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# Detection of Chemical Change of Adsorbates using Electrical Property of MoS2 Field-Effect Transistor

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博士論文

# Detection of Chemical Change of Adsorbates using Electrical Property of $MoS_2$ Field Effect Transistor

**(2 硫化モリブデンを用いた電界トランジスタ電気特性による吸着種の化学状態変化検知)**

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令和３年

**Table of Content**



## Chapter 1 INTRODUCTION

Realizing the importance of $MoS_2$ in different sensor applications[1], this PhD research emphasizes on the fabrication of $MoS_2$ based field effect transistors and their application for chemical sensing through electrical property measurement.

## Chapter 2 MATERIALS, CHARACTERIZATION TECHNIQUES AND CHARGE TRANSFER MECHANISM

Semiconductor Materials used for the $MoS_2$-FET fabrication has been introduce in this section. All the nanofabrication instruments and surface characterization techniques have been described in this chapter. Finally, surface charge transfer mechanism is given in the later part of this chapter.

## Chapter 3 *IN SITU* STUDY OF SENSOR BEHAVIOR OF $MOS_2$ FIELD EFFECT TRANSISTOR FOR METHYL ORANGE MOLECULE IN ULTRA HIGH VACUUM CONDITION

Here, I investigated the sensor behavior of the $MoS_2$-FET device with the deposition of Methyl Orange (MO) which is widely used as a chemical probe. I detected the shift of the $I_dV_g$ curve of the $MoS_2$-FET device with the increase of the coverage (□*)* of the MO molecule in *in-situ* chamber[2], shown in Fig. 1. I show that the system can detect the adsorption of MO far less than monolayer and the phase change from the first layer to the second layer growth, which is realized by the benefit of the *in situ* UHV experimental condition.

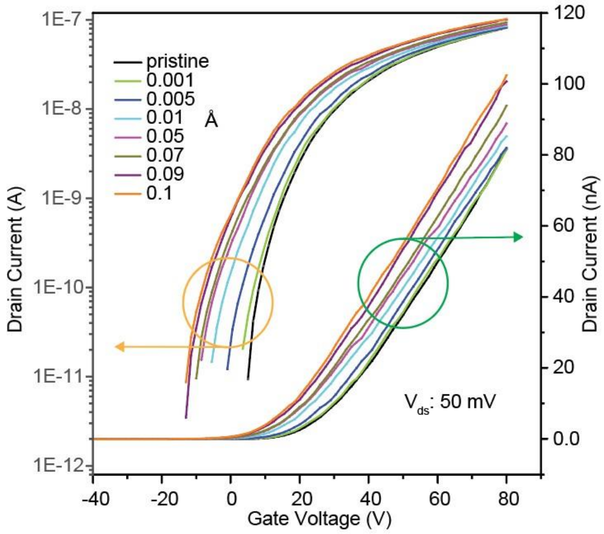


**Fig. 1 $I_d$-$V_g$ plot as a function of the MO coverage using four-layer device.**

**Chapter 4 MICROFLUIDIC TANK ASSISTED NICOTINE SENSING PROPERTY OF FIELD EFFECT TRANSISTOR COMPOSED OF ATOMICALLY THIN $MoS_2$ CHANNEL**

I investigated the sensor behavior of the $MoS_2$ FET, the channel of which is composed of four $MoS_2$ atomic layers focusing on the interaction with the solution containing target molecules. For that purpose, I made a newly designed device in which the mask covers the electrodes of the source and the drain to make the solution contact only with the channel. In addition, the micro-fluid tank was fabricated on the top of the channel to control the flow of the solution. Using the mask and tank, we performed the drop-cast process in the μm scale to transfer the nicotine molecule onto the channel (Fig. 2a). I measured the $I_d$-$V_g$ curve of the FET with the nicotine transfer to the channel and found that the threshold voltage shifted to the negative $V_g$ direction (Fig. 2b). This behavior of $V_{th}$ indicates that electrons are transferred from nicotine molecules to the $MoS_2$ channel[2, 3], which was further confirmed by analyzing the Xray photoemission spectroscopy and Raman spectroscopy together with the DFT calculation.

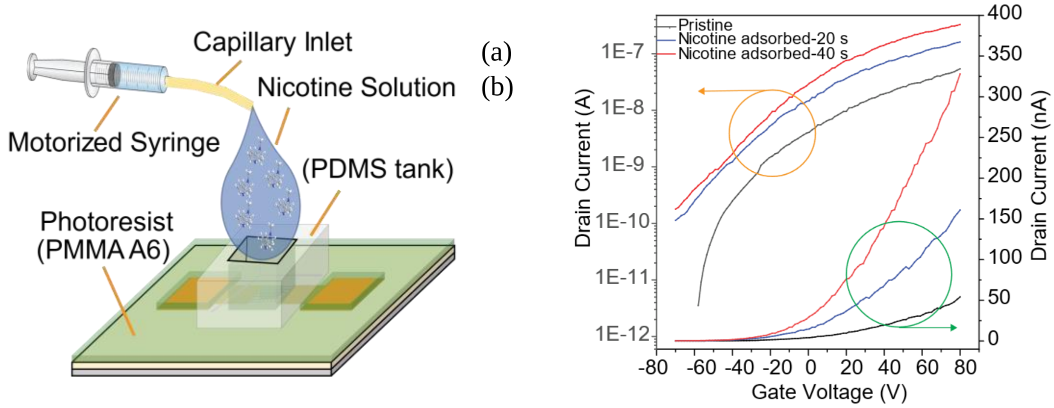


**Fig. 2 (a) Illustration of the syringe pump assisted nicotine solution passing into the tank; (b) $I_d$-$V_g$ current as a function of the back-gate voltage ($V_g$) before and after the nicotine functionalization.**

**Chapter 5 OBSERVATION OF THERMALLY REVERSIBLE ISOMERIZATION OF NITRO-SPIROPYRAN ON $MoS_2$ SURFACE BY $MoS_2$ FIELD EFFECT TRANSISTOR**

I observe the light and thermal induced structural switching of spiropyran (1′,3′-Dihydro1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-indole]) molecule through electrical property measurement by $MoS_2$-FET. UV light was irradiated on spiropyran (SP) to convert its isomer merocyanine (MC)[4], shown in Fig. 3. To reverse back to the former structure, I heat the device by external heater. Isomerization process was monitored through the measurement of $I_d$-$V_g$ of the $MoS_2$-FET device and quantitative observation was assumed form the threshold voltage determination.

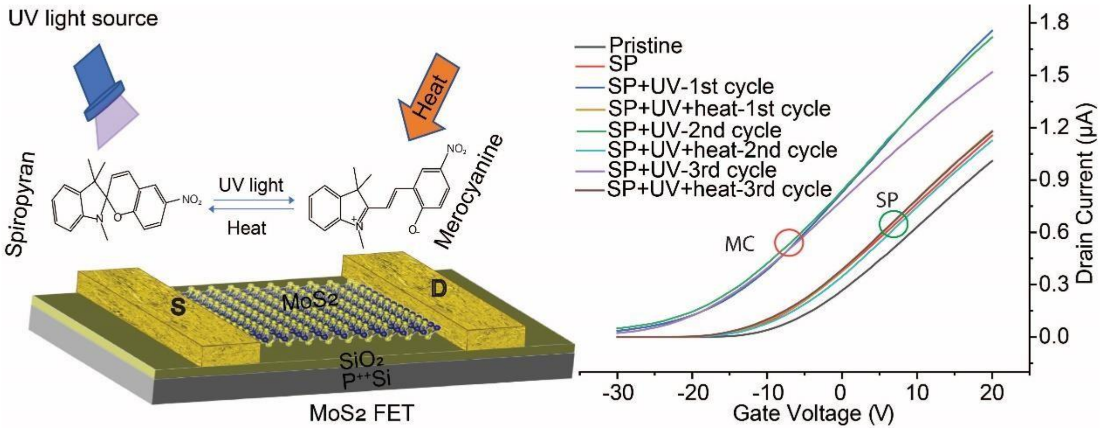


**Fig. 3 (a) Illustration of $MoS_2$-FET and SP/MC conversion upon UV/Heat application. (b) Drain current ($I_d$) as a function of gate voltage ($V_g$) for the spiropyran deposited surface after heat treatment.**

## Chapter 6 SURFACE CHARGE TRANSFER DOPING OF $MOS_2$ BY MELAMINE INVESTIGATED BY THE BACK GATED $MOS_2$ FIELD EFFECT TRANSISTORS

I report a method to tailor of the transfer characteristics of multilayer $MoS_2$-FET by using the melamine molecule through surface charge doping. Melamine solution was made using NMP as a solvent. The electrical properties were measured by Keithley 2634B in open air. The electrical properties of the back gated multilayer $MoS_2$ FETs were increased after doping at room temperature in open air (shown in Fig. 4a). The charge carrier density of multilayer $MoS_2$ was increased doubled after melamine doping. The left shift of threshold voltage after doping process revealed that melamine molecule imposes n-doping[2, 3] to the multilayer $MoS_2$. After doping process, the trend of downward shifting of $E_{2g}$ and $A_{1g}$ peaks in the Raman spectrum indicates increasing electron concentration for the n-type doping system, shown in Fig. 4b. The illustration of charge transfer is shown in Fig. 4c.

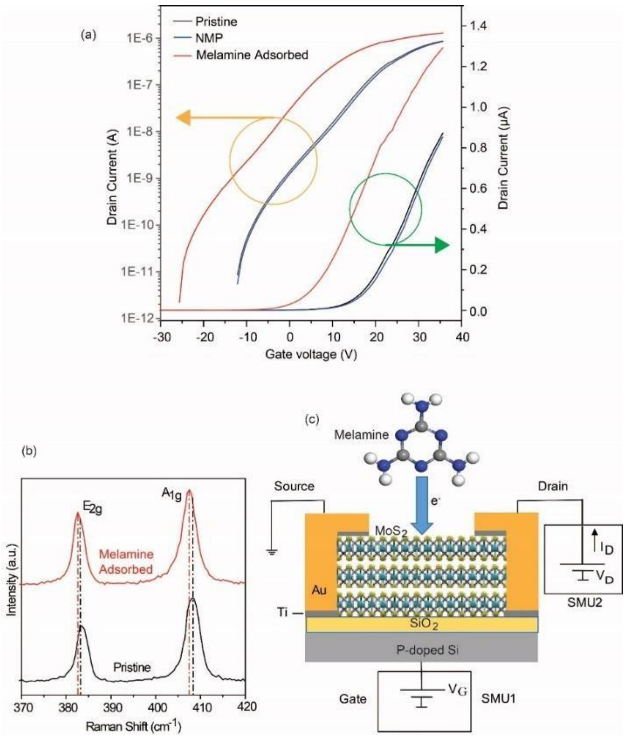


**Fig. 4 Transfer characteristics of the multilayer $MoS_2$ FET before (black), in only NMP (blue) and after surface charge doping (red) at $V_{ds}$ = 50 mV, (b) Raman spectra of the multilayer $MoS_2$ before (black) and after melamine doping process (red), (c) Surface charge transfer between melamine and $MoS_2$-FET.**

## Chapter 7 SURFACE CHARGE TRANSFER DOPING OF MULTILAYER $MOS_2$ BY CAFFEINE

I report that chemical incorporation of mechanically exfoliated multilayer molybdenum disulfide ($MoS_2$) by caffeine can tailor the electrical properties of the $MoS_2$-field effect transistors. Device was totally dipped into the caffeine solution for 15 seconds, dried by $N_2$ gun and measured the electrical properties. Transfer characteristics and Raman spectroscopy study acknowledged that caffeine results n-doping[3] in the multilayer $MoS_2$, shown in Fig. 5. Threshold voltage shifted left side after the doping process and the electrical property increased without any destruction of the device at room temperature in open air. After functionalization of caffeine molecules, the trend of downward peak shifting of $E_{2g}$ and $A_{1g}$ peaks in the Raman spectrum indicates the increase of electron concentration on the $MoS_2$ surface.

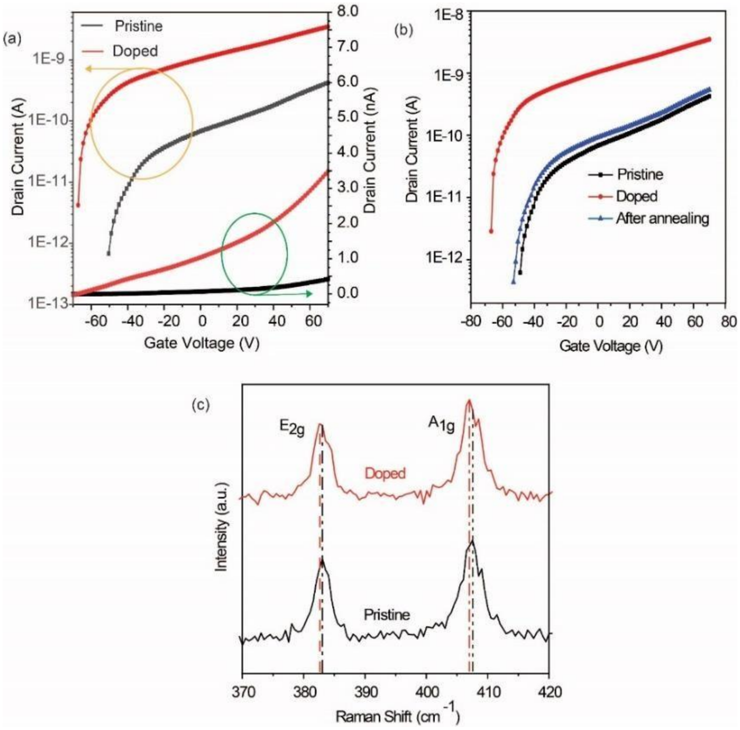


**Fig. 5 (a) Transfer characteristics as a function of back gate voltage ($V_g$) pristine (black), doped by caffeine (red), (b) Transfer characteristics as a function of back gate voltage ($V_g$) pristine (black), doped by caffeine (red), after annealing (blue), (c) Raman shift with 532 nm laser source at room temperature before and after caffeine doping.**

## Chapter 8 PRESSURE DEPENDENT P-DOPING AND N-DOPING BEHAVIOR BY $O_2$ DETECTED BY FEW LAYERS $MOS_2$-FIELD EFFECT TRANSISTORS

I show the sequential $O_2$ dosing from $E^{-5}$ Pa to 1 atm pressure on few layers $MoS_2$-FET in an in-*situ* measurement chamber. Fig. 6a shows the illustration of $MoS_2$-FET device. FET property both in air and UHV has been shown in Fig. 6b. With a very low pressure (e.g., $E^{-5}$ Pa, $O_2$ donates electron to the $MoS_2$ thus increases the $I_d$ and up to 0.1 Pa, this phenomenon retains, seen in Fig. 6c. After additional adding of $O_2$ threshold voltage started increasing and $I_d$ decreases, shown in Fig. 6d. The sensitivity of the device featuring minimum detection level of $1 \times 10^{-8}$ % of $O_2$ which is very competitive with the recent $O_2$ sensor papers. The shift of threshold voltage to the positive gate voltage after $O_2$ dosing indicates that electron is transferred from $MoS_2$ to $O_2$. We observe that certain amount of $O_2$ can mask the n-type doping behavior and starts p-type doping to the $MoS_2$ channel, consistent with the previous results[5, 6].

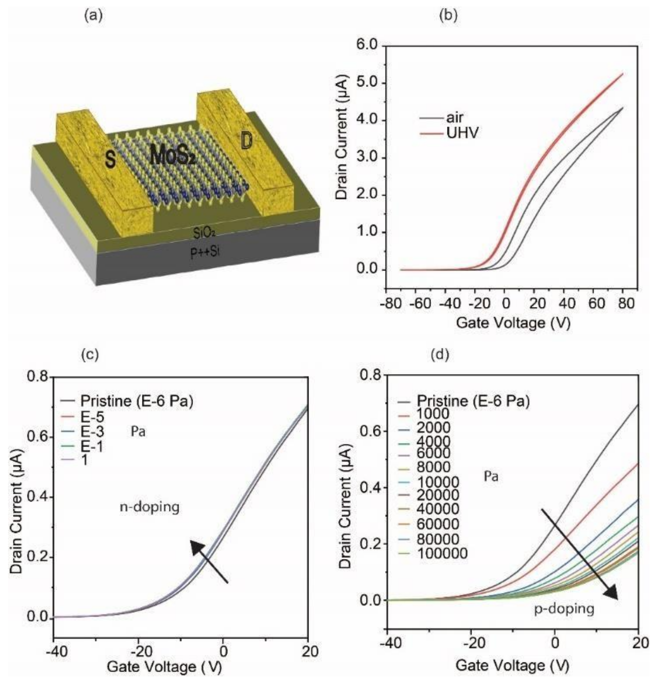


**Fig. 6 (a) Illustration of $MoS_2$-FET; (b) Transfer characteristics in air and UHV; (c) $I_d$-$V_g$ with different $O_2$ dosing with low pressure showing n-doping. (d) $I_d$-$V_g$ with different $O_2$ dosing showing p-doping.**

## Chapter 9 *IN-SITU* ADSORPTION BEHAVIOR OF METHYL RED ON $MOS_2$ AND ITS EFFECT ON THE TRANSFER CHARACTERISTICS OF MONOLAYERED $MOS_2$FIELD EFFECT TRANSISTORS

I investigate the adsorption behavior of Methyl Red (MR) and its effect on the electrical properties of the $MoS_2$ field effect transistor (FET) in an *in situ* experimental system in which the molecule deposition and the surface- and electrical-characterization of the $MoS_2$ FET are executed in a single ultra-high vacuum chamber, shown in our previous report[7]. Illustration of charge transfer is shown in Fig. 7a. The $V_{th}$ shifts towards the negative direction and the initial change with □ can be expressed with an exponential function of □, which can be accounted for with the Langmuir type adsorption of the molecule for the first layer and the charge transfer from the molecule to the substrate, shown in Fig. 7b.

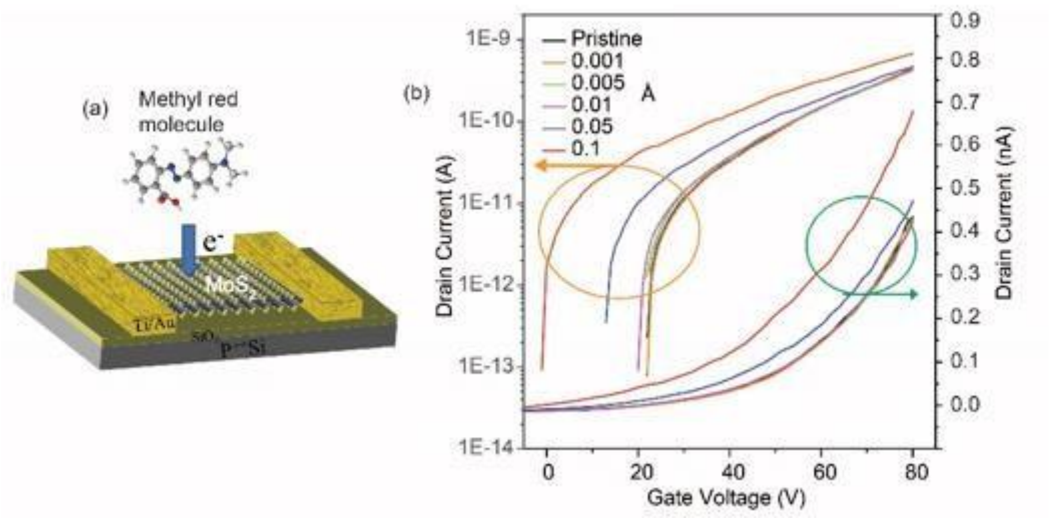


**Fig. 7 (a) Illustration of donation of electron form MR to substrate; (b) $I_d$-$V_g$ plot as a function of the MR coverage.**

## Chapter 10 GAS ENVIRONMENTAL AND PHOTO IRRADIATION EFFECT ON HYSTERESIS IN THE TRANSFER CHARACTERISTICS OF $MOS_2$ TRANSISTOR

I report the characteristic behavior of the hysteresis observed in the transfer characteristics of back-gated field-effect transistors with an exfoliated $MoS_2$ channel in various environment. We find that the hysteresis is strongly enhanced by temperature, environmental gas, or light irradiation[8-10]. Our measurements reveal characteristic behavior of the hysteresis in 1 atm oxygen environment, which I explain as oxygen molecule facilitated charge accepter on the $MoS_2$ surface, shown in Fig. 8a. The decrease in the current value in the ON state of the device may indicate that oxygen molecules are more effective charge acceptor than nitrogen molecules. I conclude that intrinsic defects in $MoS_2$, such as S vacancies, which result in effective adsorbates trapping, play an important role in the hysteresis behavior. Fig. 8b shows the hysteresis in $N_2$ environment. The hysteresis gap is lower than the $O_2$ environment is observed. This might be due to the $N_2$ is less reactive than the $O_2$.

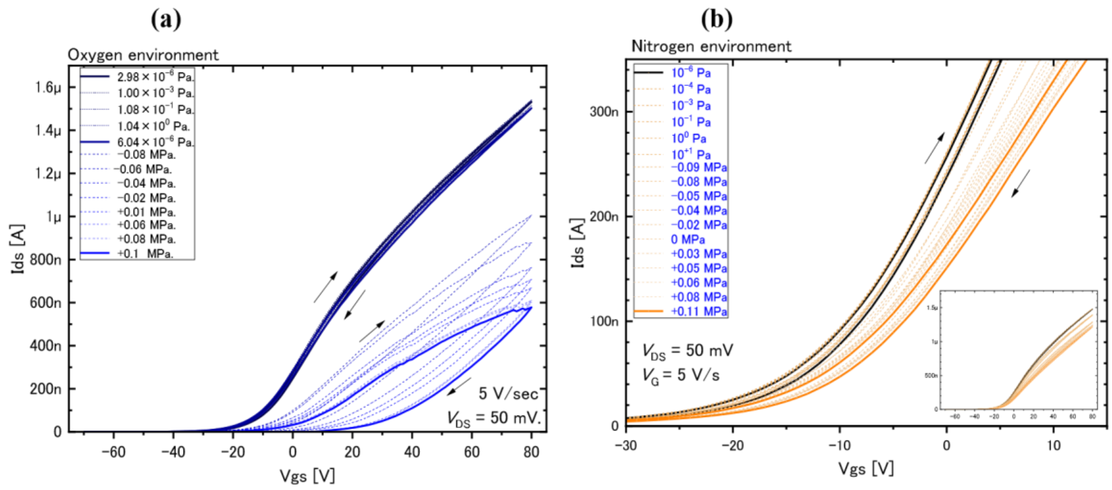


**Fig. 8 Environmental effect on hysteresis curve.; (a) Oxygen environment. (b) Nitrogen environment. Full range curve is shown in inset. In both cases, $V_{DS}$ set to 50 mV and $V_G$ sweep 5 V/sec. The sweep directions of $V_G$ are indicated by arrows.**

## Chapter 11 CONCLUSION REMARKS AND OUTLOOK

$MoS_2$-FET can be a good tool for the chemical sensing. However, my desire is to make biosensor operating in aqueous solution. The limitation is $MoS_2$ flakes are broken in solution when applying voltages. In our lab, to protect the $MoS_2$ flake being broken, $HfO_2$ or $TiO_2$ layer has been incorporated on the $MoS_2$ channel so far, but same problem remains. Still need to find the threshold thickness of other dielectric materials on the $MoS_2$ that helps to survive $MoS_2$ from being broken.

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