P. O'Boyle, and H. K. Wickramasinghe, *Appl. Phys. Lett.* **58**, 2921 (1991).
- ¹⁸A. Dols-Perez, G. Gramse, A. Calò, G. Gomila, and L. Fumagalli, *Nanoscale* **7**, 18327 (2015).
- ¹⁹R. I. Revilla, X.-J. Li, Y.-L. Yang, and C. Wang, *J. Phys. Chem. C* **118**, 5556 (2014).
- ²⁰Q. Yue, Z. Shao, S. Chang, and J. Li, *Nanoscale Res. Lett.* **8**, 425 (2013).
- ²¹W. Bao, X. Cai, D. Kim, K. Sridhara, and M. S. Fuhrer, *Appl. Phys. Lett.* **102**, 042104 (2013).
- ²²B. Chakraborty, A. Bera, D. V. S. Muthu, S. Bhowmick, U. V. Waghmare, and A. K. Sood, *Phys. Rev. B* **85**, 161403 (2012).
- ²³H.-Y. Park, M.-H. Lim, J. Jeon, G. Yoo, D.-H. Kang, S. K. Jang, M. H. Jeon, Y. Lee, J. H. Cho, G. Y. Yeom, W.-S. Jung, J. Lee, S. Park, S. Lee, and J.-H. Park, *ACS Nano* **9**, 2368 (2015).
- ²⁴A. Nipane, D. Karmakar, N. Kaushik, S. Karande, and S. Lodha, *ACS Nano* **10**, 2128 (2016).
- ²⁵Y. Shi, J.-K. Huang, L. Jin, Y.-T. Hsu, S. F. Yu, L.-J. Li, and H. Y. Yang, *Sci. Rep.* **3**, 1839 (2013).
- ²⁶H. Li, Q. Zhang, C. C. R. Yap, B. K. Tay, T. H. T. Edwin, A. Olivier, and D. Baillargeat, *Adv. Funct. Mater.* **22**, 1385 (2012).
- ²⁷J. C. Tsang, M. Freitag, V. Perebeinos, J. Liu, and P. Avouris, *Nat. Nanotechnol.* **2**, 725 (2007).
- ²⁸D. M. Basko, S. Piscanec, and A. C. Ferrari, *Phys. Rev. B* **80**, 165413 (2009).
- ²⁹K. Kaasbjerg, K. S. Thygesen, and A.-P. Jauho, *Phys. Rev. B* **87**, 235312 (2013).
- ³⁰E. H. Hwang and S. Das Sarma, *Phys. Rev. B* **77**, 115449 (2008).
- ³¹H. Schmidt, S. Wang, L. Chu, M. Toh, R. Kumar, W. Zhao, A. H. Castro Neto, J. Martin, S. Adam, B. Özyilmaz, and G. Eda, *Nano Lett.* **14**, 1909 (2014).