Electrical and Optical Characterization of MoS$_2$ with Sulfur Vacancy Passivation by Treatment with Alkanethiol Molecules

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Recent advances in the field of two-dimensional (2D) materials have drawn considerable attention due to their unique electronic and optical properties, making them promising candidates for next-generation electronic devices. Among the 2D materials, transition metal dichalcogenides (TMDs) have gained significant interest due to their tunable electronic properties and potential applications in electronics and optoelectronics. MoS$_2$, a member of the TMD family, is particularly attractive due to its direct band gap, high mobility, and transparency, making it a promising material for various applications. However, the presence of sulfur vacancies in MoS$_2$ can introduce n-type behavior, which is not optimal for some applications.

In this work, we investigate the physical properties of MoS$_2$ atomic crystals with sulfur vacancy passivation after treatment with alkanethiol molecules, focusing on their electrical, Raman, and photoluminescence (PL) characteristics. We fabricated field effect transistors (FETs) with MoS$_2$ channels and analyzed their electrical properties before and after the alkanethiol treatment. The results indicate a significant change in the electrical characteristics of the MoS$_2$ FETs, suggesting potential applications in tuning the electronic properties of MoS$_2$ through molecule adsorption.

**ABSTRACT**

We investigated the physical properties of molybdenum disulfide (MoS$_2$) atomic crystals with a sulfur vacancy passivation after treatment with alkanethiol molecules including their electrical, Raman, and photoluminescence (PL) characteristics. MoS$_2$, one of the transition metal dichalcogenide materials, is a promising two-dimensional semiconductor material with good physical properties. It is known that sulfur vacancies exist in MoS$_2$, resulting in the n-type behavior of MoS$_2$. The sulfur vacancies on the MoS$_2$ surface tend to form covalent bonds with sulfur-containing groups. In this study, we deposited alkanethiol molecules on MoS$_2$ field effect transistors (FETs) and then characterized the electrical properties of the devices before and after the alkanethiol treatment. We observed that the electrical characteristics of MoS$_2$ FETs dramatically changed after the alkanethiol treatment. We also observed that the Raman and PL spectra of MoS$_2$ films changed after the alkanethiol treatment. These effects are attributed to the thiol (−SH) end groups in alkanethiols bonding at sulfur vacancy sites, thus altering the physical properties of the MoS$_2$. This study will help us better understand the electrical and optical properties of MoS$_2$ and suggest a way of tailoring the properties of MoS$_2$ by passivating a sulfur vacancy with thiol molecules.

**KEYWORDS:** molybdenum disulfide · field effect transistor · electronic transport · molecule adsorption
vacancy sites, unsaturated Mo on the surface of MoS₂ have a tendency to covalently bond with sulfur-containing groups.²⁴⁻²⁶ Because of this, MoS₂ has been used as a dehydrosulfurization catalyst; that is, the sulfur vacancies on the basal plane of MoS₂ act as catalytic reaction sites.²⁴⁻²⁶ Therefore, molecules with thiol (−SH) functional groups will form a chemisorbed bond with MoS₂ at the sulfur vacancy positions. Makarova et al. have examined the adsorption of thiol molecules with scanning tunneling microscopy, and they indeed observed selective adsorption of thiol molecules at sulfur vacancies on the basal plane of MoS₂.²⁴ If the sulfur vacancies are important for the n-type characteristics of MoS₂ when it is used as a semiconductor device, then the treatment of thiol molecules on MoS₂ would be able to alter the electrical properties of MoS₂ by passivating sulfur vacancies of MoS₂ with thiol molecules.

In this study, we have investigated how the adsorption of thiol molecules on MoS₂ influences the physical and electrical properties of MoS₂. For this purpose, we deposited alkanethiol (HS(CH₂)ₙ−₁CH₃) molecules on MoS₂ surfaces. Alkanethiols are one of the most widely studied thiol molecules in molecular-based electronic devices.²⁷⁻³² We studied and compared the electrical characteristics of field effect transistors made with exfoliated MoS₂ flakes prior to and after alkanethiol treatment. We also studied and systematically compared the Raman and photoluminescence spectra of exfoliated MoS₂ flakes prior to and after treatment with alkanethiols.

RESULTS AND DISCUSSION

Figure 1a illustrates the fabrication process for MoS₂ field effect transistor (FET) devices. The upper and lower panels in Figure 1a show the schematics and optical microscopic images of a sample during fabrication of the device. First, we prepared the MoS₂ flakes by micromechanical exfoliation from a bulk MoS₂ crystal. The exfoliated MoS₂ flakes were transferred to a 270 nm thick SiO₂ layer on a heavily doped p++ Si substrate, which can be used as a back gate in FET devices (Figure 1a, left). We found appropriate flakes of transferred MoS₂ that can be used for fabrication of FET devices using an optical microscope, and we measured the height of the MoS₂ flakes using an atomic force microscope (AFM). Next, we used an electron beam lithography system to make the source and drain electrode patterns of the FET devices. Here, to prepare well-defined electrode patterns, we used double layers of resists: an electron resist polymer and a buffer layer polymer (Figure 1a, middle). Then, 50 nm thick Ti was deposited as the source and drain electrodes using an electron beam evaporator (Figure 1a, right). Detailed information on the device fabrication is explained in the Methods section and the Supporting Information (Figure S1).

After we fabricated the MoS₂ flake devices, we deposited alkanethiol molecules on the fabricated devices. As explained previously, the thiol molecules tend to form a chemisorbed bond with MoS₂ at the sulfur vacancy positions. Figure 1b shows the schematic
images of a MoS2 FET device before and after the alkane thiol treatment. We placed MoS2 FET devices in the alkane thiol solution for 15 h to allow alkane thiol molecules to be adsorbed on the MoS2 surface. We characterized and compared the electrical properties of the fabricated MoS2 FET devices before and after the alkane thiol treatment to examine the effect of alkane thiol absorption on the MoS2 FET devices. Furthermore, SAM-modified molecules can form a self-assembled monolayer (SAM) on a Au surface. The electrical characterization was performed using a semiconductor parameter analyzer in a probe station. We also systematically characterized some of the transferred MoS2 flakes (not a FET device structure) on SiO2/Si substrates prior to and after the alkane thiol treatment process with Raman spectroscopy and photoluminescence. Note that in the study of MoS2 FET devices, we did not use Au as the electrode because alkane thiol molecules can form a self-assembled monolayer (SAM) on a Au surface. Furthermore, SAM-modified Au electrodes may change the Fermi level of the electrodes and thus cause unwanted source–drain current changes, which may complicate the analysis.

We first measured the basic electrical characteristics of the MoS2 FET devices prior to the alkane thiol treatment. Figure 2a shows the transfer curve (source–drain current versus gate voltage, \( I_{DS} - V_G \)) of a MoS2 FET device measured at a fixed source–drain voltage \( V_{DS} = 0.5 \) V on a logarithmic scale for the source–drain current. The same transfer curve is plotted on the linear scale for the current in the inset of Figure 2a. Figure 2b displays the output curves (source–drain current versus gate voltage, \( I_{DS} - V_{DS} \)) of the device measured with gate voltages varying from 40 to \(-60 \) V with steps of 20 V. All of the electrical data were measured in a vacuum (\(\sim 10^{-9} \) Torr) to avoid unwanted effects from the ambient environment, such as those from water and oxygen. MoS2 FET devices may suffer from environmental effects.33,34 One thing to notice in Figure 2 is that there was no obvious off-state observed. This can be explained by thermally assisted tunneling through a thin Schottky barrier at the Ti/MoS2 contact.35 The Ti metal has a work function of \(-4.3 \) eV, and MoS2 has a work function in the range of \(4.6 - 4.9 \) eV. However, although the work function of Ti is smaller than that of MoS2, there is a Schottky barrier formed between the Ti and MoS2.39–41 When the Schottky barrier is low and its thickness is ultrathin as in the case of Ti/MoS2, the charges can transport via thermionic emission and thermally assisted tunneling conduction mechanisms.35 This is the reason for the absence of an obvious off-state in MoS2 with Ti contacts at room temperature.

We estimated the mobility using the following formula:

\[
\mu = \frac{dI_{DS}}{dV_G} \times \frac{W}{L} \times \frac{C_{SiO2}}{C_0},
\]

where \(W/C_0\) is the capacitance between the SiO2 channel and the p++ Si layer per unit area, where \(\varepsilon_r\) is the dielectric constant of SiO2 (~3.9), \(\varepsilon_0\) is the vacuum permittivity, and \(d\) is the thickness of the SiO2 layer (270 nm). In this study, we fabricated and characterized a total of 10 MoS2 FET devices that were prepared from mechanically exfoliated MoS2 flakes and electron beam lithography. The thickness of exfoliated MoS2 flakes was found to be in a range from 2.1 to 10.9 nm from AFM, which corresponds to a MoS2 layer number of 3–17 layers. The estimated mobility values of the MoS2 FET devices fabricated in this study were found to be in a range from 2.5 to 35.2 cm²/V s. Additionally, we calculated the carrier concentration of the MoS2 FETs using the formula \(n_0 = Q/e = C_G|V_G - V_{TH}|/e\), where \(C_G\) is the capacitance of the SiO2 dielectric layer, \(e = 1.6 \times 10^{-19}\), \(C\) is the elementary charge, and \(V_{TH}\) is the threshold voltage of the FET devices. The mobility and carrier concentrations were measured using the same condition of \(V_G = 20\) V and \(V_{DS} = 0.5\) V. We determined the \(V_{TH}\) values as the \(x\)-axis intercept from a linear fitting of the transfer curves. Then, the carrier concentrations of the MoS2 FET devices were found to be in a range from \(2.4 \times 10^{13}\) to \(7.1 \times 10^{12}\) cm².

Detailed electrical parameters of the MoS2 FET devices characterized in this study are summarized in the Supporting Information (Table S1).

After electrical characterization of the MoS2 FET devices, we deposited hexadecanethiol (HS(CH₂)₁₅CH₃) on the MoS2 FET devices. For this purpose, we dipped the MoS2 FET devices in 5 mM hexadecanethiol in ethanol solution for 15 h in a N₂-filled glovebox. Then, we rinsed the devices with ethanol and measured the electrical properties of the hexadecanethiol-treated MoS2 FET devices. For this purpose, we dipped the MoS2 FET devices in 5 mM hexadecanethiol in ethanol solution for 15 h in a N₂-filled glovebox. Then, we rinsed the devices with ethanol and measured the electrical properties of the hexadecanethiol-treated MoS2 FET devices. For this purpose, we dipped the MoS2 FET devices in 5 mM hexadecanethiol in ethanol solution for 15 h in a N₂-filled glovebox. Then, we rinsed the devices with ethanol and measured the electrical properties of the hexadecanethiol-treated MoS2 FET devices.
devices, again under vacuum conditions. Figure 3a shows the transfer characteristic curves on a logarithmic scale for a MoS2 FET device. The data represented with filled and open circular symbols are the transfer curves measured before (labeled “Pristine”) and after the hexadecanethiol treatment, respectively. The inset of Figure 3a is the transfer characteristic curves on a linear current scale. The source–drain current level dramatically decreased by ~45%, from 0.58 μA (prior to the molecular treatment) to 0.32 μA (after the molecular treatment) measured at $V_G = 20 \text{ V}$ and $V_{DS} = 0.5 \text{ V}$. The current decrease can be observed in the output characteristic curves, as shown in Figure 3b. This phenomenon can be more clearly observed in contour plots of the current. Figure 3c displays the contour plots of the source–drain current as a function of $V_G$ and $V_{DS}$ for the MoS2 FET device that were obtained from the transfer characteristics curves measured for $V_{DS}$ in the range of 0.1 to 1 V and $V_G$ in the range of −40 to 40 V before and after the hexadecanethiol treatment. Here, one can clearly notice that the channel current in the device decreased after the molecular treatment.

The observation of the current decrease phenomenon in MoS2 FETs after the alkanethiol treatment can be explained in the following manner. Thiol molecules have a sulfur atom at the end group, and the sulfur-containing groups have a tendency to form covalent bonds with unsaturated Mo edges of vacancy defects on the surface of MoS2.24–26 In the vacancy defect sites there are free electrons in unsaturated Mo atoms that do not belong to any chemical bond, and these electrons can behave as charge carriers. However, after the thiol molecule treatment, the thiol molecules are chemically absorbed at the sulfur vacancy sites on the surface of MoS2, which decreases the number of free electrons in MoS2. Also, note that the adsorbed alkanethiol molecules or possible solution residue may behave as defects such as scattering centers, which can also cause additional effects such as the current decrease after the molecule treatment (see Figure S5 in the Supporting Information). The density of the sulfur vacancy has been estimated to be on the order of $10^{13} \text{ cm}^{-2}$ from aberration-corrected transmission electron microscopy (TEM) images.22 It is desired to estimate the percentage of sulfur vacancies that are occupied by alkanethiol molecules after the molecule treatment using atomic resolution TEM or other analyses, which is unfortunately beyond the scope of our study.

We consistently observed a similar current decrease phenomena with other MoS2 FET devices in response to the alkanethiol treatment, and the current contour plots for other MoS2 FET devices before and after the treatments are provided in the Supporting Information (Figures S2 and S3). To confirm that the reason for the current decrease in the devices is indeed due to the effect of the adsorbed alkanethiol molecules, we treated MoS2 FET devices in the same way that we processed alkanethiol-treated MoS2 FET devices but in an ethanol solution that did not contain any alkanethiol molecules. The electrical characterization results for the ethanol-treated devices are shown in the Supporting Information (Figure S5). In this case, the source–drain current of the ethanol-treated MoS2 FET device did not decrease significantly compared with the case prior to the ethanol treatment. Also notice that the decreased current of alkanethiol-treated MoS2 FETs with ethanol treatment.
recovered the channel current to the value of the pristine condition when we annealed the devices at elevated temperatures over 473 K (see Figure S7 in the Supporting Information).

The current reduction after the thiol molecule treatment can be due to the molecules acting as trap sites or the molecules passivating sulfur vacancies and decreasing the carrier concentration. To find out the dominant mechanism among these, we performed temperature-variable $I$–$V$ measurements for the devices before and after the alkanethiol molecule treatment. We first measured the $V_G$–$I_{DS}$ curves of the MoS$_2$ FET device in the temperature range from 80 to 320 K as shown in the left part of Figure 4a. Then, we treated alkanethiol molecules to the device and measured again; the results are shown in the right part of Figure 4a. From Figure 4a, we can notice that the current level of the device decreased and the threshold voltage shifted in the positive gate voltage direction while the sub-threshold swing (SS) value did not change significantly.

Figure 4b shows the carrier concentration (black symbols) and threshold voltage (blue symbols) of the device before and after the molecule treatment. Filled and empty square symbols in this figure represent the data that were measured before and after the molecule treatment, respectively. The carrier concentration was estimated at a $V_G$ of 20 V. We can see that the carrier concentration dramatically decreased and the threshold voltage dramatically shifted to the positive gate voltage direction after the molecule treatment. We also estimated the mobility and SS value of the device, and the results are summarized in Figure 4c. We observed that there was no significant difference in SS values before and after the molecule treatment. The SS value is related with the number of trap sites. If the number of trap sites increases, the SS value would increase. However, the SS value did not change significantly after the molecule treatment, which means that the thiol molecules would not mainly act as trap sites; instead it is more likely that the molecules are passivating sulfur vacancies and decreasing the carrier concentration. In other words, although both the molecules acting as trap sites and the molecules passivating sulfur vacancies and decreasing the carrier concentration can be the reason for the source–drain current reduction, the passivating effect from absorbed alkanethiol molecules seems to be a more dominant effect of the current reduction phenomenon. Furthermore, the SS value did not vary significantly as the temperature was varied. This also supports our interpretation. Note that the mobility of the device decreased after the molecule treatment. This can be explained by a hopping transport model.$^{22}$ Electrons in the MoS$_2$ can transport through the sulfur vacancy sites by hopping. With this model, the average distance between the sulfur vacancy sites would increase after the molecule treatment by passivating sulfur vacancy sites of MoS$_2$. Therefore, it will make the hopping probability decrease and mobility

![Figure 4](http://pubs.acs.org/doi/abs/10.1021/acsnano.5b04400)
Figure 5. (a) Optical image of a MoS2 flake that was used for Raman and PL studies. (b) Raman spectra measured from a circled region marked in (a) before and after the hexadecanethiol treatment. (c) Raman mapping image of the E1_g mode and A1_g mode before (left) and after (right) the hexadecanethiol treatment. We added dotted lines to indicate the MoS2 flakes in this figure.

decrease as well. Note that if the behavior of the Ti–MoS2 contact were changed after the molecule treatment, it would change the electrical properties of the devices. However, the contact effect cannot be the dominant reason for our observation. For example, we calculated the effective barrier height with the following formula for a 2D transport channel: $\ln(C_0/T^{1/2}) = -(e/kT)\phi_B + \text{const.}$ With this calculation, the effective barrier height was estimated to be changed by $\sim0.03$ meV after the molecule treatment (at $V_G = 40$ V), which indicates that the contact effect would not be significant in our study. Also note that the characteristics of contacts between MoS2 and the Ti electrode are not determined by just comparing Fermi levels of Ti and MoS2. The sulfur vacancy causes the $E_F$ of MoS2 to increase, and this result leads to a narrow Schottky barrier for the Ti/MoS2 contact with a sulfur vacancy. In our case, we treated alkanethiol molecules after the device fabrication. Therefore, the Ti/MoS2 contact region was already covered by Ti and the alkanethiol molecules were absorbed on the channel only, but not on the Ti/MoS2 contact region. Besides, the alkanethiol molecules cannot form a self-assembled monolayer on the Ti surface, so molecule treatment does not change the electronic properties of Ti. Therefore, the contact behavior would not be changed before and after the molecule treatment.

If a MoS2 surface is covered with molecules, then the vibration characteristics of a MoS2 film will be altered. Because Raman spectroscopy has been used as a powerful tool in studying two-dimensional materials, we measured and compared the Raman spectrum of a MoS2 flake prior to and after alkanethiol treatment under the same conditions. We used a Raman system with a $\sim1$ mW, 532 nm wavelength laser. With the Raman spectroscopic study, one can find two characteristic normal modes of vibration in MoS2, an E1g mode and an A1g mode. The E1g peak in the Raman spectrum is the result of in-plane vibrations of Mo and S atoms in opposite directions, and the A1g mode is associated with the S atoms’ out-of-plane vibration in the opposite direction. Figure 5a shows the optical image of a MoS2 flake. We can approximately determine the thickness of the MoS2 flake from the contrast of the optical image. The black-circled region in Figure 5a is a single-layer MoS2 flake piece. Figure 5b shows the Raman spectra of a single-layer MoS2 flake before and after hexadecanethiol treatment. The black and red curves in Figure 5b were measured before and after the hexadecanethiol treatment, respectively. In the case of pristine MoS2 flakes, i.e., MoS2 flakes prior to the hexadecanethiol treatment, E1g and A1g modes were observed at 383.0 and 402.3 cm$^{-1}$, respectively, which suggests that the circled region is indeed a single-layer MoS2 flake (the difference of the E1g and A1g peak positions is 19.3 cm$^{-1}$). An important finding is that both E1g and A1g modes shifted to a higher wavenumber (blue-shifted). The E1g mode blue-shifted from 383.0 cm$^{-1}$ to 387.6 cm$^{-1}$ and the A1g mode blue-shifted from 402.3 cm$^{-1}$ to 406.9 cm$^{-1}$. The blue-shift of the E1g and A1g modes can be explained by the molecule adsorption. The chemically absorbed alkanethiol molecules on the MoS2 surfaces slightly suppress atomic vibrations and lead to a higher force constant of vibration, causing the wavenumber blue-shift. Figure 5c displays the Raman spectra mapping around the peak position of the E1g and A1g modes. In this figure, we added dotted lines to indicate the MoS2 flakes. After the alkanethiol treatment, the peak positions for both the E1g and A1g modes in every part of the MoS2 flakes shifted in the direction of higher wavenumbers. We also investigated the effect of another
alkanethiol molecule, octanethiol (HS(CH_2)_7CH_3), on MoS_2 by comparing the Raman spectra mapping images of MoS_2 flakes before and after treatment with octanethiol. The results demonstrated that a blue-shift in the Raman data was consistently observed in this case as well (see Figure S9 in the Supporting Information), which suggests that the changed effect is due to the sulfur-containing thiol molecules. Note that the Raman spectra of the MoS_2 flakes did not change noticeably when they were treated with only ethanol solution that did not contain alkanethiol molecules. Furthermore, when we continued to deposit alkanethiols on the MoS_2 flakes that had been treated with ethanol, we consistently observed the blue-shift phenomenon in the Raman spectra (see Figure S9 in the Supporting Information). All these observations suggest that the alkanethiol molecules are the main reason for the blue-shift in the Raman data of the MoS_2 flakes and for the changes in the electrical parameters in the MoS_2 FETs.

In addition to Raman spectroscopy, we also measured the photoluminescence (PL) spectra of MoS_2 before and after the hexadecanethiol treatment. Notice that MoS_2 can be affected by the incident laser’s polarization of PL, known as a valley polarization phenomenon in MoS_2, and we did not use any polarization filter in order to prevent unwanted effects from the valley polarization. Figure 6a shows the PL mapping image of pristine MoS_2 flakes (left image) and hexadecanethiol-treated MoS_2 flakes (right image). Figure 6b displays the PL spectra that were acquired from the circled regions shown in Figure 6a. Generally, two resonance peaks can be observed in the PL spectra of MoS_2 flakes at ~625 and ~670 nm, which are due to the spin–orbital splitting of the valence band and direct excitonic transitions in MoS_2, respectively. We observed that with the hexadecanethiol treatment the PL peaks shifted slightly from 621 nm to 618 nm and from 673 nm to 668 nm and that the intensity of the PL peak decreased noticeably (Figure 6b). Moreover, the PL peak signals from the interband transition in the bulk MoS_2 flake region (marked with A) disappeared, and those in the multilayer MoS_2 flake region (marked with B) shifted from a yellow to a green color, i.e., in the smaller wavelength direction (Figure 6a), which indicates that the PL peaks shifted in a high-energy direction. This phenomenon can be explained as follows: generally the PL peak depends on the energy band structure of materials. In MoS_2, a sulfur vacancy provides an electron donor level within the band gap of MoS_2. Now, when we treat the MoS_2 with alkanethiol molecules, the number of donor levels in the band gap of MoS_2 decreases by passivating the sulfur vacancy sites of MoS_2 with the alkanethiol molecules. As a result, the intensity of the PL spectrum decreases and the peak position shifts slightly in the high-energy direction, and note that because the PL peak shift is slight, it can be considered that the band gap of MoS_2 was not changed noticeably by the alkanethiol molecule treatment. As a comparison experiment, we measured the PL spectra on MoS_2 flakes that were treated with ethanol solution without alkanethiol molecules. The result was that the PL spectra of the ethanol-treated MoS_2 flakes did not change noticeably (see Figure S10 in the Supporting Information). Additionally, to further verify chemisorption of alkanethiol molecules on the surface of MoS_2, we measured the binding energy of MoS_2 prior to and after the hexadecanethiol molecule treatment using an X-ray photoelectron spectroscopy (XPS) system. The result was that the XPS characteristic peaks’ positions of the MoS_2 shifted after the alkanethiol molecule treatment, which indicates that the chemical environment of the MoS_2 was indeed changed (see Figure S8 in the Supporting Information).

As we discussed above, alkanethiol molecules can be chemically absorbed at the sulfur vacancy sites on the surface of MoS_2, and this is the reason for the current decrease, the threshold voltage shift, the Raman peak shift, and the changes in PL spectra with the treatment with thiol molecules. The number of sulfur vacancy sites depends on the surface area of the MoS_2 channel. Thus, the effect of alkanethiol molecules depends on the surface area of the MoS_2 channel. Additionally, this effect depends on the thickness of the MoS_2 flakes because MoS_2 is a two-dimensional layered material and the height is a major factor in determining the surface to volume ratio of the MoS_2 layer. Figure 7a displays the current difference versus height data plot. We measured the channel current for...
all the MoS₂ FET devices that we fabricated and calculated the current difference as \( \frac{I_{\text{Pristine}} - I_{\text{After}}}{I_{\text{Pristine}}} \). Here, \( I_{\text{Pristine}} \) and \( I_{\text{After}} \) are the current levels of the devices that were measured at \( V_G = 20 \) V and \( V_{DS} = 0.5 \) V prior to and after the alkanethiol treatment. For this study, we fabricated a total of 10 MoS₂ FET devices that were prepared from mechanically exfoliated MoS₂ flakes, of which the thickness varied from 2 to 11 nm. As can be observed in the plot of Figure 7a, the current difference is proportional to the inverse of the thickness of the MoS₂ channel. The blue dashed curve in this plot was added to show this dependence. Figure 7b displays the plot of the current difference versus the surface area to volume ratio. We calculated the values of surface area to volume ratio as \( \frac{2hl + w}{hlw} \), where \( h \) is the thickness of the MoS₂ channel, \( w \) is the channel width, and \( l \) is the channel length. As shown in Figure 7b, the current difference of the MoS₂ FETs depended on the MoS₂ channel's surface area to volume ratio. The results in Figure 6 show that the effect of the alkanethiol adsorption to the MoS₂ surface on the channel current of MoS₂ FET decreases as the thickness of the MoS₂ channel increases (i.e., the surface area to volume decreases). We also calculated the carrier concentration difference and mobility difference of the characterized MoS₂ FET devices, and the results are provided in the Supporting Information (Figure S6).

We now explain the effect of alkanethiol molecule adsorption on the MoS₂ surface using the energy band diagrams as shown in Figure 8. Figure 8a and b show the energy band diagram before and after the alkanethiol adsorption. The Ti metal as the source—drain electrode has a work function of \( \sim 4.3 \) eV, and MoS₂ has a work function in the range 4.6-4.9 eV. However, although the work function of Ti is smaller than that of MoS₂, there is a Schottky barrier formed between the Ti and MoS₂.\(^ {39,41} \) Figure 8b shows the energy band diagram after the alkanethiol molecule treatment. When the MoS₂ devices are treated with alkanethiol molecules, the alkanethiol molecules that are chemically adsorbed at the surface of MoS₂ can capture the electrons of unsaturated Mo in MoS₂ and deplete the MoS₂ channel. Thus, alkanethiol molecules act as an energy barrier, resulting in the decrease of the channel current (Figure 3).

CONCLUSION

In summary, we fabricated MoS₂ FETs and measured their physical properties before and after alkanethiol molecule treatment to investigate the effect of passivating sulfur vacancy on the surface of MoS₂. After treatment with alkanethiol molecules, we observed that the source—drain current of the MoS₂ FETs decreased dramatically. In addition, the Raman spectrum peaks...
(E1,2g and A1g) of the MoS2 flakes exhibited a blue-shift, and the PL peaks disappeared or slightly shifted after the alkane thiol treatment. From the temperature-variable electrical characterization, the changes in physical and electrical properties of MoS2 flakes and MoS2 FET devices are a result of the alkane thiol molecules capturing the electrons in MoS2 by passivating sulfur vacancy sites (unsaturated Mo) on the MoS2 surface. Our study may foster a way of tailoring the electrical and optical properties of MoS2 by sulfur vacancy passivation using sulfur-containing molecules.

**METHODS**

The MoS2 flakes used in this study were exfoliated using the micromechanical exfoliation method from a bulk MoS2 crystal purchased from SPI Supplies, USA. Then, the exfoliated MoS2 flakes were transferred from 3M Scotch tape to SiO2 on a heavily doped p+ Si wafer (resistivity ~5 x 10^{-7} Ω cm), which can be used as a back gate. After finding the location of a multilayer MoS2 flake using an optical microscope, the MoS2 flakes’ height was measured with an NX 10 AFM system (Park Systems). To make patterns of electrodes, we spin-coated methyl methacrylate (MMA) (8.5%) and MMA (9% concentration in ethyl lactate) as a base layer and poly(methyl methacrylate) (PMMA) 950 K (5% concentration in anisole) as electron resist at 4000 rpm. After the spin-coating of each layer, the sample was baked at 180 °C for 90 s. The electrodes of MoS2 FETs were patterned using an electron beam lithography system (JSM-6510, JEOL) with a 30 kV exposure. The pattern development was performed with an methyl isobutyl ketone/isopropyl alcohol (1:3) solution with a development time of 50 s. The electrical characteristics of the device were measured using a semiconductor parameter analyzer (Keithley 4200-SCS) in a probe station (JANIS model ST-500). Also, the Raman and PL characteristics of the MoS2 flakes were measured using a Raman system (CRM 200, WiTec, Germany).

**Conflict of Interest:** The authors declare no competing financial interest.

**Supporting Information Available:** The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b04400. The device fabrication, characteristic parameters of MoS2 FET devices, contour plots of the source–drain currents for other MoS2 FET devices, electrical data of a MoS2 FET with ethanol treatment, static data of mobility difference and carrier concentration difference, electrical data of alkane thiol-treated MoS2 FET at elevated temperatures, XPS data of MoS2 flakes before and after alkane thiol treatment, Raman and PL data with ethanol and octanethiol molecules, as well as supplementary figures and a table (PDF).

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