ELECTRONIC APPLICATION OF TWO DIMENSIONAL MATERIALS

by

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Dedicated to my Lord and Savior Jesus Christ To my supporting father and mother To beloved husband Yee Rui Koh

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ABSTRACT

Recent advances in atomically thin two-dimensional materials have led to various promising technologies such as nanoelectronics, sensing, energy storage, and optoelectronics applications. Graphene with sp2-bonded carbon atoms densely packed in a honeycomb crystal lattice has attracted tremendous interest with excellent electrical, optical, mechanical, and chemical properties. In this work, graphene's mechanical properties, chemical properties, and piezoelectric properties are explored as graphene is implemented in the automotive electrical distribution system. Graphene is useful in friction reduction, corrosion protection, and piezoelectric energy harvesting cell improvement. Besides graphene, transition metal dichalcogenides (TMDs), which are the metal atoms sandwiched between two chalcogen atoms, have also attracted much attention. Unlike graphene, many TMDs are semiconductors in nature and possess enormous potential to be used as a potential channel material in ultra-scaled field-effect transistors (FETs). In this work, chemical doping strategies are explored for the tunnel FETs applications using different metal phthalocyanines and polyethyleneimines as dopants. TMDs FETs can also be used as a selective NO₂ gas sensor with a polydimethylsiloxane filter and a highly sensitive photo-interfacial gated photodetector application.

1. GRAPHENE APPLICATIONS

1.1 Graphene

Graphene is a single layer of carbon atoms tightly packed in a honeycomb lattice structure with an in-plane covalent bond and weak interlayer van der Waal force (Figure 1.1). Out of four carbon atoms, three carbon atoms exhibit sp^2 hybridization. With the unique lattice structure, graphene has zero bandgap behaving like a metal. The mobility of charges can reach 25,000 cm²·V⁻¹·s⁻¹ at room temperature [1]–[3] and graphene has high thermal conductivity above 3000 WmK⁻¹ [4]–[6]. Graphene is also the most robust 2D material ever measured with Young's modulus of 1Tpa and intrinsic strength of 130 GPa, fracture strength (~125 GPa) [7], [8] and elastic tensile strain of 25%[9]–[11]. Graphene is chemically inert [12]–[15], impermeable to gases[15]–[17], and has excellent lubricity[18]–[20] with high transparency of 97.7%[21]. A lot of research has implemented graphene as transparent flexible electrodes, field-effect devices [22]–[24], corrosion barriers [15], and micro-and nanoelectromechanical systems [25] with the focus on mechanical, electrical, thermal, and chemical applications of graphene.



Figure 1.1. Structure of Graphene

In this study, we utilized different graphene properties for various automotive applications. Multilayer graphene can be an appropriate conductive solid and liquid lubricant due to the sheet-like structure, outstanding lubricity, and high electrical conductivity. Graphene-based liquid lubricant usually incorporates graphene as additives in ethanol, water, or oil [26]. Plasma-enhanced chemical vapor deposition (PECVD) grown graphene can serve as a solid lubricant to metal surfaces[27], [28]. Graphene can serve as a corrosion protective coating with excellent chemical inertness, great impermeability, high toughness, and hydrophobicity [29], [30]. Last, we can also

implement graphene filler in the energy harvester cell due to graphene's high mechanical strength, high electrical conductivity. The addition of graphene oxide flake can increase the piezoelectric effect by increasing the β -phase content of polymer composites cells.

1.2 PECVD Graphene Growth

Common ways to prepare graphene include chemical vapor deposition (CVD), mechanical exfoliation, epitaxial growth, and chemical reduction of graphene oxide. Typically, the CVD technique can be used to deposit graphene coatings on metals with the mixtures of gases Ar/ H₂/ CH₄ flowing through a quartz tube at deposition temperature 1000 °C [31]–[34]. Plasma enhanced chemical vapor deposition (PECVD) is a modified CVD process with remote plasma to assist dissociation of hydrocarbon precursors at relatively low temperatures [30], [34]–[36] (Figure 1.2). Via the PECVD method, good quality graphene can be grown on arbitrary substrates, such as metals [37], dielectrics [30], and semiconductors [35], in contrast to conventional CVD growth at much higher temperatures for single-layer Graphene on copper (Cu) and multi-layer Graphene on nickel (Ni) substrates [33]. Thus low-temperature PECVD can be utilized as a controllable graphene synthesis on a wide range of metal substrates.



Figure 1.2. Illustration of graphene growth using plasma-enhanced chemical vapor deposition. Plasma is introduced to break down precursors and accelerate the nucleation and growth at lower temperatures and on any arbitrary substrates.

1.2.1 Sample Preparation Before PECVD Graphene Growth

Samples Cleaning Process

To ensure chamber cleanliness and preserve graphene quality, a cleaning procedure would be applied to the substrates before putting them into the PECVD chamber. There are two kinds of samples to grow graphene on, thin-film samples and metal terminals. Samples are cleaned via sonication in the toluene /acetone /isopropanol alcohol, each in sequence for five minutes. After drying up with the air gun, the samples are put into the PECVD chamber. Graphene is grown on the terminals from 400°C to 750 °C using methane (CH4) or acetylene (C_2H_2) as precursor gas and argon as the carrier gas. Remotely ignited RF plasma (550 W) provides the energy needed to break methane molecules into carbon radicals that enabled rapid graphene deposition significantly reduced temperature compared with the conventional CVD method.

Chamber Cleaning Procedure Before and After Graphene Growth

Before and after the graphene growth, the chamber cleaning process needs to be run in the PECVD system. Critical parameters such as process time, furnace temperature, flow rate, chamber pressure, and RF power at each step of the procedure during the cleaning process are listed in Table 1.1.

	Time		Furnance	Flow rate	Pressure	RFPower
Seg	[Hour:Min:Soc]	Process Name	Temperature	[Ar: H2:CH4-High:CH4-Low]	[PT Vac 1000: 10]	[Setpoint: Reverse: Forward]
	[Trous in insec]		[oC]	[SLPM:SCCM:SCCM:SCCM]	[Torr]	[W]
0	00:00:02	Setup-Initial Conditions	1000	0:0:0:0	1000:10	0:0:0
1	00:00:30	Pumpdown Part 1 (65mTorr)	1000	5:100:200:20	1000:0.065	0:0:0
2	00:00:30	Cycle Ball Value	1000	5:100:200:20	1000:10	0:0:0
3	00:03:00	Pumpdown Part 2 (65mTorr)	1000	5:100:200:20	1000:0.065	0:0:0
4	00:01:00	Leak Back (50mTorr)	1000	0:0:0:0	1000:0.050	0:0:0
5	00:00:05	Check T	1000	0:0:0:0	1000:10	0:0:0
11	00:00:30	Start Flows	1000	25:0:0:0	1000:10	300:0:0
12	01:00:00	Air Plasma Clean	1000	25:0:0:0	1000:10	400:0:0
13	00:00:05	Turn off plamsa and increase temp & Pressure.	1000	0:0:0:0	1000:10	0:0:0
14	01:00:00	Bakeout	1000	0:0:0:0	1000:10	0:0:0
15	00:00:02	Evacuate	460	0:0:0:0	1000:10	0:0:0
16	00:02:00	Unload and evacuate	460	0:0:0:0	1000:10	0:0:0
17	00:00:05	Back to atm Pressure	460	5:0:0:0	1000:10	0:0:0
18	00:00:30	Pumpdown Part 1 (65mTorr)	460	5:100:200:20	1000:0.065	0:0:0
19	00:00:30	Cycle Ball Value	460	5:100:200:20	1000:10	0:0:0
20	00:03:00	Pumpdown Part 2 (65mTorr)	460	5:100:200:20	1000:0.065	0:0:0
21	00:01:00	Leak Back (50mTorr)	460	0:0:0:0	1000:0.050	0:0:0
22	00:00:30	Open valve	460	5:100:200:20	1000:0.065	0:0:0
23	00:00:30	close valve	460	5:100:200:20	1000:0.065	0:0:0
24	00:02:00	process pump off	460	5:100:200:20	1000:0.065	0:0:0
25	00:00:5	end of recipe	460	1:0:0:0	1000:10	0:0:0
40	00:10:00	abort due to alarm- safe state	0	1:0:0:0	1000:10	0:0:0

Table 1.1. PECVD chamber cleaning procedure

1.2.2 PECVD Graphene Growth Processes

High-Temperature Process using Methane as Precursor

The recipe for PECVD 750°C graphene growth using methane as a precursor is shown in Table 1.2. Critical parameters such as process time, furnace temperature, flow rate, chamber pressure, and RF power at each step of the procedure during the cleaning process are listed below. Critical parameters can be adjusted to fit the purpose to ensure the desired thickness and quality of graphene are grown on the target substrate. After high-temperature graphene growth, Raman analysis can be used to check if graphene growth is successful or not.

		01	0	1	0	1
Seg	Time [Hour:Min:Sec]	Process Name	Furnance Temperature	Flow rate [Ar: H2:CH4-High:CH4-Low]	Pressure [PT Vac 1000: 10]	RFPower [Setpoint: Reverse: Forward]
			[oC]	[SLPM:SCCM:SCCM]	[Torr]	[W]
0	00:00:02	Setup-Initial Conditions	780	1:0:0:0	1000:10	0:0:0
1	00:00:30	Pumpdown Part 1 (65mTorr)	780	5:100:200:20	1000:0.065	0:0:0
2	00:00:30	Cycle Ball Value	780	5:100:200:20	1000:10	0:0:0
3	00:03:00	Pumpdown Part 2 (65mTorr)	780	5:100:200:20	1000:0.065	0:0:0
4	00:01:00	Leak Back (50mTorr)	780	0:0:0:0	1000:0.050	0:0:0
5	00:00:05	Check T	780	0:0:0:0	1000:10	0:0:0
6	00:02:00	Push sample into Hot zone	780	0:0:0:0	1000:0.005	0:0:0
7	00:02:00	Stablelize temperature	765	0:0:0:0	1000:0.005	500:0:0
8	00:01:00	Introduce Ar and H2	760	0.1:05:0:10	1000:0.005	500:0:0
9	00:05:00	Start plasma for reduction	760	0.1:05:0:10	1000:0.005	500:0:0
10	00:03:00	Shut off Ar/H2	760	0.2:20:0:0	1000:0.005	500:0:0
11	00:20:00	Introduce CH4	760	0:0:0:10	1000:0.005	500:0:0
12	01:00:00	Growth AT 750C(500W plasma)	760	0:0:0:10	1000:10	500:0:0
13	00:30:00	Pull sample out from Hot zone	450	0.1:0:0:0	1000:10	0:0:0
14	00:00:05	Back to atm Pressure	450	0.1:0:0:0	1000:10	0:0:0
15	00:00:05	end of recipe	450	1:0:0:0	1000:10	0:0:0
40	00:10:00	abort due to alarm- safe state	0	1:0:0:0	1000:10	0:0:0

Table 1.2. PECVD 750°C graphene growth procedure using methane as the precursor

Low-Temperature Process using Acetylene as Precursor

The recipe for PECVD 450°C graphene growth using acetylene as a precursor are shown in Table 1.3. As same as mentioned in the session on high-temperature graphene growth, all the key parameters can be adjusted to ensure the desired thickness and quality of graphene on the target substrate. After low-temperature graphene growth, Raman analysis can be used to check if graphene growth is successful or not.

Seg	Time [Hour:Min:Sec]	Process Name	Furnance Temperature	Flow rate [Ar: H2:CH4-High:CH4-Low:C2H2]	Pressure [PT Vac 1000: 10]	RFPower [Setpoint: Reverse: Forward]
			[oC]	[SLPM:SCCM:SCCM:SCCM]	[Torr]	[W]
0	00:00:02	Setup-Initial Conditions	460	0:0:0:0:0	1000:10	0:0:0
1	00:00:30	Pumpdown Part 1 (65mTorr)	460	5:100:200:20:20	1000:0.065	0:0:0
2	00:00:30	Cycle Ball Value	460	5:100:200:20:2	1000:10	0:0:0
3	00:05:00	Pumpdown Part 2 (65mTorr)	460	5:100:200:20:2	1000:0.065	0:0:0
4	00:01:00	Leak Back (50mTorr)	460	0:0:0:0:0	1000:0.050	0:0:0
5	00:01:00	Check T	460	0:0:0:0:0	1000:10	0:0:0
6	00:02:00	Push sample into Hot zone	460	0:0:0:0:0	1000:0.005	0:0:0
7	00:02:00	Stablelize temperature	460	0:0:0:0:0	1000:0.005	0:0:0
8	00:00:05	Start C2H2(10 sccm)	460	0:0:0:0:10	1000:10	500:0:0
9	00:00:05	Start H2(3 sccm)	460	0:3:0:0:10	1000:10	500:0:0
10	01:00:00	Growth at 500W C2H2(10 sccm)	460	0:5:0:0:10	1000:10	500:0:0
11	00:30:00	Pull sample out from Hot zone	460	0.03:0:0:0:0	1000:10	0:0:0
12	00:00:05	Back to atm Pressure	450	0.5:0:0:0:0	1000:10	0:0:0
13	00:00:05	Back to atm Pressure	450	1:0:0:0:0	1000:10	0:0:0
14	00:00:05	Back to atm Pressure	450	2:0:0:0:0	1000:10	0:0:0
15	00:00:05	end of recipe	450	0:0:0:0:0	1000:10	0:0:0
40	00:10:00	abort due to alarm- safe state	0	0:0:0:0:0	1000:10	0:0:0

Table 1.3. PECVD 450°C graphene growth procedure using acetylene as the precursor

1.2.3 Sample Characterizations After PECVD Graphene Growth

The usual methods to characterize graphene include SEM, TEM, AFM, Raman spectroscopy, etc. SEM and the optical microscope can be used for checking the uniformity coverage of graphene on the substrate. AFM is an effective way for the characterization of graphene thickness. TEM can observe the morphological feature of Graphene and count the number of graphene layers accurately. Raman spectroscopy can provide a quick and effective way for graphene structure and quality [38].

Raman Characterization

Raman spectroscopy is a typical method to characterize graphene quality as we grow inhouse using the PECVD method. Raman Spectroscopy uses a 532 nm excitation laser as the laser source. The peaks at D band 1350 cm⁻¹, G band 1580 cm⁻¹, and 2D band 2700 cm⁻¹ are presented in the graphene samples spectrum[39] (Figure 1.3). The higher the D band, the Graphene exists more defects and vice versa—the lower intensity of the D peak, the fewer defects in the graphene layer. The G band is due to the sp2-bonded carbon atoms in a two-dimensional hexagonal graphite layer. The higher the 2D band indicates a lower layer number of Graphene. Raman spectroscopy can clearly distinguish a single layer from a bilayer or a few graphene layers with the relative position of 2D peaks and the intensity ratio of the 2D band and G band.



Figure 1.3. Typical Raman spectrum of PECVD grown Graphene on Cu/SiO₂/Si substrate

The PECVD growth recipes and temperatures are chosen based on the samples' melting point. Figure 1.4 shows the Raman analysis of graphene grown on Au terminals and Ag terminals at the different growth temperatures. As the temperature increases, 2D peak intensity around 2730 cm⁻¹ increases, indicating higher growth temperature can yield better graphene film quality.



Figure 1.4. PECVD graphene quality is characterized by Raman analysis. Higher 2D peak intensity around 2730 cm⁻¹ indicates better graphene quality as the growth temperature increases on (a) Au and (b) Ag terminals.

Atomic Force Microscopy (AFM)

The thickness of the PECVD grown graphene is confirmed with AFM. The samples used for AFM characterization are thin film samples with the desire metal surface deposited on SiO₂ substrate. After graphene is grown on the target thin film substrate, PMMA is spin-coated and baked at 180 °C on the graphene/metal/SiO₂ stack before chemically etched away the metal layer. After the wet etching, the PMMA/graphene stack is transferred to the SiO₂ substrate and gets dried in the air overnight. When the sample is completely dry, PMMA coating is removed by soaking the sample in acetone at 70 °C for 4 hours and rinsing with clean acetone and isopropanol alcohol. Then the sample is blow-dried by an air gun. Graphene thickness is characterized using atomic force microscopy (AFM) directly on the SiO₂ substrate. The same thickness is expected on metal terminals since both types of samples go through the same graphene deposition process and conditions. One-hour graphene growth yield to ~3 nm confirmed using atomic force microscopy (AFM) on the thin-film sample (Figure 1.5).



Figure 1.5. AFM thickness profile of graphene on SiO₂ substrate after etch and transfer. Graphene growth used 450°C PECVD recipe. The thickness of graphene is around ~3nm.

1.3 Insertion Force Reductions of Metal Terminals using Graphene Coatings

1.3.1 Introduction

Many electrical connectors, terminals, and cables are used in the automotive, aerospace, electronics, and housing industry. Electrical connectors and terminals are widely used in the automotive industry. It is desirable to mate the electrical connections using a lower insertion force

to improve the assembly process ergonomics while maintaining good electrical conduction over the vehicle's lifetime. Traditionally, the industry implements lubricant between electrical components to reduce friction, reducing friction force, and improving durability [40]. The typical lubricants have been liquid oil-based materials with fatty acids [41], solid lubricant as metal [42], sulfide [43], and oxide nanoparticles [44] additives [45]. Usually, lubricants face challenges of low friction characteristics, thermal stability [46], and material compatibility [47].

Multi-layer graphene is capable of serving as a solid lubricant[48], [49]. The strong intralayer covalent bonds advance to maintain unchanged electrical conduction as the terminals in contact. The weak interlayer van der Walls interactions smooth out the roughness and reduce the friction of the metal surface during dynamic motion. Multi-layer graphene shows decreasing friction coefficients by a factor of 6 on sliding steel interfaces compared with a pristine steel surface, both in the air and dry nitrogen environment [50]. Graphene-based liquid lubricant that incorporates graphene in ethanol, water, and oil [26] as additives can also reduce wear rate compared with base lubricant without graphene. Usually, graphene is obtained by mechanical exfoliation [51], chemical vapor deposition (CVD) [33], [34], [52], [53], and reduction of graphite oxide (GO) [26], [38], [54] with decreasing graphene quality [55]. However, the graphene quality may also affect the lubrication performance by the preparation process. The synthesized graphene usually showed a friction coefficient lower than bulk graphite, which suggests higher quality graphene would be a better lubricant [56].

In this chapter, high performance multi-layer PECVD graphene is grown on gold (Au) and silver (Ag) terminals as a solid lubricant, and cost-effective reduced graphene oxide coating is coated on Tin (Sn) terminals. Repetitively engage and disengage a pair of female and male terminals has been performed.

1.3.2 High Quality PECVD Graphene as Lubricant

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Multi-layer graphene, serving as a conductive solid lubricant, is coated on the metal surface of electrical terminals. In this work, multi-layer PECVD graphene is grown on gold (Au) and silver (Ag) terminals as a solid lubricant. Repetitively engage and disengage a pair of female and male terminals has been performed. This insertional process test is the first time demonstration using PECVD graphene to successfully reduce the insertion force and the wear of industrial standard electrical terminals. This graphene layer reduces the wear and the friction between two sliding metal surfaces while maintaining the same level of electrical conduction when a pair of terminals engage. The friction between the metal surfaces was tested under dry sliding in a cyclical insertion process with and without the graphene coating. Comprehensive characterizations were performed on the terminals to examine the insertion effects on graphene using scanning electron microscopy (SEM), four-probe resistance characterization, lateral force microscopy (LFM), and Raman spectroscopy. With the thin graphene layers grown by plasma enhanced chemical vapor deposition (PECVD) on gold (Au) and silver (Ag) terminals, the insertional forces can be reduced by 74 % and 34 % after the first cycle and 79 % and 32 % after the 10th cycle of terminal engagement compared with pristine Au and Ag terminals. The resistance of engaged terminals remains almost unchanged with the graphene coating. Graphene stays on the terminals to prevent wear-out during the cyclic insertional process and survives the industrial standardized reliability test through high humidity and thermal cycling with almost no change.

1.3.2.1 Methods

Graphene Growth

PECVD Graphene is deposited on electrical terminals at a temperature range from 400°C to 750°C recipes as described in Chapter 1.2. Before the graphene growth process, both samples are cleaned before putting into the chamber. The growth recipes and temperatures are chosen based on the samples' melting point. Graphene quality is confirmed with Raman analysis before insertion test.

Insertion Test

Due to the specific design of the paired terminals and the purpose of the work, typical friction characterization tests such as pin on disk testing are not suitable to measure the friction between sliding metal/metal interfaces. Insertion force measurement is used to study the friction between sliding metal/metal interfaces. Insertion force testing is performed on an MTS 810 material test system with a 5 lb load cell, a Kistler 5010 amplifier, a Tektronix MDO3014 oscilloscope, and in-house-made fixtures (Figure 1.6 (a)). The terminals are fixed in the fixtures

that are mounted on the MTS test system. Careful alignment of the male and female terminals is ensured for every test (Figure 1.6). The female terminal is fixed on the bottom station while the male terminal moves downward and upward for 7 mm at the rate of 0.025 mm/s per engaging and disengaging cycle. All terminals have gone through ten cycles of measurements before and after the reliability test. The testing conditions fulfill the USCAR standard. Engaging and disengaging forces are extracted by subtracting the baseline from the peak force (Figure 1.8 (a)).

a)

b)

c)

Figure 1.6. Alignment process of the male and female terminals to the MTS tensile tester. (a) Terminals are aligned to the fixture on the table-top. (b) Fixtures are aligned to the MTS tensile tester with the assistance of two alignment bars. (c) Before the insertion test, the two alignment bars are removed from the fixture.

Electrical Testing

Four-point current-voltage measurements were taken on the terminals by measuring the voltage drop between two points in the inner loop while running current in the outer loop (Figure 1.10). The voltage is measured by an SR830 DSP Lock-in Amplifier while the current is applied using a 6221 DC and AC Current Source. Electrical testing on both Au and Ag terminals, with and without graphene coating and before and after reliability testing, has been performed on ten sets of samples ten times each to obtain a statistical comparison between each condition.

Reliability Testing

Since electrical terminals need to have good heat, humidity, and corrosion resistance to provide good electrical contacts during the vehicle's lifetime, they need to pass the accepted reliability test defined by SAE-USCAR specification [57]. In this work, both Au and Ag terminals with and without graphene were subjected to forty cycles of reliability test that lasted for 20 days. For each cycle, terminals experience thermal and humidity environments in 10 sequential steps (Figure 1.9 (c)). Insertion force testing and electrical characterizations have been performed on terminals before and after the reliability test.

Scanning electron microscope (SEM) Characterization

SEM pictures of the terminal surface morphology were taken using Hitachi S4800.

Lateral Force Microscopy (LFM) Characterization

LFM is another method implemented to study the friction between sliding metal/metal interfaces. LFM measures the deflection of the cantilever in the horizontal direction. The lateral deflection of the cantilever is a result of the force applied to the cantilever when it moves horizontally across the sample surface, and the magnitude of this deflection is determined by the frictional coefficient, the topography of the sample surface, the direction of the cantilever movement, and the cantilever's lateral spring constant.

LFM is performed on the terminals using Veeco Dimension 3100 AFM. The LFM cantilever is a 40° triangle shape n-type silicon tip with an Al coating (HQ: NSC19/AL BS), purchased from Umash with a force constant of $K_N = 0.5$ N/m. TGF11 silicon calibration grating

from MikroMasch is used to calibrate the LFM intrinsic results converting the voltage reading to friction force nN in Figure 1.13.

Atomic Force Microscopy (AFM) Characterization

The thickness of the PECVD grown graphene is confirmed with AFM. During the growth, Au/ SiO₂ samples will be put into the growth chamber together with the Au terminals. After the graphene growth, the thickness of the graphene/Au/SiO₂ should be the same as the terminals. The thickness of graphene is measured using AFM (Figure 1.5) after the wet etching Au layer.

1.3.2.2 Results and Discussion

Frictional force change is monitored when the male terminals' tip touches the female terminals in contact with the wire region. When a pair of terminals are in contact, the largest insertion force occurs when the male terminal's tip touches the female terminal's bulge. Both male and female terminals are mounted on a fixture before loading into an MTS tensile tester. Careful alignment among terminals, fixtures, and the MTS system has been checked before the insertional test (Figure 1.6. The force signals sensed by the piezoelectric load cell are amplified and recorded by an oscilloscope. When the terminals are in contact during the engage or disengage movement, the sudden rise of the force will be recorded. By calculating the difference between the magnitude of the peak force and the baseline, engage force and disengage force are recorded for each cycle of the insertion test. A set of representative measurements for engaging and disengaging movement with the respective forces are shown in Figure 1.8 (a). Negative values are intentionally applied to the disengaging forces to plot both forces together to distinguish the engaging and the disengaging forces. Each set of terminals has gone through ten cycles of insertion tests, and ten pairs of terminals have been tested to take averages and record error bars.



Figure 1.7. (a) Both the male and female terminals come with a metal box region and a wire region. When a pair of male and female terminals are in contact, the largest insertion force occurs when the male terminals' tip touches the female terminal's bulge. (b) The set-up for insertion measurements.

The magnitude of the forces is compared between a pair of Au terminals and another pair that has received the PECVD graphene coating for both engaging and disengaging movement. A significant insertion force reduction has been observed in the graphene-coated pair, as shown in Figure 1.8 (b). To confirm the force reduction comes from graphene's effect instead of the PECVD process, a set of Au terminals treated with the same plasma and temperature condition as the graphene growth process but without introducing carbon precursors are tested. There is no graphene grown on the Au terminals' surface. Even though the plasma treatment at elevated temperature also reduces terminals' insertion force, graphene coating can further reduce the insertional forces (Figure 1.8 (b)).



Figure 1.8. 10 cycles of insertion force testing on terminals with and without graphene coating. Each data point is the average value of 10 sets of terminals with an error bar showing the variation. (a) For each cycle, the magnitude of the engaging and disengaging force is extracted by subtracting the baseline from the peak force. (b) The engaging (black) and disengaging (red) force of a set of bare terminals is larger than terminals with plasma treatment at elevated temperature (green and blue) (c) The engaging and disengaging force of graphene-coated Au terminals (green and blue) is smaller than bare Au terminals (black and red). (d) Comparison of graphene-coated Ag terminals (green and blue) and bare Ag terminals (black and red).

Sample variations exist in pristine terminals before the graphene coating. Statistical studies of the graphene effect on the terminals are performed by measuring both engaging and disengaging force on ten sets of terminals of each type, eliminating some variations in terminals due to the manufacturing processes. The graphene coating effect on the terminals is based on statistics instead of isolated measurements. By plotting the average values with error bars, both forces start with higher values at the beginning cycle and saturate after a few insertional cycles (Figure 1.8 (c)). After coating both male and female terminals with PECVD graphene, engage force reduces 74 %

after the first cycle and 79 % after the 10th cycle compared to pristine Au terminals. For the disengaging force, it reduces 83 % after the first cycle and 81 % after the 10th cycle. Compared ten sets of graphene-coated Ag terminals with ten sets of pristine Ag terminals, 34 % reduction at the first cycle, and 32 % reduction at the 10th cycle for the engaging force, and similarly 32 % and 29 % for the disengaging cycles, as shown in Figure 1.8 (d). The reduction of insertion force through graphene coating is more substantial in Au terminals than Ag terminals.

Graphene coating lubricates metal surface can also be monitored using LFM. By measuring the cantilever's lateral bending when the cantilever moves horizontally across the terminal surface, the frictional force of the metal surfaces can be observed. By carefully doing calibration using the "wedge" method [58]–[60], the difference in the graphene-coated terminal's friction force and the bare terminal can be determined. The calibration is carefully performed in the supplemental session. The friction forces of Au and Au-graphene terminals are extracted from LFM measurements (Figure 1.13 (d)). With graphene coating, the friction of Au terminals can be reduced from the range of 2 N to 1 N, which is comparable to the insertion force measurement using a tensile tester.

Forty cycles of reliability tests have been performed in a 20-day period on Au terminals with and without graphene coating by changing the temperature and increasing the humidity (Figure 1.9 (c)). Figure 1.9 (a) compares five sets of pristine Au terminals before and after the reliability tests. After the extensive thermal and humidity treatment, the insertion forces decrease for the first few insertional cycles but then recover to the original values measured before the reliability tests (Figure 1.9 (a)). The initial force reduction is suspected due to the stress relaxation during the thermal cycles [61]. The thermal treatment may also increase the average metal grain size, decreasing the surface roughness and leading to the engaging and disengaging force decrease during initial cycles. However, the harsh treatment could damage the terminal surfaces so that the friction forces become large again after some movement. In contrast, for five sets of graphene-coated Au terminals, the engaging and disengaging forces are consistently smaller for all insertional cycles after the reliability tests (Figure 1.9 (b)), indicating a robust terminal surface with the graphene coating. Similar results have been observed on pristine Ag terminals and graphene-coated ones.



Figure 1.9. 40 cycles of the reliability tests on Au terminals with and without graphene coating
(a) Both the engaging and the disengaging forces of Au terminals (black and red) reduce after the reliability test for the first few cycles (green and blue). (b) Both the engaging and disengaging forces of graphene-coated Au terminals (black and red) drop consistently for all insertional cycles after the reliability tests (green and blue). (c) One cycle of thermal and humidity process. Repeated cycles are made in a continuous 20-day period to complete the reliability tests.

Electrical measurements have been performed on both pristine terminals and graphenecoated terminals. Graphene is a semi-metal with sheet resistivity of ~700 Ω/\Box [62], much more resistive than the underlying Au or Ag terminals. However, the graphene coating may prevent natural oxidation of the metal terminals. Graphene effect on the terminal resistance can be determined using four-probe electrical measurements to eliminate the contact resistance and to extract more accurate terminal resistance. Four alligators are clipped at the same locations of the terminals for every measurement. The graphene coating slightly increases the resistance of the Au and Ag terminals (Figure 1.10 (a) and (b)). The terminal resistances after the reliability tests are measured, and no apparent changes are observed for both pristine terminals and graphene-coated terminals.



Figure 1.10. Four-probe electrical measurement on terminals before and after reliability tests. (a) Graphene coated Au terminals (red) show higher resistance than bare Au terminals (black).
Resistance barely changes after reliability cycling (square), considering the slightly large error bars and accuracy of the volt-meter reading. (b) Graphene-coated Ag terminals (blue) show higher resistance than bare Ag terminals (green). Resistance stays roughly the same after reliability cycling (square). Statistical results came from ten samples for each condition measured ten times.

The quality of graphene on the terminals is characterized by Raman Spectroscopy using a 532 nm excitation laser as described in session 1.2.3. As seen in Figure 1.11 (a), after ten cycles of insertion testing, graphene quality remains unaltered, indicating that graphene stays on the terminals after insertion. Thermal and humidity reliability tests do not affect the graphene coating on the terminals with no changes in the graphene characteristics observed after the reliability tests (Figure 1.11 (b)).



Figure 1.11. (a) Raman spectra before and after insertion testing. no sign of detachment of graphene due to mechanical friction. (b) Raman of terminals before and after reliability testing.

From Figure 1.12, it is clear that the Ag surface is smoother with lower surface roughness after the graphene growth. After the reliability test, both the pristine Ag terminal and the graphene-coated terminal do not show a noticeable difference.



Figure 1.12. (a) and (b) The SEM of Ag terminals and graphene-coated Ag terminals. (c) and (d) Ag terminals and graphene-coated Ag terminals after reliability testing.

Figure 1.13 (a) is the schematics of the trapezoidal steps etched into a silicon substrate with a 10um pitch and a 1.75um step height. LFM friction measurements on the terminal surface are made through forward and reverse scans. An example of the friction loop on the Au terminal is presented in Figure 1.13 (c). The friction force can be determined by using the wedge calibration method. The half-width of the experimentally observed friction loop, W, is converted to the friction force through a lateral calibration constant, α , using Equation 1.1[63].

Equation 1.1:

$$F_L = \alpha W$$

 F_L = Lateral friction force W =half-width of friction loop α =lateral calibration constant

Lateral calibration constant α is obtained through the LFM calibration using the TGF11 grating[60]. The trapezoidal steps under an angle θ are 54.74°. Δ is the friction loop offset. F_N is the applied normal force, and F_A is the adhesion force, which can be obtained through the Forcedistance graph during the calibration, as shown in Figure 1.13 (b). F_N and F_A can be obtained by Figure 1.13 (b) and Equation 1.3 and 1.4. To get the deflection in the units of nm, S_NU_N and S_NU_A need to be normalized by the slope (5.336 x 10⁶) to convert the unit of V² to nm. After obtaining the normal force F_N and adhesion force F_A from Equations 1.3 and 1.4, solving Equation 1.2 provide two possible solutions for friction coefficient μ . Between the two solutions of μ , only the one smaller than 1/tan θ is a real solution, while the other yields an unreasonable negative calibration loop of Au terminal times α yields to the friction force, as shown in Equation 1.1. By measuring the friction loop of the Au terminals and Au-G terminals, friction forces extracted from LFM measurement are shown in Figure 1.13 (d). Using LFM to characterize the Au and Au-G terminals' friction, it is clear that graphene coating results in lower friction compared with the bare terminals. The average number of the friction force is similar to the result (Figure 1.8 (c)).

Equation 1.2:

$$\sin\theta(F_N\cos\theta + F_A)\,\mu^2 - \frac{\Delta}{W}\,(F_N + F_A\cos\theta)\mu + F_N\sin\theta\cos\theta = 0$$

 $\theta = 54.74$ °

 F_N = the normal force

 F_A = the adhesion force μ = the friction coefficient of the flat surface Δ = friction loop offset

Equation 1.3:

$$F_N = k_N S_N U_N$$

Equation 1.4:

$$F_A = k_N S_N U_A$$

k_N =normal spring constant of the cantilever

S_N =normal deflection sensitivity

U_N =voltage difference between the contact setpoint and the scanning setpoint

U_A =voltage difference between the contact setpoint and the voltage point when the cantilever jumps out of contact

Equation 1.5:

$$\alpha = \frac{1}{W} \mu \frac{F_N + F_A \cos \theta}{(\cos^2 \theta - \mu^2 \sin^2 \theta)}$$

In this case:

$$\begin{split} &S_N U_N = 0.5680 \ / \ 5.336 \ x \ 10^6 = 107 \ x \ 10^{-9} \ m = 107 \ nm \\ &S_N U_A = 1.322 \ / \ 5.336 \ x \ 10^6 = 248 \ x \ 10^{-9} \ m = 248 \ nm \\ &F_N = 0.5 \ x \ 107 = 53.5 \ nN \\ &F_A = 0.5 \ x \ 248 = 124 \ nN \\ &\Delta = 2.684 \\ &\mu_1 = 0.05239 \\ &\mu_2 = 3.806 \\ &1 \ / tan\theta = 0.7070 \\ &\mu_1 = 0.05239 \ is \ only \ valid, \ because \ \mu_1 < 1 \ / tan \ \theta \\ &\alpha = 28.74 \ nN \ V \end{split}$$



Figure 1.13. (a) schematic of the trapezoidal steps on the TGF11 silicon calibration grating. (b)
 Force-distance graph (c) the forward trace and reverse trace friction loop measured on an Au terminal (d) Friction forces of Au and Au-graphene terminals extracted from LFM measurements.

There are mainly three reasons that multi-layer graphene coating can reduce the friction of terminals during the insertion movement. First, multi-layer graphene is a layered material with weak van der Waals bonding between each layer, and they can easily slide against each other during the insertion movement. The friction force between sliding graphene layers on the male and female terminals is smaller than between sliding metal surfaces. Second, from the SEM images shown in Figure 1.12, terminal surface roughness gets reduced after graphene coating. With smaller surface roughness, a reduced contact area decreases the friction force between the sliding metal /metal interface. Finally, we would like to briefly mention that the puckering effect discovered in atomically thin graphene sheets and leads to high friction does not apply here since the puckering effect does not affect the interface beyond four-layer graphene, as shown in the reference [64]. Given that our PECVD graphene coating on terminals is thicker than four layers, the puckering effect would not be significant.

1.3.2.3 Conclusion

Given high mechanical strength, fracture strength, and lubricity properties, In this work, multi-layer PECVD graphene is grown on Ag and Au terminals as a solid lubricant. Repetitively insertional processes have been performed on these metal terminals as the male terminal's tip touches the female terminal's inner bulge. The insertional forces can be reduced by 74 % and 34 % after the first cycle and 79 % and 32 % after the 10th cycle of terminal engagement, compared with pristine Au and Ag terminals. The resistance of engaged terminals remains almost no change with the graphene coating. Graphene deposited on the terminals prevents wear-out during the cyclic insertional process and survives the industrial standard reliability test with high humidity and thermal cycling.

1.3.3 Cost Effective Reduced Graphene Oxide Solutions as Lubricant

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We have previously shown that plasma-enhanced chemical vapor deposition (PECVD) of graphene on gold (Au) and silver (Ag) terminals can significantly reduce the insertion force (friction force during the terminal insertion process) in session 1.3.2. However, the cost of this deposition method is relatively high, and its high-temperature process (> 400 °C) makes it impractical for materials with low melting temperatures. For example, tin (Sn) coating with a melting temperature of 232 °C is commonly used in electrical connectors, which cannot sustain the high-temperature process. A lubricant that is cost-effective and process-compatible to Sn terminals is appealing to explore.

Polyalphaolefin (PAO) base oil is one of the most common synthetic base oils used as industrial and automotive lubricants. It is commonly used in automotive fluids and hydraulic, gear, and bearing oils. It can operate in extremely cold or hot climates. The reduced graphene oxide (rGO) suspended in PAO base oil can be a good liquid lubricant to lower friction and preserve wear durability. The friction coefficient can be 30% lessened, and the rubbing surfaces have shown fewer scratches with the rGO additive compared to using the PAO base oil lubricant only. Besides, 0.5 wt.% rGO-PAO solution has the lowest friction coefficient among all concentrations [65].
In this study, reduced graphene oxide was prepared using a low-cost solution process and applied to metallic terminals. The reduced graphene oxide (rGO) suspended in polyalphaolefin (PAO) base oil was coated on Sn terminals via a dip-coating method. Insertion force tests with and without the rGO coating were performed on Sn terminals. The reduction of friction between two sliding metal surfaces while preserving the same level of electrical conduction has been successfully demonstrated. Comprehensive characterizations with four-probe resistance measurements and Raman spectroscopy were performed. Besides, we carried out a systematic study of the lubrication effect from both PAO and rGO for comparison. Given the advantages of low-cost and simple synthesis processes, rGO in PAO solution can be employed to lubricate electrical terminals to significantly reduce insertion force while maintaining good electrical conduction.

1.3.3.1 Methods

Sample Conditions

Sn and Au terminals tested in this work are commonly used in the automotive industry. The PAO coating and the 0.5 wt% PAO-rGO coating are coated on both male and female Sn terminals to compare the lubricant effects. PECVD graphene coating is also compared with the PAO-rGO coating on Au terminals. All sample conditions on Sn and Au terminals are tested with the insertion test and the electrical test.

Reduced Graphene Oxide Coating on The Terminals

The process to dip coating the rGO-PAO liquid lubricant on terminals is shown in Figure 1.14. A mixture of 0.5 wt.% rGO and PAO oil is created in a falcon tube. The rGO-PAO liquid lubricant is then sonicated in a sonication bath for 30 minutes before Sn terminals are dipped in the solution and taken out for the air-dry process. The rGO-PAO coating remains on the terminals after drying in the air for at least 24 hours. This lubrication coating costs less than 2 cents per terminal, making it a cost-effective graphene solution coating.



Figure 1.14. The process to coat the rGO-PAO liquid lubricant on terminals.

Insertion Test

Insertion test is performed on both bare terminals and the rGO-PAO coated terminals follow the same procedure as shown in session 1.3.2. Careful alignment of the male and female terminals is ensured for every test. The testing conditions fulfill the USCAR standard [57].

Electrical Test

To check whether the rGO-PAO lubricant modifies the terminal resistance, four-point current-voltage measurements are taken on the terminals by measuring the voltage drop between two points in the inner loop while running current in the outer loop. The testing procedure is the same as described in session 1.3.2. Electrical testing on Sn terminals with and without graphene coating has been performed on five sets of samples ten times each to obtain a statistical comparison between each condition.

Raman Characterization

The quality of rGO-PAO coating on the terminals is characterized by Raman Spectroscopy using a 532 nm excitation laser [66], [67]. The 2D peak around 2700 cm⁻¹ is the characteristic peak of the stacking order. The G peak around 1580 cm⁻¹ is the in-plane vibration of the sp2 carbon atoms. The D peak around 1350 cm⁻¹ is related to defects and disorder. The characteristics peak of PAO oil is at 2900 cm⁻¹ [68]. The Raman characteristics of the rGO before and after ten cycles of the insertion test are shown in Figure 1.18 in the session of 1.3.3.2 Results and Discussion.

1.3.3.2 Results and Discussion

The frictional force between metal surfaces can be determined by measuring the metallic terminal's insertion force during the engaging and disengaging process. PECVD graphene was coated on Au and Ag terminals as a solid lubricant [36]. A linear correlation was observed between the metal surface's friction coefficient and the insertion force of electrical terminals: a higher insertion force indicates the metal surface with a higher friction coefficient.

Sample variations exist in pristine terminals. Statistical studies of insertion forces on five pairs of terminals of each type are performed to eliminate manufacturing process variations. Hence, our conclusion of the lubricant coating effect of the rGO-PAO coating to the terminals is based on statistics instead of isolated measurements. Ten cycles of insertion force test on these three kinds of Sn terminals are shown in Figure 1.15, based on the USCAR standard. The insertion force' magnitude is compared between pristine Sn terminals and the Sn terminals with two kinds of lubricants: 1. PAO oil (Figure 1.15 (a)) and 2. rGO-PAO coated (Figure 1.15 (b)) on both male and female sides.



Figure 1.15. Ten cycles of insertion force testing on Sn terminals with and without lubricant coating. Each data point is the average value of 5 sets of terminals with an error bar showing the variation. The engaging and disengaging force of pristine Sn terminals is labeled in black for direct comparisons. The engaging force is plotted in positive values and the disengaging force is plotted in negative values for easy display and reading only. (a) The engaging and disengaging force of Sn terminals coated with PAO oil are labeled in red. (b) The engaging and disengaging force of Sn terminals coated with rGO-PAO are labeled green.

Percentage reduction of insertion force of lubricated Sn Terminals compare with pristine Sn terminals is shown in Table 1.4. By coating with the PAO oil coating, a 14% reduction of the engaging force and an 11% reduction of the disengaging force are observed in the 1st cycle of insertion, compared with the pair of pristine Sn terminals. By coating the rGO-PAO lubricant, the engaging force can be lowered by 54%, and the disengaging force can be reduced by 35%. A similar trend is observed in the 10th cycle of the measurements. Sn terminals and Sn terminals coated with PAO oil coating and rGO-PAO coating show lower insertion force in the 10th cycle than the 1st cycle. Therefore, it is concluded that the rGO-PAO is a more effective lubricant to Sn terminals than the PAO oil coating.

% Reduction in Sn	P.	40	rGO-PAO					
Terminals	Engage	Disengage	Engage	Disengage				
1 st Insertion	14%	11%	54%	35%				
10 th Insertion	30%	60%	75%	47%				

Table 1.4. Percentage reduction of insertion force of lubricated Sn Terminals compared with pristine Sn terminals

Both the PECVD graphene coating and the rGO-PAO coating are applied to Au terminals to compare the lubricant effect to Au terminals. The insertion force of pristine Au terminals is larger than that of Au terminals coated with both kinds of coatings. Percentage reduction relative to the pristine terminals is presented in Table 1.5. Similar to the Sn terminals, further reduction is observed in Au terminals with the rGO-PAO coated compared with the PAO lubricant only. For the 1st cycle of insertion, the PAO oil coating provides a 3% and 2% reduction in the engaging and disengaging forces than pristine Au terminals. By coating the rGO-PAO lubricant, the engaging force can be lowered by 21%, and the disengaging force can be reduced by 24%. A similar trend is observed in the 10th cycle of the measurements.

% Reduction in Au	Р	AO	rGO-PAO			
Terminals	Engage	Disengage	Engage	Disengage		
1 st Insertion	3%	2%	21%	24%		
10 th Insertion	14%	13%	45%	33%		

 Table 1.5. Percentage reduction of insertion force of lubricated Au Terminals compare with pristine Au Terminals

Comparison of percentage reduction of insertion force of Au terminals coated with PECVD graphene and rGO-PAO liquid lubricant in the 1st cycle and 10th cycle of insertion test is shown in Figure 1.16. PECVD graphene can reduce the insertion force of terminals for more due to three reasons. First, high-temperature annealing and plasma treatment during the PECVD graphene growth process has reduced the terminals' surface roughness. In contrast, no thermal or mechanical treatment has been implemented during the rGO-PAO liquid lubricant coating process. All reduction in insertion force is attributed to the lubricant itself without any process effect. Second, PECVD graphene coating is more conformal on terminals when compared to the dipping process used for the rGO-PAO lubricant. The non-uniform coating on the terminals results in less insertion force reduction and more variations. Third, the graphene quality determined by the preparation process may also affect the lubrication performance. Synthesized graphene usually showed a higher friction coefficient than bulk graphite, suggesting better graphene quality could lead to a superior lubricant [56]. PECVD graphene is grown on the Au terminals with a controlled process and shows higher quality graphene than the cost-effective reduced graphene oxide



Figure 1.16. Comparison of percentage reduction of insertion force in the 1st cycle and the 10th cycle of insertion tests for Au terminals coated with PECVD graphene and the rGO-PAO liquid lubricant.

Electrical measurements of terminal resistance have been made on both pristine Au and Sn terminals and the rGO-PAO coated terminals. Graphene is a semi-metal with sheet resistivity of $\sim 700 \ \Omega/\Box$ [62], much more resistive than metal terminals. To check whether the additional rGO-PAO lubricant layer modifies the terminal resistance or not, four-probe electrical measurements are employed. No noticeable resistance changes have been discerned on the lubricated terminals with the three lubricant conditions (Figure 1.17). Therefore, we conclude that the rGO-PAO coating can be an excellent lubricant to metallic terminals. Similar measurements and observations have been made on Au terminals with the rGO-PAO coating as well.



Figure 1.17. Four-probe electrical resistance measurements on pristine Sn terminals and Sn terminals coated with the PAO lubricants and the rGO-PAO lubricants. Statistical results come from five pairs of samples for each condition measured ten times.

Raman spectroscopy has been used to characterize the quality change of the rGO coating on the terminals due to the insertion test. The rGO characteristics before and after ten cycles of the insertion test are shown in Figure 1.18. Before the insertion test, there existed very thick rGO flakes on the terminal surface, which showed distinguished characteristic peaks (D, G, and 2D) in the measured Raman spectra. There are also areas on the terminal where the G peak signal is very weak, with a small 2D peak indicating a thinner or non-uniform rGO coating. The peak around 2900 cm⁻¹ is the characteristics peak of PAO oil [68]. After ten cycles of the insertion test, Raman measurements on thin rGO flakes look very similar to those measured before the insertion test. In contrast, the insertion process might have damaged the thick rGO coating may remain on the terminal surface after the insertion test.



Figure 1.18. The quality of the rGO is characterized using Raman. (a) Microscope image of the laser beam on a thick rGO flake found on the Sn terminal surface before the insertion test. (b) Microscope image of the laser beam on the Sn terminal (off the flake) before insertion test. (c) microscope image of the laser beam on the rGO flake on the Sn terminal after insertion test. d) corresponding Raman characteristics of (a) to (c).

To confirm the long-term lubricant effect with the rGO-PAO coating, we have performed 100 cycles of insertion test (Figure 1.19) on Sn terminals with and without the coating. The rGO-PAO lubricant coating slows down the wear of terminals while reducing the insertion force. After the 100 cycles of insertion test, Sn terminals show increases of engaging force from 2.2 N (1st cycle) to 8.6 N (100th cycle) as the Sn coating get removed during the insertion test. The underneath Cu/Ni surface is exposed after the 100 cycle insertion test. Sn terminals coated with the rGO-PAO coating maintain low insertion force throughout 100 cycles of insertion with the engaging force of 1.32 N at the 1st cycle and 0.95 N at the 100th cycle. Less damage on the male terminal is observed on the Sn terminals coated with rGO-PAO compared with Sn bare terminal, as shown in Figure 1.19 (b). A similar trend is observed in the disengage forces.



Figure 1.19. (a) Insertion force tests on Sn terminals with and without the rGO-PAO lubricant coating in the 1st cycle, 10th cycle, and 100th cycle. (b) Sn terminal and Sn terminal with the rGO-PAO coating before and after 100 cycles of insertion test. After 100 cycles, the Cu/Ni surface is exposed at the male Sn terminal, indicating some Sn coating got removed during the insertion test. Sn terminals coated with the rGO-PAO coating show less damage in comparison.

1.3.3.3 Conclusion

Given superior mechanical strength, fracture strength, and lubricity properties, reduced graphene oxide can be an applicable lubricant to metal surfaces in a liquid form. In this work, we have demonstrated:

1. A cost-effective rGO-PAO solution is applied to Sn terminals to reduce insertion force during the cyclic insertional process while maintaining good electrical connections despite the additional coating layer.

- 2. The rGO-PAO lubricant is dip-coated onto Sn terminals by a simple process.
- The reduction of insertion force is noted and resulted from the lubrication effect of both PAO base oil and rGO.
- 4. After ten cycles of the insertion test, rGO may be damaged and thinner as the male terminal's tip rubs the bulge inside the female terminal. However, Raman characteristics reveal that some rGO coating may remain on the terminal surface after the insertion test.

Based on the advantages of a low-cost and simple process, this rGO-PAO solution can be an effective lubricant to metal-to-metal interfaces when high-temperature coating techniques such as CVD and PECVD graphene cannot be implemented.

1.4 Graphene as Corrosion Protection on Metal Surfaces

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Inside an automobile, hundreds of connectors and electrical terminals in various locations experience different corrosive environments. These connectors and electrical terminals need to be corrosion-proof and provide good electrical contact for a vehicle's lifetime. Saltwater and sulfuric acid are some of the main corrosion concerns for these electrical terminals. Currently, various thin metallic layers such as gold (Au), silver (Ag), or tin (Sn) are plated with a nickel (Ni) layer on copper alloy (Cu) terminals to ensure reliable electrical conduction during service. Graphene can serve as a corrosion protective layer due to its excellent chemical stability and prevent electrochemical oxidation of metallic terminals. In this work, the corrosion protection effects of thin graphene layers grown by plasma-enhanced chemical vapor deposition (PECVD) on Au and Ag terminals and thin-film devices were investigated. Various mechanical, thermal/humidity, and electrical tests were performed. In addition, a systematic corrosion study of different metallic surfaces when exposed to saltwater, sulfuric liquid phase, and EIA 364-65B class IIA gas phase was performed. All tested cases confirm that the graphene layer substantially reduces corrosion rate compared with the samples with no graphene coating. The resistance of the metallic terminals remains almost unchanged when compared to that of bare terminals.

1.4.1 Introduction

Metal corrosion is a critical concern in the electronics, automobile, and aerospace industries. Most metals are chemically unstable and corrode over time, especially when they are exposed to extreme environments. Metal tends to convert into its oxide form. The formation of oxides causes metal components' properties such as mechanical strength and electrical conductivity to degrade. Usually, corrosion can be controlled by depositing organic thio-based monolayers, polymeric coatings, or inert metals between the metal and corrosive environments [12]–[14]. However, thio-based monolayers cannot survive temperatures above 100 °C. Polymeric coatings are usually very thick and have pores and pinholes, leading to corrosion with the highly crosslinked molecule [13]. Choosing inert metal coatings may likely increase the cost of production. Besides, most of the existing coatings may change metal's physical properties and decrease thermal and electrical conductivities as time passes [14]. Therefore, effective and affordable corrosion protection is vital to extend component durability and lifetime.

For connectors and electrical terminals inside the automobile to be functionally effective, they need to be waterproof, corrosion-proof and provide electrical contact under harsh and corrosive environments. Saltwater and sulfuric acid are some of the major corrosion concerns of these electrical terminals. Currently, gold (Au), silver (Ag), and tin (Sn) metals are plated on Cu terminals to ensure good electrical contact and sustain severe corrosive environments.

In this work, thin PECVD graphene coating as a corrosion protection layer on the Cu, Ag, and Au surfaces was investigated. Various mechanical, thermal, and electrical tests were performed. Systematic studies of saltwater and sulfuric liquid phase corrosion tests, the mixed flowing gas phase corrosion tests, and the humidity-high temperature tests have been performed on various metal terminals and thin-film samples. All cases tested to confirm that the graphene layer substantially reduces the corrosion rate on terminals with the coating compared with no graphene coating.

1.4.2 Methods

Sample Conditions

Two types of samples are tested in this work: 1. Metal thin-films on SiO₂ substrate and 2. Metal terminals. Both thin-film samples and terminal samples are tested for corrosion rate with

and without PECVD graphene coating. The samples' conditions tested in different corrosive environments are listed in Table 1.6.

	Sample Conditions						
Test Envir	Thin- SiO ₂ S	flims on Susbtrate	Terminals				
	Cu	Ag	Ag	Au			
Liquid Phase Test	NaCl	>	>				
	H_2SO_4	>	>				
Mixed Flow Gas Test	H ₂ S, Cl ₂ , NO ₂ , SO ₂		>	>			
Humidity-High Temperature Test	Thermal /Humidity			>	~		

Table 1.6. Sample conditions (Bare and graphene coating) tested in various corrosive environments

Four-terminal thin-film devices are fabricated on SiO_2 substrates with different channel widths (2 µm, 6 µm, 10 µm, 14 µm, and 18 µm) and a fixed channel length (300 µm) and channel thickness (120 nm). Cu thin film is deposited on the SiO_2 substrate using a PVD evaporator, and Ag thin film is deposited on the SiO_2 substrate using a CHA evaporator. The SEM image with the patterned four-terminal devices' dimension is shown in the inset of Figure 20(a). The Cu and Ag thin-films samples are tested in the liquid phase NaCl and H₂SO₄ and the mixed flow gas corrosive environments.

Figure 20 (b) shows the optical image of metal electrical terminals. The Ag and Au terminals tested in this work are commonly used in the automotive industry. These terminals are cleaned in toluene, acetone, and isopropanol alcohol sonication for 5 minutes sequentially before any treatment or test.



Figure 1.20. (a) The SEM image of thin-film four-terminal devices on SiO₂ substrate (b) The optical image of metal electrical terminals.

PECVD Graphene Growth

PECVD Graphene is deposited on thin-film devices and electrical terminals at a temperature range from 400°C to 750°C recipes as described in Chapter 1.2. Before the graphene growth process, both samples are cleaned before putting into the chamber. The growth recipes and temperatures are chosen based on the samples' melting point. Graphene quality is confirmed with Raman analysis before corrosion study.

Corrosion Test Conditions

Since electrical terminals need to have good heat, humidity, and corrosion resistance to provide reliable electrical contact during the vehicle's lifetime, they need to pass the accepted corrosion and the humidity-high temperature tests.

I. Liquid Phase Corrosion Test

The liquid phase corrosion tests are performed on Cu and Ag thin-film devices, follows Ford's internal standard. The 5% NaCl and 25% H₂SO₄ test fluids cover the entire SiO₂ substrate. The resistance change is monitored at each hour. The electrical test has been performed on fourterminal devices before and after the liquid phase corrosion test.

II. Mixed Flow Gas Corrosion Test

A prevalent method for accelerating corrosion is Mixed Flow Gas (MFG) testing. Mixed Flow Gas testing was developed in the early 1980s at Battelle Memorial Institute to replicate the corrosion rates measured via copper and silver test coupons in various industrial environments. In the MFG test, the temperature and humidity levels are elevated and give an acceleration factor of 180. A typical Battelle MFG test lasts 20 to 30 days, equating to 10 to 15 years of field life. Other MFG test standards have been developed by Electronic Industries Association (EIA) and International Electrotechnical Committee (IEC)[69]. For our case, the mixed flow gas corrosion test has been tested on Ag terminals for 14 days at Molex LLC at the standard of EIA 364-65B Class IIA[69]. The Class IIA test condition is listed in Table 1.7. Resistance of the terminal is monitored before and after the mixed flow gas corrosion test.

Table 1.7. Gas-phase corrosion testing conditions in 14 days in the standard of EIA 364-65B

	Gas Composition (ppbv)								
Class IIA	H_2S	Cl ₂	NO ₂	SO_2	T (°C)	% RH			
	10	10	200	100	30	70			

III. Humidity – High Temperature Test

To ensure the long-term durability of the terminals requires verifying their functionality after aging tests. The automotive industry uses humidity-temperature cycling tests for this purpose. High humidity and temperature test can accelerate galvanic and electrolytic corrosion and cause electrical and mechanical degradation. This is helpful to evaluate the terminal connector's electrical durability. Temperature cycling can cause wear and fretting corrosion[70]. The 20-day repeated cycles of the humidity-high temperature test have been performed on Ag and Au terminals, following USCAR standard. The insertion force and the electrical resistance have been measured on terminals before and after the test. For each cycle, terminals experience thermal and humidity environments in 10 sequential steps, as shown in Figure 1.21 at the temperature range of -40 °C to 150 °C and the humidity range of uncontrolled to 80 %.



Figure 1.21. One cycle of thermal and humidity process. Repeated cycles are made in a continuous 20-day period to complete the humidity-high temperature test (reprinted from [36]).

Insertion Test

Au and Ag terminals with and without graphene coating have gone through ten cycles of insertion and extraction before and after the humidity-high temperature test to evaluate whether the test modifies the electrical terminal's insertion force. The image of the terminals and the method to extract and insert are shown in our previous work [36]. The insertion test is performed on an MTS 810 material test system with a 5 lb load cell, a Kistler 5010 amplifier, a Tektronix MDO3014 oscilloscope, and in-house-made fixtures. The terminals are fixed in the fixtures that are mounted on the MTS test system. Careful alignment of the male and female terminals is ensured for every test. The female terminal is fixed on the bottom station while the male terminal moves downward and upward for 7 mm at the rate of 0.025 mm/s per engaging and disengaging cycle.

Electrical Test

The electrical measurements have been performed on both thin-film devices and terminals with and without graphene coating. The four-probe electrical measurements are employed to check whether the graphene layers change the sample resistance and are effective as an active corrosion barrier. The voltage drop between the two inner electrodes is measured while the current is passing through the outer electrodes. Four-probe electrical measurements can eliminate contact resistance and extract more accurate device resistance.

For the thin-film devices, the electrical measurements are performed using the Keithley semiconductor analyzer 4200-SCS. Five devices are measured for each channel width and length, and for each test condition, before and after any treatment to obtain a statistical understanding of the resistance change.

For the terminals, the voltage is measured by an SR830 DSP Lock-in Amplifier while the current is applied using a 6221 DC and AC Current Source. Electrical tests have been performed on five samples for a statistical comparison between each condition. Four alligator clips are clipped at the same location on the terminals for every measurement.

1.4.3 Results and Discussion on Thin Film Devices

Four-point resistance measurements have been performed on both Cu and Ag thin-film devices before and after the NaCl and H_2SO_4 corrosion tests. Five sets of devices are included in the statistics for each data shown in Figure 1.22. PECVD graphene is grown on these thin-film samples as a corrosion protection coating. As shown in Figure 1.22 (a) and Figure 1.22 (b), the Cu and Ag device resistance increases with the decreasing width expected from Ohm's law. The device resistance is reduced after the graphene coating due to the native oxide on the metal being effectively removed during the graphene growth.

The resistance change of Cu and Ag devices after a 5% NaCl corrosion test is shown in Figure 1.22 (c) and Figure 1.22 (d). The test fluids cover the entire substrate during the corrosion test to monitor the graphene effect as corrosion protection. After two hours of NaCl tests, Cu with graphene coating has less resistance change than no graphene coating for all channel widths (Figure 1.22 (c)). For example, for the channel width of 6 μ m, a 22% resistance increase was measured on bare Cu devices after 2 hours of NaCl corrosion test, while only a 12% resistance increase was measured in devices with the graphene coating. Similar results have been found in the Ag devices after 31 hours of the NaCl corrosion tests (Figure 1.22 (d)). The Ag devices with graphene coating show almost no resistance change, while the bare Ag devices show a ~55% resistance increase. We conclude that the graphene coating effectively reduces the corrosion rate of Cu and Ag in a 5% NaCl corrosive environment.



Figure 1.22. (a) Resistance as a function of device width for bare Cu devices and graphene-coated Cu devices before the corrosion test. (b) Resistance as a function of device width for bare Ag devices and graphene-coated Ag devices before the corrosion test. (c) Percentage resistance change of Cu and graphene-coated Cu after 2 hours of NaCl corrosion test. (d) Percentage resistance change of Ag and graphene-coated Ag after 31 hours of NaCl corrosion test. (e)
Percentage resistance change of Cu and graphene-coated Cu after 1 hour of H₂SO₄ corrosion test. (f) Percentage resistance change of Ag and graphene-coated Ag after 31 hours of H₂SO₄ corrosion test.

For the Ag and Ag-G thin film devices, the SEM images are presented in Figure 1.23 (a) and (b). The thin film Ag-G devices show less corrosion than the Ag devices. However, graphene can not completely stop the corrosion. The PECVD graphene is grown at a much lower temperature compared with traditional CVD graphene. The PECVD graphene with more defects and grain boundaries may allow chemical species to pass through and attack the metal substrate underneath. If the corrosion test is performed for a more extended period, corrosive media will eventually attack the whole metal from the surface to the bulk.



Figure 1.23. The SEM images of (a) Ag and (b) Ag-G thin-film devices after the mixed flow gas phase corrosion test.

1.4.4 Results and Discussion on Metal Terminals

Terminals- Subjected to Mixed Flow Gas

The Ag terminals and graphene-coated Ag terminals (Ag-G) have gone through EIA 364-65B Class IIA mixed flow gas test for 14 days. Electrical measurements are performed before and after the mixed flow gas test.

Figure 1.24 compares the bare Ag terminals and graphene-coated Ag terminals before and after the gas phase corrosion test. After the corrosion tests, Ag and Ag-G terminals are corroded on the surface with the color changes in Figure 1.24 (a). However, the terminals' resistance only increases slightly, plotted in Figure 1.24 (b). This indicates that corrosion only occurs at the surface for both bare Ag and graphene-coated Ag terminals instead of the whole terminals. After the gas phase corrosion test, the graphene coating protects the terminals in the mixed flow gas environment with little resistance change.



Figure 1.24. (a) Ag and Ag-G terminals before and after gas corrosion tests. (b) Resistance of the two types of terminals before and after 14 days mixed flow gas corrosion test.

The SEM images of Ag and Ag-G terminals before the mixed flow gas corrosion test are shown in Figures 1.25 (a) and (b). Figure 1.25 (c) and (d) show corroded surfaces after the mixed flow gas corrosion test. Both Ag and Ag-G terminals show similar corroded surfaces after the mixed flow corrosion test. For the Ag and Ag-G thin film devices, the SEM images are presented in Figure 1.23 (a) and (b).



Figure 1.25. The SEM images of (a) Ag and (c) Ag-G terminal before the corrosion test. The SEM images of (b) Ag and (d) Ag-G terminal after the corrosion test.

Terminals- Subjected to Humidity-High Temperature Test

Since these electrical terminals need to have good heat, humidity, and corrosion resistance to provide good electrical contacts during the vehicle's lifetime, forty cycles of the humidity-high temperature test have been performed in a 20-day period on Au terminals with and without graphene coating. Figure 1.26 (a) and (b) compares five sets of the bare Au and Au-G terminals before and after the humidity-high temperature test. Graphene is grown on the terminal using a 400°C recipe. After the extensive thermal and humidity treatment, the insertion forces decrease for the first few insertional cycles but then recover to the original values measured before the humidity-high temperature test (Figure 1.26 (a)). The initial force reduction is suspected due to the stress relaxation during the thermal cycles [61]. The thermal treatment may also increase the average metal grain size, decrease surface roughness, and lead to the engaging and disengaging force decrease during initial cycles. However, the harsh treatment could damage the terminal surfaces so that the friction forces become large again after some movement. In contrast, for five sets of graphene-coated Au terminals, the engaging and disengaging forces are consistently smaller for all insertional cycles after the humidity-high temperature test (Figure 1.26 (b)), indicating a robust terminal surface with the graphene coating. Similar results have been observed on bare Ag terminals and graphene-coated ones.



Figure 1.26. (a) Ten cycles of the insertion force tests on bare Au terminals before (black) and after (red) the humidity-high temperature test (b) Ten cycles of the insertion force tests on Au-G terminals before (green) and after (blue) the humidity-high temperature test.

Four-probe electrical measurements were tested on Au and Au-G terminals before and after the humidity-high temperature test to check whether the humidity and thermal stress modified the terminals' resistance. The graphene coating slightly increases the resistance of the bare Au and Au-G terminals (Figure 1.27). After the humidity-high temperature test, no apparent resistance changes for both bare terminals and graphene-coated terminals are observed. Similar observations have also been seen on the Ag terminals.



Figure 1.27. Four-probe electrical measurements on Au (black) and Au-G (red) terminals before and after the humidity-high temperature test. Statistical results came from ten samples for each condition measured ten times.

1.4.5 Conclusion

In this work, PECVD graphene is deposited on Cu, Ag, and Au surfaces. Systematic studies of these metal terminals and thin-film samples are performed after liquid phase corrosion, gasphase corrosion, and humidity-high temperature tests. All tested cases confirm that the graphene layer substantially reduces the corrosion rate compared with samples with no graphene coating. The metallic terminals' resistance remains almost unchanged compared to that of bare terminals under the mixed flow gas corrosion test and the humidity-high temperature test. Thin PECVD graphene coating can protect the metallic surface under corrosive environments. For low melting point metal, such as Sn surface, the PECVD method is not practical. In addition, scaling the growth and reducing the cost would be critical to implement this technique.

1.5 Energy Harvesting with Reduced Graphene Oxide Piezoelectric Composite Cell

Most of the material in this section of the chapter is in manuscript drafting, "PVDF-TrFE Energy Harvesters Optimization using Reduced Graphene Oxide and Barium Titanite Additives", Suki Naifang Zhang, Yu Chieh Chiu, Selva Vadivelmurugan, Babak Arfaei, and Zhihong Chen

1.5.1 Introduction

Ongoing energy crises such as oil shortages and problems such as environmental pollution have become challenging to the automotive industry. Energy harvesting is a promising solution that can produce renewable and clean energy. Energy harvesting technologies capture unused and wasted energy and convert it into a more usable form[71]. And it provides significant potential for the current automotive industry as improving vehicle energy efficiency and fuel economy as collecting the solar, wind, hydro, thermal, and mechanical energies[71]–[74]. For vehicles, lost heat, braking energy, and vibration energy are the main targets of energy harvesting[75]–[77]. As such, interest in recovering energy lost due to vibration during automotive travel is escalating.

Piezoelectric materials are widely used in energy harvesting applications as they can convert unused dissipating mechanical energy from various sources into electric current or voltage. Piezoelectric materials can provide higher energy conversion efficiency compared to other materials[78], [79] and the most representative piezoelectric materials are piezoelectric ceramics and piezoelectric polymers[80]. When mechanical vibration is applied to the piezoelectric polymer film, electrical charges are induced between the two surfaces. Some polymers have strong piezoelectric effects when subjected to mechanical stretching or external excitation, which can be adopted as generator materials for energy harvesting purposes. Polyvinylidene fluoride (PVDF) is one of the most attractive polymers due to its pyro, piezo, ferro electroactive properties and additional high thermal and chemical stability. PVDF and its copolymers, such as PVDF-TrFE, and their high sensitivity and flexibility make it a suitable application in an energy harvesting device.

PVDF usually contains different crystalline phases such as α , β and γ [81]. The piezoelectric active β and γ phase are most interested in sensing, actuation, and generator applications. To obtain β phase PVDF, the most common strategies can be mechanical stretching of α phase, applying a high electric field and or high pressure, or add nucleating fillers such as BaTiO₃, reduced graphene nanoparticles as so on. PVDF-TrFE possesses advantages over the host

polymer PVDF since it has a much more crystallinity β phase than the parent polymer PVDF. The enhancement of the formation of the β -phase does not require any additional processes such as stretching and poling[82]. The chain conformation for different phases of PVDF, respectively α , β , and γ phases, is shown in Figure 1.28. The chain conformation for different phases of PVDF, respectively α , β , and γ phases, is shown in Figure 1.28. In the β phase, it contents all trans(TTT) Planar zigzag structure. For the α it has TGTG'(trans-gauche-trans-gauche) structure. For the γ phase, it has T₃GT₃G' structure[83]. Since each chain possesses a dipole moment perpendicular to the polymer chain, the β phase contains the highest dipole moment per unit cell compare with the other two phases[84].

Compared with the piezoelectric ceramics, the polymer piezoelectric materials' disadvantage is low polarization and piezoelectric properties. Lead content ceramics such as lead zirconate titanate (PZT) and lead magnesium niobate lead titanate (PMN-PT) usually have large dielectric and piezoelectric constants. Still, toxic lead-based ceramics often is not favored by the application. Instead, BaTiO₃ is a good candidate with a high piezoelectric constant, and it is biocompatible[85]. Additional BaTiO₃ as nucleating fillers may improve the β -phase alignment and overall composite dielectric of PVDF energy harvester.

In this work, we design an energy harvesting system with flexible piezoelectric composites cell and study the additive effects from r-GO and BaTiO₃ to PVDF-TrFE as the goal to achieve higher electrical energy output from automotive vibration.



Figure 1.28. Diagrams of the chain conformation for α , β , and γ crystalline phases of PVDF[80].

1.5.2 Methods

Piezoelectric Cell Preparation

PVDF-TrFE copolymer was purchased from Poly K Technologies. PVDF-TrFE 80/20 is chosen explicitly since it has a high Curie temperature around ~135 °C. Reduced graphene oxide (rGO) was purchased from Graphenea. Barium Titanate (BaTiO₃) was purchased from US-Nano. The average particle size is around 200 nm. Solvent Dimethylformamide (DMF) is used to dissolved PVDF-TrFE. The piezoelectric cell (PVDF-TrFe-BaTiO₃-rGO) is prepared as follows.

In order to prepare a (PVDF-TrFe)x-(BaTiO₃)y-(rGO)z solution in the ratio of x=70 y=30 and z=0.7. We would take 0.7g of PVDF-TrFE (80-20), 0.3g BaTiO₃, and 0.007g rGO powders and mixed them in a flask with 10 ml DMF solvent. Stir the mixture solutions with a magnetic bar on the hot plate at 110 °C overnight for well mixed. Thermal energy will melt PVDF-TrFE and form a uniform slurry of the PVDF-TrFe-BaTiO₃-rGO solution. When the solution is ready, dropcast the mixture solutions on a clean SiO₂ substrate and following with hot plate annealing at 110°C overnight to ensure all the solvent evaporated. The PVDF-TrFe-BaTiO₃-rGO composites thin film can be peel off from the substrate if the solvent is completely removed. Different compositions of PVDF-TrFe-BaTiO₃-rGO piezoelectric cells studied in this work are listed in Table 1.8. Different concentrations of each component are tested to find the optimal composition for the piezoelectric energy harvesting cell. Typical each piezoelectric cell is around 1cm² by 1cm². Copper tapes are used as flexible electrodes of the piezoelectric cells. Both sides of the piezoelectric cell are covered with copper tape in a parallel plate capacitor structure. Lead wires are soldered onto copper tape charges transfer. Charges which are harvested from vibration would be stored in the capacitor for LED lighting. Figure 1.29 shows the piezoelectric composites after peeling off from the SiO₂ substrate and the piezoelectric energy cell after Cu tape electrode and wire leads are in place.

				<u>Vary rGO</u>			<u>D</u> 3	
PVDF-TrFe Content	BaTiO₃ Content	rGO Content	PVDF-TrFe Content	BaTiO ₃ Content	rGO Content	PVDF-TrFe Content	BaTiO₃ Content	rGO Content
70	0	0	70	30	0	70	0	7
50	50	0.5	70	30	0.7	70	3	7
60	40	0.4	70	30	3	70	10	7
			70	30	5	70	20	7
			70	30	7	70	30	7
			70	30	14			

Table 1.8. Different compositions of PVDF-TrFe-BaTiO₃-rGO piezoelectric cells in this work.



Figure 1.29. a) The piezoelectric composites, after peeling off from the SiO₂ substrate. Different colors are due to varying concentrations of the PVDF-TrFe, BaTiO₃, and rGO contents. b) The piezoelectric energy cell with Cu tape electrode and wire leads.

Experimental Setup

The circuit design for energy harvesting using PVDF-TrFe-BaTiO₃-rGO piezoelectric cells is shown in Figure 1.30. The task is divided into three parts: 1. vibration generation, 2. energy harvester cell development, and circuit development for energy storage and lighting. The PVDF-TrFe-BaTiO₃-rGO energy harvester is placed in the center of the vibration generator (a shaker). A sinusoidal wave has generated using a function generator at 70 Hz. The signal is amplified using an amplifier as mimicking the vibration generated from the automobile. Different G vibrations can be tuned using the amplifier as the input of vibrational force to the samples. The typical vibration condition is 9G at 70 Hz in this work. The sample is completely insulated and taped down on the stage of the shaker using insulation tape (Figure 1.4). AC to DC conversion was performed using the voltage rectifier. The output DC voltage was collected and stored in a 470 uF capacitor. The

voltmeter can read stored charges in the capacitor. Typical charging measurement takes 8 minutes per run of the experiment, and we collect five sets of measurements in each condition to eliminate sample variations. Tabletop Energy Harvesting Setup is shown in Figure 1.31.



Figure 1.30. Lab testing circuit design



Figure 1.31. Tabletop energy harvesting setup

1.5.3 Results and Discussion

Figure 1.32 shows the capacitor charging output and open circuit output of various PVDF-TrFe-BaTiO₃-rGO piezoelectric cells as increasing BaTiO₃ and rGO concentration. Device output rising with the increasing BaTiO₃ and rGO concentration. Adding rGO into the composites favors the β phases dipole alignment can induce the increased energy output. During polymer crystallization, dipole interactions happen between PVDF and DMF, and the r-GO acted as a nucleation center. C-F bonds' strong dipoles would rotate around the chain backbone's C-C bonds and made the PVDF chains align to the graphene surface, which enhanced the β phase content[86]. Adding BaTiO₃ nanoparticles to the composites also improves the device performance since BaTiO₃ has a higher dielectric constant than PVDF-TrFe.



Figure 1.32. The capacitor charging output of various PVDF-TrFe-BaTiO₃-rGO piezoelectric cell as increasing a) BaTiO3 content and b) rGO content. The open-circuit output of various PVDF-TrFe-BaTiO₃-rGO piezoelectric cells as increasing a) BaTiO₃ content and b) rGO content.

Reliability Test

The PVDF-TrFe-BaTiO₃-rGO energy harvester with (x:y:z=70:30:7) has been tested under extreme conditions -80 °C and 125 °C for ten days for reliability purposes. These two samples were original in the same piece of composites film. Identical thickness and quality were chosen before the reliability test. The intrinsic performance of two pieces of samples is almost the same. The harvester was put on hotplates for ten days at 125 °C and in the fridge at -80 °C. The samples are taken out from the hotplate and the refrigerator every day and take the electrical charging measurement until the 10th day. Before and after ten days, reliability tests at 125 °C and -80 °C were shown in Figure 1.33. The sample does not show performance degradation after ten days of reliability test at 125 °C and -80 °C. The oxidation of the Cu electrode causes a more significant variation of output after ten days at 125 °C. As the contacts get oxidized, a more substantial device performance variation contributing to the more significant error bar is collected at the capacitor.



Figure 1.33. Intrinsic charging performance of the PVDF-TrFe-BaTiO₃-rGO composites harvesters and the performance after 125 °C and -80 °C 10 days reliability test.

As the PVDF-TrFe-BaTiO₃-rGO (70:30:0.7) piezoelectric cell is put at the center of the vibration generator, the piezoelectric cell converts the vibrational energy to electrical energy and stored at the capacity as the piezoelectric cell experiencing 9G vibration. The harvested electrical energy can light up a small LED, as shown in Figure 1.34. Before the vibration test, a LED light bulb is shown on the circuit board connecting to the rectifier. As the piezoelectric cell is on the shaker experiencing the vibration in the dark, the LED light bulb is lighted by the harvested energy.



Figure 1.34. a) Before the vibration testing, a LED light bulb is on the circuit board. b) During the vibration, the LED light bulb is light up by the harvested energy.

Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX)

SEM and EDX are used to characterize the piezoelectric energy harvesting cell. SEM/EDX is carried out on the system of Hitachi S4800 Field Emission SEM. Figure 1.35, SEM/EDX shows the surface morphology of the piezoelectric cell and distinguishes the BaTiO₃ signal from rGO/ PVDF-TrFe. Since both rGO AND PVDF-TrFe Contents C atoms, EDX can not be used to determine the signal between rGO and PVDF-TrFe.



Figure 1.35. a) The SEM image of PVDF-TrFe-BaTiO₃-rGO piezoelectric cell. b) EDX signal from oxygen atoms, c) EDX signal from titanium atoms, d) EDX signal from carbon atoms, e) EDX signal from fluorine atoms, and d) EDX signal from barium atoms

X-ray diffraction (XRD)

XRD characterizations were carried out using a Panalytical X'pert Pro diffractometer with Ni Beam Attenuator CuK α ($\lambda = 0.15404$ nm). XRD of different PVDF-TrFe-BaTiO₃-rGO piezoelectric composites with various concentrations of PVDF-TrFe, BaTiO₃, and rGO content is shown in Figure 1.36 (a). The black curve comes from the pure PVDF-TrFe thin film. As the rGO is added into the PVDF-TrFe, the red curve starts to show the characteristic peak of rGO at 27° at label A compared with PVDF-TrFe. As the BaTiO₃ was added into PVDF-TrFe, the green curve show several characteristics peaks contributed by the BaTiO₃ content at label B. No rGO peak AT label A is observed on the green curve since no rGO is added into the composite. The broadband contains two peaks at 2θ =18.42° and 20.24° (label C) is the characteristic peak for PVDF-TrFe. In the XRD pattern of PVDF-TrFe, the peaks at 18.42° and 20.24° correspond to the non-polar crystalline α phase and polar crystalline β phase, respectively, at label C [87]. At the same concentration of PVDF-TrFe and BaTiO₃, but varying the rGO concentration from 7 to 14, higher rGO characteristics peaks intensity are observed compared with blue and cyan curved. A linear relationship is observed on the XRD signals as increasing BaTiO₃ concentration and rGO concentration (Figure 1.36 (b) and (c)).



Figure 1.36. a) XRD of the different PVDF-TrFe-BaTiO₃-rGO piezoelectric composites with various concentrations of PVDF-TrFe, BaTiO₃, and rGO content.

Fourier-transform infrared spectroscopy (FTIR) Analysis

The presence of the α , β and γ phases produced by PVDF-TrFe-BaTiO₃-rGO thin film was accessed using FTIR spectroscopy. Figure 1.37 shows the FTIR β phase peak as the PVDF-TrFe, BaTiO₃, and rGO content varying in the piezoelectric composites.



Figure 1.37. a) FTIR of different PVDF-TrFe-BaTiO₃-rGO piezoelectric composites at the β peak.

To benchmark, this PVDF-TrFe-BaTiO₃-rGO piezoelectric cell, commercial PZT disk, commercial PVDF cell, and other piezoelectric cells with PZT additives are compared in Figure 1.38. Comparing the PVDF-TrFe-BaTiO₃-rGO piezoelectric cell performance with Commercial PZT disk and PZT PVDF cell, Our piezoelectric cell has comparable performance as commercially packaged PVDF cell. Still, the commercial PZT disk outperforms our piezoelectric cell (Figure 1.11 (a)). Comparing our PVDF-TrFe-BaTiO₃-rGO piezoelectric cell performance with the PZT additive piezoelectric cell under the same measurement conditions, Our piezoelectric cell has better performance than other piezoelectric cells made in the lab (Figure 1.38 (b)). Commercial PZT disk and commercial PVDF cell have optimal packaging design compared with our piezoelectric cell. Our device output performance is comparable with the commercial PVDF cell; with a better packaging design, our piezoelectric cell may perform better than the existing commercial PVDF product.



Figure 1.38. a) Comparison of the PVDF-TrFe-BaTiO₃-rGO piezoelectric cell performance with Commercial PZT Disk and PZT PVDF cell b) Comparison of the PVDF-TrFe-BaTiO₃-rGO piezoelectric cell performance with PZT additive piezoelectric cell.

1.5.4 Conclusion

We developed PVDF-TrFe-BaTiO₃-rGO piezoelectric composites cell to harvest vibrational energy from a shaker to charge the capacitor in this work. We found that both rGO and BaTiO₃ can improve the device output performance. These new PVDF-TrFe-BaTiO₃-rGO composites are very flexible and can survive ten days of reliability testing at 125°C and -80°C without performance degradation. We will start package these PVDF composites and maximize charging performance by stacking the PVDF composites and optimizing the circuit to improve the output performance.

2. TRANSITION METAL DICHALCOGENIDES APPLICATIONS

2.1 Transition Metal Dichalcogenides (TMDs)

Ultrathin 2D nanomaterials attract attention after Novoselov and Geim's team exfoliated graphene from graphite using the mechanical cleavage method in 2004[88]. Graphene descendants TMDs, which are almost as thin, transparent, and flexible as graphene[89], [90] also sparked intense research interests in different research areas. TMDs are 2D aligned transition metals covalently bonded between two layers of chalcogenide atoms[91], as shown in (Figure 2.1). Unlike graphene is a gapless semimetal, these 2D materials can be metallic, semi-metallic, semiconducting, insulating, or superconducting by changing different chemical compositions and structural configurations [90]. Many TMDs are semiconductor in nature and processes high surface to volume ratio[92], high carrier mobility[93][94], superior mechanical strength[95], great flexibility[96], and lack of surface dangling bonds which allows TMDs to be used in different electronics and optoelectronics applications[97]–[103].



Figure 2.1. Crystal structure of TMDs

Compare with conventional 3D semiconductors (Si, Ge, and III-Vs), TMDs offer several promising advantages, such as better electrostatic gate control, which help to mitigate the short channel effect in the ultra-scaled FET[90], [97], [104]. "channel length (L_{CH}) scaling" factor " λ " given by $\lambda = (\sqrt{t_{OX}t_{BODY}}\varepsilon_{BODY})/\varepsilon_{OX}$, where t_{OX} and t_{BODY} are the thicknesses of the gate oxide and channel, respectively, and ε_{OX} and ε_{BODY} are their respective dielectric constants. Critical technological roadblocks include its contact, doping, and mobility (μ) engineering to move further

on an actual application. In this work, controllable air-stable doping of TMDs would be explored for next-generation low power electronics applications.

Due to the layered structure with a large surface area and surface volume ratio, TMDs also serve advantageously in gas sensing and allow rapid charge transfer reaction upon exposure to the gas molecules. TMDs gas sensors can show an instantaneous change in the electron/hole conductivity due to gas molecule absorption and desorption. Currently, 2D TMDs gas sensors have been demonstrated for the detection of various gas molecules. In this work, selective TMDs gas sensors are explored for health monitoring applications.

Common photodetectors, photoFETs devices, rely on the absorption effect by the channels or the photogenerated carriers modulating the channel's electric field [105]. Due to ultra-thin t_{body} and high on/off ratio, TMDs can be used as a detector of photogenerated carriers when TMDs conductivity changed with the light absorption in the substrate. In this work, a depleted semiconductor-oxide-semiconductor (TMD) photodetector was explored for light-sensing applications.

2.2 Chemical Doping Strategies on Transition Metal Dichalcogenides (TMDs)

2.2.1 Introduction

There is little doubt that as electronic devices' miniaturization is evolving, rapid improvement over conventional transistors is in urgent need[104]. Owing to their ultra-thin bodies without surface dangling bonds, two-dimensional (2D) TMDs devices can be more aggressively scaled-down than Si transistors without suffering from short-channel effects. Although researchers have scaled the channel length of TMD transistors down to 10nm[97], the realization of high-performance devices is limited by the availability of materials with the right bandgap size, high carrier mobility, and low contact resistance between metal contacts and the semiconductor[106]. Moreover, controllable air-stable doping of the TMD channels to lower the parasitic resistances and allow complementary metal oxide semiconductor (CMOS) device operations remains a challenge.

Ion implantation has been especially important in the evolution of three-dimensional (3D) semiconductor technologies, such as silicon. However, this doping method has been largely and understandably avoided in TMDs, due to per unit volume defect enhancements inherent in 2D

materials compared to their 3D counterparts[107]. On the other hand, alternative doping methods, such as addition (covalent modification) and physisorption (surface charge transfer), have been overwhelmingly utilized with TMDs[108]. Unlike substitutional doping, where impurities are implanted into the intrinsic semiconductor by atomic replacement, covalently attached and physisorbed impurities are less invasive for 2D materials. Dopant species used with TMDs either stable but have relatively little doping effects or are short-lived but offer temporary large effects. Degenerate level of doping for molybdenum disulfide (MoS₂) and tungsten diselenide (WSe₂) has been achieved with potassium[102], benzyl viologen (BV)[109], hydrazine[110], and NO₂[111] However, these dopants suffer from stability. Some of them will distort the crystalline lattice of the TMD material through covalent modification. Physioadsorbed impurities are considered the most non-invasive dopants available as no alterations are made to the crystalline lattice. In contrast, covalent alterations are often found to diminish the device carrier mobilities[109].

2.2.2 Metal Phthalocyanine (Pcs) Doping to TMDs

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We have identified a few physisorbed phthalocyanine (Pc) molecules that can be either ntype or p-type dopants for both MoS₂ and WSe₂ by monitoring the threshold voltage shift in fieldeffect transistors (FETs) using these TMDs as channel materials (Figure 2.2 (a)). These Pc molecules can chelate up to 70 different elements from the periodic table[112], giving rise to a much wider variety of organometallic compounds with potentially vastly different properties. It is often desirable to be able to predict the doping level and stableness of the selected dopants. However, this predictive approach is still in its infancy today since the doping process can be influenced by multiple factors, not limited to redox potential, doping mechanism, and geometry of the dopant at the dopant/semiconductor interface. We will show that our compound selection allows us to tune doping levels according to the Pc effectiveness as a dopant.

Pc molecules are chosen as a basis for molecular doping because they show good chemical stability and bind to most metal atoms in the periodic table. To quantitatively evaluate doping levels, we fabricated back-gated TMD FETs and monitored their threshold voltage (V_{TH}) changes before and after doping. We were able to freely modulate the doping levels in both types of TMD

devices using various metallated Pc molecules that include platinum phthalocyanine-4,4',4'',4'''tetra-sulfonic acid tetrasodium salt (PtTsPc), copper phthalocyanine-4,4',4'',4'''-tetra-sulfonic acid tetrasodium salt (CuTsPc), iron phthalocyanine-4,4',4'',4'''-tetra-sulfonic acid tetrasodium salt (FeTsPc), sodium phthalocyanine-4,4',4'',4'''-tetra-sulfonic acid tetrasodium salt (Na₂TsPc), and copper(II) 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluoro-29H, 31-Hphthalocyanine (F-CuTsPc) (Figure 2.2 (b-f)). After doping, we successfully reverse the doping effect, recovering the original V_{TH} values by re-solubilizing the dopants in a suitable solvent.



Figure 2.2. (a) Schematic of a back-gated few-layer MoS₂ or WSe₂ FET, chemically doped with metallated Pc molecules. Chemical structures of different Pc molecular dopants (b-f): (b) PtTsPc, (c) CuTsPc, (d) FeTsPc, (e) Na₂TsPc and (f) F-CuTsPc.
As shown in Figure 2.2 (b-f), different metals that vary in work function can be incorporated into the Pc core. The periphery of the molecule can be modified with substituents such as fluorine atoms, which inevitably alter Pc's electronic properties. We have successfully deduced doping outcomes by considering the work function of the metal incorporated into the Pc core. We present highly stable dopants for MoS₂ and WSe₂ and demonstrate a high level of n-type and p-type doping of WSe₂ with physisorbed Pc species. We also report that with respect to the work function of metals substituted into Pc, the doping polarity can be switched from n-type to p-type (or vice-versa), a level of control with no similarity to date. We further investigated the doping effect of adding electron-withdrawing substituents on the periphery of Pc molecules with mixed results but hoping that it may lead others in rationally tailoring such organics to achieve desirable doping effects.

2.2.2.1 *Methods*

Device Fabrication

 $3-5 \text{ nm MoS}_2$ and WSe₂ flakes were mechanically exfoliated using scotch tape and transferred onto heavily doped Si substrates with 90nm SiO₂ on top. The thicknesses of the flakes were characterized using AFM. Source and drain contacts were patterned using e-beam lithography, followed by e-beam evaporation of 60nm Ni metal. Pc molecules.

Electrical Characterization

Transfer characteristics of the tested TMD devices were measured using an HP 4156C semiconductor parameter analyzer. To analyze these metallated Pc molecules' doping levels without a false hysteresis effect, all electrical characteristics of TMD devices were measured under pulsed voltages to eliminate charging effects from SiO₂. Positive drain biases were chosen to monitor the electron current conduction, and negative drain biases were used for the hole current conduction. V_{TH} is recorded by linear extrapolation of sub-threshold slopes from the transfer characteristics (I_{ds} - V_{gs}) curves[113]. After introducing dopants to TMD devices by soaking in aqueous dopant solutions, the same pulse measurements were performed as those measured before doping. All device characteristics were color-coded with the associated dopants annotated in the Figures. Doping effects in TMD devices were verified by threshold voltage (V_{th}) shifts and changes

in the on-state currents[114]. A large number of devices were used to calculate the average V_{th} shifts with averages and standard deviation for all dopants.

Dopant Deposition

The dopants were deposited by soaking the device substrate in 50mg/mL of aqueous Pc solution for 12 hours. After soaking, the substrate was immediately spun using 2000 rmp, 60s dwell, and 4s ramp on/off time to remove excess dopants, and annealing was performed under vacuum at 120°C for 4 hours. F-CuTsPc was not water soluble and could not be made into an aqueous solution. We dissolved 10mg/mL of F-CuTsPc in hot chloroform. The F-CuTsPc solution was dropped at the air/water interface of a Langmuir trough, and the barriers were compressed to 23 mn/m. The F-CuTsPc was then deposited onto the device substrate by Langmuir-Schaefer transfer, and annealing was performed under vacuum at 120°C for 4 hours.

Na₂TsPc and PtTsPc Synthesis

Non-metallated H₂Pc was purchased from Alfa Aesar. Na₂Pc was synthesized using similar protocols for Pc metalation. 0.3g of H₂Pc ($3.6 \times 10-4$ mol), a small piece of sodium metal cut from hexane, and 50 mL of anhydrous DMF were refluxed under nitrogen atmosphere at 60°C for 12 hours. About 5 mL of isoamyl alcohol (3-Methylbutan-1-ol) was slowly added to the reaction flask, and after 2 hours, the reaction was quenched in isopropyl alcohol the solvent evaporated by rotavapor. The solid was filtered and washed three times with chloroform. The solid was collected and dissolved in water. The product was verified by observing the ultraviolet absorbance spectrum associated with metalation to confirm the metal-Pc species. After metalation, the UV-absorbance spectrum of porphyrins changes in two ways. There is a blueshift in the major Soret Band and the Q Bands diminish into a doublet, as we observed. PtTsPc was synthesized in a slightly similar manner where 0.3g of H₂Pc (3.6×10^{-4} mol), 0.6g of PtCl₄ (1.8×10^{-3} mol), and 50 mL of anhydrous DMF were refluxed under nitrogen atmosphere at 60°C for 12 hours. The reaction was monitored by absorption spectroscopy as well. The product was washed three times with chloroform. The solid was collected, dissolved in water, and the final product was dialyzed against water for three days.

2.2.2.2 Results and Discussion

Figure 2.3 (a-d) compare transfer characteristics of WSe₂ devices before and after doping with PtTsPc, CuTsPc, FeTsPc and Na₂TsPc, respectively. Synthesis procedures of the dopants are described in the method session. All devices originally exhibit typical ambipolar characteristics due to an intrinsic near mid-gap Schottky barrier (SB) line-up[115], [116] even when high work function metal contacts such as Ni were used. After being doped by PtTsPc, CuTsPc, and FeTsPc compounds, devices showed large positive V_{TH} shifts, suggesting p-type doping of the WSe₂ channels (Figure 2.3 (a-c)). In the meantime, an enhancement in the p-branch (hole) on-current by 1-2 orders of magnitude and strong suppression of the n-branch (electron) on-current were also observed, indicating a reduction in the p-type contact resistance (R_c) due to a decreased SB line-up to the valence band[117]. In contrast, the Na₂TsPc doped device (Figure 2.3 (d)) presents an opposite, n-type doping effect as evidenced by the left V_{TH} shift and an improved n-branch on-current because of the SB alignment closer to the conduction band upon doping.

Now let's compare the effectiveness of each dopant. Figure 2.3 (a) shows a +33V V_{TH} shift of a WSe₂ device on a 90nm SiO₂ substrate after doping with PtTsPc. The range of the V_{TH} shifts across all devices was found to be +18 to +40 V (Figure 2.3 (e)). A doping density of 9.6×10^{12} /cm² is calculated from the total charges induced by doping, Q = C_{OX}* Δ V_{TH}=15.3×10⁻¹⁵ C. Figure 2.3 (b) and (c) present WSe₂ devices before and after CuTsPc and FeTsPc doping, with a +32V and +27V V_{TH} shift, respectively. Typical hysteretic behaviors of these devices are shown in the inset of Figure 2.3 (b). Although the V_{TH} shift range is similar between PtTsPc, CuTsPc, and FeTsPc, the mean V_{TH} shift establishes a general doping trend among these three p-type dopants with respect to the work function of the metal substituent (Figure 2.3 (e). It appears that the doping level difference between the CuTsPc and PtTsPc is smaller than expected, with the mean V_{TH} shift of CuTsPc doped devices being slightly above the linear doping trend. Currently, the majority of approaches for introducing solution-based dopants to TMDs are through drop-casting or soaking. Due to the lack of controllability of such methods, it is unlikely to avoid batch-to-batch variations. Our statistical studies show that CuTsPc and PtTsPc exhibit less doping variation on WSe₂ (Figure 2.3 (e and f)).



Figure 2.3. Transfer characteristics of WSe2 devices before and after applying metalphthalocyanine dopants of (a) PtTsPc, (b) CuTsPc, (c) FeTsPc and (d) Na2TsPc. Figure (e) shows the trend of correlating VTH shift after molecular doping with the work functions of the metal core atoms in dopants (a)-(d). Figure (f) shows the statistical distribution of V_{TH} shift for dopants (a)- (d).

We further investigated Pc doping by exploring the opposite end of our p-type doping trend by selecting Na₂TsPc, a lower work function metal substituted into the Pc core (Figure 2.3 (e)). Whereas the n-branch currents of PtTsPc, CuTsPc, and FeTsPc doped devices were suppressed by about four orders of magnitude, such is not the case in Na₂TsPc doped devices (Figure 2.3 (d)). Our results show a clear n-type doping for Na₂TsPc devices with a mean -13V V_{TH} shift (Figure 2.3 (d)), and the range in V_{TH} shift across all devices was found to be a -1V to -38V (Figure 2.3 (e and f)). Also, there is suppression of the p-branch and enhancement of the n-branch currents in Na₂TsPc doped devices, which suggests that the SB line-up to the conduction band is reduced.

Given the work function of Pt, Cu, and Fe (5.65eV, 4.65eV, and 4.5eV, respectively), it is clear that higher p-doping levels can be achieved in WSe₂ devices by adopting higher work function metals into Pc. In contrast, upon Pc's metalation with a lower work function metal, such as Na²⁺(2.75eV), the doping polarity is shifted from p-type to n-type doping. Therefore, by using different metallated Pc species, we obtained a combination of p-type and n-type doping in WSe₂, with a predictable trend in respect to the work function of the metallated species (Figure 2.3 (e)). Given this linear relationship, it should remain possible to utilize other dopants that fit within this work function trend to establish a preselected doping level.

The Pc family of molecules have various stabilities, which is highly dependent on which atom is part of the metal-N center[118], since destabilization mostly depends on the reduction of the metal coordinating N atoms[119]. To investigate the stability, we measured the transfer characteristics of the CuTsPc- and FeTsPc-doped WSe₂ FETs after 16 days and 18 days upon initial doping, shown in Figure 2.4. The doping levels of these devices remain unchanged with no observation of V_{TH} shift or on-current reduction. This indicates that doping with these physisorbed metal-phthalocyanine molecules has remarkable stability while achieving high doping levels. Unfortunately, we found that our PtTsPc doped devices did not have good stability with the doping effect lost after 2 days exposed to atmospheric conditions.



Figure 2.4. Stability test of Metal-phythalocyanines dopants on WSe₂ FETs, (a) 16 days (CuTsPc) (b) 18 days (FeTsPc).

We expanded our doping efforts by using three Pc dopants, CuTsPc, FeTsPc, and Na₂TsPc, on MoS₂ FETs (Figure 2.5 (a-c)). Different from WSe₂, undoped MoS₂ devices show n-type unipolar characteristics. The n-branch current is expected to reduce in conjunction with a positive V_{TH} shift when p-type doping is introduced to MoS₂, while the opposite should be observed for ntype doping. Remarkably, a similar doping trend of the work function dependence is observed, with V_{TH} shift of +18V, +6V, and -4V in CuTsPc, FeTsPc, and Na₂TsPc doped devices, respectively. A linear relationship is also observed between the doping level and metal work function in MoS₂ devices. Overall, it is interesting to note that, using the same dopants and doping conditions, stronger doping effects are observed in WSe₂ compared to MoS₂. Figure 2.5 (d) shows the stability of CuTsPc doped MoS₂ devices after 35 days exposed to the atmosphere. Compared to other surface adsorption experiments utilizing molecular doping of TMDs, no other dopants are comparable to this chemical stability with a time interval of up to 4 weeks.



Figure 2.5. Transfer characteristics of (a-c) Metal-phythalocyane doping on MoS₂ FET devices, (a) CuTsPc, (b) FeTsPc, (c) Na₂TsPc. (d) Stability test of CuTsPc on MoS₂ devices.

As shown above, CuTsPc exhibits the best combination of higher doping level, less device variation, and better stability for both WSe₂ and MoS₂ devices. This motivated us to look into variants of CuTsPc, such as fluorinated CuTsPc (F-CuPc), to achieve even stronger p-type doping. The fluorine atoms on the periphery of F-CuPc withdraw electrons away from the metal center, where most of the electron density is localized. (19) Reduction in electron density would inherently dampen the extent of electron donation from dopant to TMD. Figure 2.6 illustrates the doping effect of F-CuTsPc on MoS₂ devices, suggesting a more substantial p-type doping effect when using fluorination.



Figure 2.6. Effect of fluorination on Metal-phthalocyanine doping by comparing doping effects of CuTsPc and F-CuTsPc on MoS₂ devices. Doping effects on I_{ON} and V_{TH} shift are shown by arrows.

2.2.2.3 Conclusion

In this study, we highlighted the utility of Pc chemical doping on WSe₂ and MoS₂ devices. By taking advantage of the highly versatile Pc molecule, we could modify the doping levels by tuning the metal substituent's work function in a rather predictable way. As a result of these efforts, we've achieved high levels of p-type doping in both WSe₂ and MoS₂ devices, and we were also able to switch the doping polarity by using low work function metal inserted into Pc. Furthermore, we reported that the doping effect of CuTsPc is minimally impacted after 35 days of exposure to ambient conditions. This is the longest spanning stability test reported on doped TMD devices. We believe that searching for higher doping levels utilizing similar compounds or other Pc variants will be beneficial in this case.

2.2.3 Linear Polyethyleneimine (LPEI) Doping to TMDs

Part of the material in this section of the chapter is in manuscript drafting, "Molecular Doping Strategies for 2D Transition Metal Dichalcogenides and Thoughts to Consider", Christopher J. Benjamin, Suki Zhang, and Zhihong Chen

We utilize a class of organic polymer, polyethyleneimine (PEI), to chemically dope 2D TMDs, MoS₂ and WSe₂. Researchers have used PEI with many types of semiconductors for decades as an n-type dopant. However, the current logic for using PEI focuses on the consistency and reliability of this polymer to act as an n-type dopant without any further justification. PEI structure has 1°, 2°, and 3° amines, linear and branched forms, and each with unique physiochemical properties to be considered (Figure 2.7). We pull from existing, general polymer indices and apply a rational approach to chemically doping MoS₂ and WSe₂ with PEI. The overall polymer size, geometry, charge, and shape conformability are all factors to consider when applying polymers to interfaces[120]–[125].

The doping of MoS_2 with branched PEI (BPEI) has been reported, with an n-type (electron-donating) voltage threshold shift (V_{TH} shift) around a -4V[125], [126]. The linear PEI (LPEI) form, where the functional groups are exclusively 2° amines, has less electron-donating tendencies than 3° amine groups present on BPEI. We demonstrate that by considering the increased geometrical conformability, site adaptivity, and surface loading of LPEI, we can achieve degenerate doping levels on MoS₂ and WSe₂. On the other hand, chemical doping efforts to date have utilized BPEI[127]–[129], as opposed to the LPEI we report here along with another research group as of 2015[130].

Furthermore, we probe the effect of pH on the doping levels achieved with LPEI, adding another level of control to evaluate potential chemical dopants for 2D materials. The work reported with LPEI in 2015 showed non-degenerate doping of graphene[131]. On the other hand, we achieved degenerate levels of doping using LPEI with MoS₂ and WSe₂, demonstrating a higher level of doping even though the positioning of the conductance band in graphene is more favorable to n-type doping than MoS₂ and WSe₂[132]. Our report is the first of its kind to consider this set of physicochemical parameters for chemically doping

TMD's. We hope that it would inspire other researchers to consider such rational approaches that apply to other molecules to achieve targeted doping levels.



Figure 2.7. a) Labels for the doped device architecture. b) Intrinsic device architecture and device architecture for devices doped at pH=4 and pH=11. c) Energy diagram for electron injection into TMD before and after doping.

2.2.3.1.Methods

Device Fabrication

MoS₂ and WSe₂ flakes were mechanically exfoliated using the scotch tape method, and the 3-5 nm flakes were transferred onto p-doped Si with 90nm SiO₂ substrate. The source and drain contacts were patterned with e-beam lithography process with e-beam evaporated Nickel contact

Excess metal was removed with acetone, leaving the patterned metal behind. Flake thickness was measured using AFM.

Electrical Characterization

We used an HP 4156C semiconductor parameter analyzer to characterize our devices in a vacuum-free environment. False hysteresis was found to be eliminated using pulse measurements running at 0.1 seconds "on" and 10 seconds "off". A positive drain bias was used for the electron current of the channel, followed by collecting the transfer characteristics and extracting the V_{th} shift using linear extrapolation of the sub-threshold slopes. We collected data from multiple devices for each dopant to ensure accuracy in reporting our results.

Dopant Deposition

For high pH samples, LPEI was added to warm water until a pH of 11 was maintained and monitored by litmus paper. For low pH samples, LPEI has added to a water solution, and the addition of formic acid continued until a pH of 7 was achieved. After measurement of the intrinsic device characteristics, the samples were soaked in these dopant solutions overnight. After retrieval were spun at 2000 rpm for 90 seconds with a spin coater to remove excess LPEI.

2.2.3.2. Results and Discussion

PEI was elected in this study due to the variety of supramolecular structures and physicochemical properties, such as polymer type and change of pH environments. We observe the doping effect of LPEI as a response to pH by monitoring the change in V_{TH} shift, referencing pristine MoS₂ and WSe₂. We use tape exfoliated TMD from bulk MoS₂ and WSe₂ deposited onto SiO₂ dielectric with nickel source/drain, with the devices under the influence of a global back gate (Figure 2.7). For the pristine devices, MoS₂ devices show n-type unipolar transfer characteristics. In contrast, WSe₂ devices show ambipolar characteristics due to the Fermi level close to the midgap of the valence and conductance band. Multiple device characteristics were collected to ensure accuracy in reporting this doping effect.



Figure 2.8. a) Transfer characteristics of MoS₂: Before doping (black), LPEI at pH=7 (red) and LPEI at pH=11 (green) and b) Transfer characteristics of WSe₂: Before doping (black), LPEI at pH=7 (red) and LPEI at pH=11 (green)

As shown in Figure 2.8 (a), MoS₂ started with nFET characteristics before dopant introduction. As MoS₂ gets exposed to LPEI at pH=7, stronger n-doping is observed on MoS₂ devices compared with the literature value with BPEI [131]. A similar result is observed on the WSe₂ devices in Figure 2.8 (b). WSe₂ started with ambipolar characteristics before LPEI interacts with the channel. After LPEI at pH=7 is in contact with WSe₂, WSe₂ showed n-doped characteristics with the V_{th} shift to a more negative value for over 20V while n-branch on-current increased and p-branch on-current decreased. Both MoS₂ and WSe₂ characteristics indicated LPEI provided n-doping to the channel. The doping effect pulled the channel band diagram down and favors the Schottky barrier aligned closer to the conduction band and allows more electron travels from source to drain.

As we tune the pH value of LPEI to pH=11, we can change the doping level of TMDs. In Figure 2.8, After exposure of LPEI to MoS₂ and WSe₂ devices, we observed a more substantial n-type doping effect compared to pH=7 as we monitored the V_{th} shift and n-branch on-current. Almost degenerate n-doping level is observed on MoS₂ devices as indicated that the off state of the device pushed out of the -60V to +60V transfer characteristics window. At pH=11, 40V V_{th} shifts to more negative applied gate voltage compared with the 20V V_{th} shift with pH=7. This result indicates with we can tune the n-doping level to MoS₂ by changing the doping environments of LPEI. A similar effect is observed on the WSe₂ device. The degenerate n-doping level is achieved with over 60V V_{th} shift and increase electron current.

To test whether our measurements result from doping and not forming a parallel channel in the dopant layer, the backdated device on the LPEI polymer is tested with nickel source/drain contacts. The low picomolar results show no parallel channel formed in the dopant layers, verifying that the current levels represented in this report are not artificial and a direct result of the LPEI doping effect..

2.2.3.3. Conclusion

In this work, LPEI was shown to provide remarkable n-type doping to MoS₂ and WSe₂ devices. This doping effect was shown to be a stark improvement in comparison to BPEI in previous literature. We demonstrate that by considering PEI doping's physiochemistry, a level of doping modulation and control can be asserted over these devices. Such approaches to choosing chemical dopants for 2D transistor devices have yet to be realized. For the following 2D next-generation devices to come closer to fruition, the same level of control and predictability in doping levels that exist for traditional, bulk 3D silicon devices must also be met with 2D materials. We provide a basis for reaching this goal, and we hope such approaches become commonly used for chemically doping 2D materials in the future.

2.3 Selective Electronic NO₂ Sensors using Polydimethylsiloxane Filter on WSe₂ Devices

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Atomically thin two-dimensional (2D) materials are ideal gas sensing materials with ultrahigh sensitivity due to the high surface-to-volume ratio, low electronic noise, and tunable Fermi level alignment. However, obtaining selectivity to a target analyte in the presence of other confounding gases in the environment remains an issue preventing selective gas sensing using 2D materials. We fabricate a selective nitrogen dioxide (NO₂) sensor using WSe₂ by adding a simple oil layer as a filter in the present work. For this proof of concept study, we used polydimethylsiloxane (PDMS) due to its dipole moment being similar to NO₂ (~0.3 D). This PDMS layer helps selectively detect NO₂ and filter out both more polar gases, such as ammonia (NH₃) and hydrogen sulfide (H₂S), as well as non-polar gases, such as carbon monoxide (CO), that are likely to be present in the background environment. Not only did we obtain a selective response for single components, but we also observed an improved sensing response (around 200%) when NO₂ is mixed with other gases compared to the intrinsic WSe₂ device without modification. The obtained results were found to be reproducible and reversible. The charge transfer effect of different gases to WSe₂ devices was characterized by an Atomic Force Microscope (AFM) through phase imaging technique.

2.3.1 Introduction

The push for personalized medicine has created a market for wearable real-time monitoring solutions to identify physiological changes and environmental contaminants to enable total exposure health monitoring. To enable the goals of total exposure health, real-time environmental monitoring solutions, including sensing toxic gas molecules, is critical[133], [134]. Air pollutant hazardous gases like NO_x and CO are commonly produced from vehicles, energy sources, power plants, and etc.[135]–[138]. More specifically, nitrogen oxides (NO_x)s are a family of reactive gases produced endogenously by humans as a signaling molecule (NO). It is released into the atmosphere by breathing or emitted by automobiles, trucks, turbines, and power plants (NO₂). For environmental monitoring applications, NO₂ is more relevant. NO₂ is not only a strong oxidizing agent and air pollutant, but it also reacts in the atmosphere to form ozone (O₃) and acid rain[139]·[140]. Continuous NO₂ exposure may cause respiratory diseases[136], [138], [141], [142], but it cannot be detected by the human senses. Ideally, NO₂ gas sensors should detect NO₂ in the presence of other interfering gas species and enable detection in explosive environments, i.e., in combustible materials without further modification (intrinsically safe).

Commercially developed NO_2 gas sensors are mainly based on metal oxide semiconductors due to their high sensitivity. However, they require elevated temperatures, inconsistent with intrinsically safe devices (200-400°C)[143]. This makes the metal oxide cross-reactive with volatile organic compounds, conferring poor selectivity and muddling deployment where more than one gas species is present. While NO_x is a p-type dopant (electron-withdrawing), most other volatile compounds are n-type dopants (electrondonating) and thus will reduce the magnitude of the NO_x sensor. Finally, the need to maintain elevated temperatures increases the power consumption of the device[134], reducing the suitability for deployment in real-time, wearable devices.

Transition metal dichalcogenides (TMDs) are 2D aligned transition metals covalently bonded between two layers of chalcogenide atoms. Since graphene was first isolated from highly oriented pyrolytic graphite (HOPG) in 2004[88], [144], 2D TMDs have drawn a lot of attention to their electronics and optoelectronics device applications due to the high carrier mobility, superior mechanical strength, flexibility, optical transparency, and high thermal conductivity[101], [110], [143], [145]. Atomically thin tungsten diselenide (WSe₂) is one of the members of the TMDs family with a thickness-dependent bandgap. For bulk WSe₂, the bandgap of 1.35eV increases to 1.54eV for bilayer and 1.64 eV in monolayer[102] due to quantum confinement effects[103]. TMDs also serve advantageously in gas sensing due to their layered structure with large surface area and surface volume ratio, allowing rapid charges transfer reaction upon exposure to the gas molecules and thus show an instantaneous change in the electron/hole conductivity. Currently, 2D TMDs gas sensors have been demonstrated for the detection of various gas molecules. Many studies about MoS₂ FET gas sensor applications have been reported[134], [143], [146], especially with NO₂[134] and NH₃[147]. Fewer studies on WSe₂ have been performed. At room temperature, WSe₂ has been found that it has responsivity to NO₂, NH₃, H₂S, SO₂ individually[148] NO₂[145] [149] [150] and SO₂[148][,][151] are p-type dopants to TMDs while NH₃ [147]-[149] and H₂S[148][,][152]are n-type dopants. An oxidizing gas such as NO₂[113] is believed to withdraw electrons from the WSe₂ and increase the p-branch currents or decrease n-branch currents with a corresponding increase in threshold voltage (Vth). In contrast, a reducing gas such as NH₃ can donate electrons to the WSe₂ resulting in increased n-branch currents or decreased p-branch currents with a corresponding decrease in Vth. Thus, monitoring the current changes and threshold voltage shift can indicate the sensitivity of WSe₂ to the gas molecules. However, current technology still faces challenges like selectivity among different gas-phase analytes[147].

Polymers have been exploited in the past to confer selectivity[153]. Using non-volatile polymers in the liquid state provides a simpler mechanism to create a diffusion barrier that can be modified and blended easily for the analyte of interest, where analytes permeability into the oil will be defined by their dipole moments. Polydimethylsiloxanes (PDMS) are known gas-permeable polymers that also are bio-compatible and thus suitable in wearable devices[154]. Siloxanes, such as PDMS, have a minimal dipole moment (~0.3) and therefore are predominantly

hydrophobic without further modification[155]·[156]. Additionally, siloxanes are known to both be electrical passivating[157]–[159] and chemically inert with most gases and VOCs[160]·[161].

Thin films of PDMS are already often used as a highly selective gas permeable/liquid impermeable membrane in microfluidic devices to enable degassing[162]·[163]. The rate of gas permeation through these solidified PDMS devices is directly proportional to the product of solubility of the gas and the rate of diffusion of the dissolved gas in PDMS, which relies on the size of the gas molecule[164]. Moving to a liquid phase polymeric barrier should eliminate heterogeneity due to pore sizes, creating a simpler methodology for conferring selectivity.

In this work, we investigate the sensing performance of WSe₂ exposed to four gas analytes (NH₃, H₂S, NO₂, CO) both in isolation and in mixtures. The WSe₂ sensor without the PDMS coating demonstrated a response to all four test gases. By adding this thin layer of uncured, viscous PDMS as a semi-selective coating, the responsiveness of the WSe₂ device to NO₂ was unchanged, but the selectivity of the device was substantially improved. Future work will pursue alternative viscous oil coatings on-top of these TMDs to tune the selectivity to different classes of compounds, integrate electronics for real-time testing, and develop device geometries that will enable retention of these oil coatings on wearable type devices.

2.3.2 Methods

Devices Fabrication and Characterization

Exfoliated WSe₂ flakes are transferred onto 90nm SiO_2/p^{++} Si substrates using the scotch tape method. A PMMA resist was deposited on the substrate via spin-coating, baked at 180°C for 5 min before the PMMA was patterned using e-beam lithography. The post-exposed PMMA e-beam resists were developed in 75% isopropanol for 1 min, followed by e-beam metal evaporation of 15nm Ti and 65nm Au as the source and drain contacts.

The schematics of the final WSe₂ gas sensor are illustrated in Figure 2.9 (a). After WSe₂ gas sensor fabrication, in some instances, a layer of PDMS oil is then drop cast on the sample to create a semi-selective barrier towards gas-phase analytes and allowed to wet the surface thoroughly. The thickness of the oil was estimated at ~0.5 mm. The thickness of WSe₂ and the phase images are measured using Atomic Force Microscope (AFM, Bioscope II from Veeco) after source-drain contacts are placed on top of the WSe₂ flake. Figure 2.9 (b) shows the SEM images

of the WSe₂ device taken using SEM (Nanofabrication instrumentation, Raith) with device size $\sim 1 \mu m$ by $1 \mu m$.

Gas Sensing Measurement

The electrical measurement is measured before and after gas exposure using a Keithley 4200 parameter analyzer. The devices are placed into a modified flow cell fabricated from a falcon tube. House air with the spiked single analyte is directly flowing into the falcon tube. Mixture gases are pre-mixed in bags before flowing into the improvised flow cell. The back-gating method is used to investigate the field-effect transistor (FET), where the heavily doped p-Si substrate as the back-gate electrode in all measurements. The WSe₂ transfer characteristics are measured before and after exposing individual gases or mixed gases, both with and without the PDMS filter. Sensor responses for WSe₂ devices are determined by monitoring both V_{th} shifts and the changes in the on-state currents.

A list of the single analyte gas mixtures (balance is 80% N₂, 20% O₂) measured using the WSe₂ devices in a stop-flow system is listed in Table 2.1. The stop-flow system was implemented as follows. A falcon tube was modified with NPT fittings at the inlet and outlet. After the target gas flows into the falcon tube and purges air out for at least 1 min, the falcon tube is closed, and the target gas mixture remains in contact with the WSe₂ device until the exposure time ends. For proof-of-concept testing to determine the response of the WSe₂ sensors towards analytes with and without the silicone oil filter, we either performed high concentration exposures for relatively short time periods or low concentration exposures for more extended time periods. The PDMS coating we used is SYLGARDTM 184 silicone elastomer, Part A, with a viscosity of 5100 cP. Measurements were acquired pre and post-exposure.

Testing of WSe₂ devices for multiple analyte mixtures was performed with the following gas mixtures (balance gas of 80% N₂, 20% O₂): a) 5 ppm H₂S with 2.5 ppm NO₂, b) 5 ppm H₂S with 25 ppm CO and 2.5 ppm of NO₂ and 25,000 ppm of CH₄ c) 5 ppm H₂S with 25 ppm CO and 2.5 ppm of NO₂ and 5000 ppm of CO₂. Multiple analyte gas testing is performed in an open system (continuous flow cell), with air passing between two holes in the falcon tube. 250cc/min of these multiple analyte mixtures are continuously pumped into the falcon tube for 40 minutes. All gas bottles for both single analyte and multi-analyte mixtures were purchased from CalGasDirect.



Figure 2.9. a) Schematics of the WSe₂ gas sensor with im-proved selectivity using PDMS filter, NO₂ is the target gas for the sensor, highlighted in the red circle. b) SEM of the WSe₂ device.

Gas		ppm	Exposure Time (min)
	NO ₂	5 & 1000	10 & 1
Reactive	H ₂ S	10	10
Analytes	СО	100	1
	NH ₃	50	10
Inert	CO ₂	5000	10
Analytes	CH ₄	25000	10
Analyte Gas Mixtures	H ₂ S-NO ₂	5-2.5	40*
	H_2 S-CO-NO ₂ (CH ₄)	5-25-2.5	40*
	H_2S -CO-NO ₂ (CO ₂)	5-25-2.5	40*

Table 2.1. Gaseous conditions for single gases and mixture gases measurements (*open system(250cc/min),10L).

2.3.3 Results and Discussion

FET Characterization of Sensors to Single Analyte Exposures

The transfer characteristics of the WSe₂ FET when V_{ds} = 1 V before and after gas exposure are shown in Figure 2.10. We tested the response in the presence and absence of NO₂ through the following steps: 1) intrinsic WSe₂ transfer characteristics before gas exposure (black). 2) first NO₂ gas exposure (5 ppm NO₂, 10 mins, green). 3) return to baseline upon removal of NO₂ by applying a vacuum (blue). 4) Repeat exposure to NO₂ (pink). In Figure 2.10 (a), it is observed that 5 ppm NO₂ gas causes the p-branch current level to increases by one order of magnitude and a positive V_{th} shift by almost 10 V (black to green). Application of vacuum to desorb the NO₂ analyte enables partial recovery from its original state (blue). After the second exposure to NO₂, the sensor produces nearly the same transfer curve compared to the first exposure (pink). This demonstration shows that unaltered WSe₂ FETs can be used as a reversible NO₂ gas sensor.

Figure 2.10 (b)shows the transfer characteristics of the same WSe₂ sensor in a linear scale. With 5 ppm NO₂ gas can increase the p-branch current 11 times (green) compared with the intrinsic performance (black) at V_{gs} = -20 V. With the 2nd NO₂ gas exposure, the sensor can also maintain seven times (pink) higher current than the device after applying a vacuum.

Figure 2.10 (d), we then tested a higher exposure for a shorter period of time to determine both the sensor response and the reversibility of this exposure to higher analyte concentrations. Exposure of the sensor to 1000 ppm of NO₂ gas for 1 min resulted in a three order of magnitude increase in the current in the region of the transfer curve corresponding to the p-branch on-current. The V_{th} increases by 30 V after gas exposure. These shifts, as expected, were more significant than observed at 5 ppm of NO₂. Applying a vacuum can partially recover the WSe₂ channel to the original state, enabling repeated use.

To help confer selectivity, we tested the sensor response in the presence of a thin PDMS oil layer. As shown, PDMS does not change the intrinsic characteristics of the WSe₂ sensor (Figure 2.10 (c)), red versus black curves). After exposure of the PDMS coated sample to 5 ppm NO₂, a positive V_{th} shift and an increased current are observed of similar magnitude ($2.5x10^{-7}$ A/µm vs. 8.2 $x10^{-7}$ A /µm) to the non-PDMS coated sensor. Applying a vacuum can remove the analyte results with a complete return to baseline (blue). A second exposure to 5 ppm NO₂ results in a similar sensor response (pink).

Both WSe₂ devices with and without the PDMS oil demonstrated similar changes in terms of 1) one order of magnitude in current increase corresponding to the p-branch, and 2) \sim 10 V V_{th} shift. This indicates that PDMS allows NO₂ to pass through to the WSe₂ surface and does not materially affect the sensitivity of the WSe₂ channel in a stop-flow, equilibrium-based system.



Figure 2.10. Transfer characteristics of the WSe₂ sensors with exposure to a) 5 ppm NO₂ in log scale, b) 5 ppm NO₂ in linear scale, c) 5 ppm NO₂ with PDMS filter toWSe₂ gas sensors, and d) 1000 ppm NO₂. Before gas exposure is in the black line (BD) with no PDMS coating and red line with PDMS coating (BD-PDMS). The first gas exposure is in the green line ((AD1) with no PDMS coating and (PDMS-AD1) with PDMS coating). The first vacuum is in the blue line ((AD1-VON1) with no PDMS coating and (PDMS-AD1-VON1) with PDMS coating). The second gas exposure is in the pink line as labeled ((AD1-VON1-AD2) with no PDMS coating and (PDMS-AD1-VON1-AD2) with PDMS coating)

The permeability and selectivity of the WSe₂ devices coated with PDMS were also tested against other chemical analytes such as H₂S, NH₃, CO, CO₂, and CH₄ (Figure 2.11). The transfer characteristics for the WSe₂ devices in response to H₂S, NH₃, and CO, both with and without a PDMS oil filter is shown in Figure 2.11.

From Figure 2.11 (a) and Figure 2.11 (c), we observe that exposure to H_2S and NH_3 creates shifts in the transfer curve indicative of n-doping of WSe₂, with a negative V_{th} shift, increased nbranch current, and decreased p-branch current. From Figure 2.11 (e), CO demonstrates a transfer curve shift indicative of p-doping of WSe₂, with positive V_{th} shift and increased p-branch current. After H₂S, NH₃, and/or CO gas exposure to the WSe₂ sensor device, the transfer curve changes by a half order of magnitude for current in all three cases, as shown in Figure 2.11 (a), (c), and (e), respectively. When running the same tests with the WSe₂ flake coated with PDMS, we no longer observe a change in the transfer curve Figure 2.11 (b), (d), and (f), indicating that the sensor now is unresponsive to those analytes and is at least semi-selective.

The experimental results for the uncoated sensor are consistent with Wang et al.'s first principle calculation in which charge depletion on the WSe₂ surface is found with the adsorption of NO₂, whereas NH₃ presents a charge accumulation near the WSe₂[149]. In comparison, after coating PDMS on the WSe₂ devices, the transfer curves show minute if any changes unless the analyte is NO₂, demonstrating that PDMS helps filter out the doping effects from H₂S, NH₃, and CO for the WSe₂ device while retaining sensitivity to NO_xs. More specifically, PDMS (0.316 D) is believed to prohibit the permeation/exposure of dissimilar gas such as polar gases H₂S (0.97 D), NH₃ (1.47 D), and non-polar gases CO (0.11 D). Hence, gases with dissimilar dipole moments are not absorbed and not able to react with the WSe₂ surface. Thus, no change of doping was observed upon exposure to H₂S, CO, or NH₃. In contrast, gases with similar dipole moments to PDMS like NO₂ should absorb readily into the PDMS and react with the WSe₂ sensor, creating a change in FET properties.



Figure 2.11. Transfer characteristics of the WSe₂ sensors with exposure to a) 10 ppm H₂S and b) 10 ppm H₂S with PDMS filter, c) 50 ppm NH₃, and d) 50 ppm NH₃ with PDMS filter, e) 100 ppm CO and f) 100 ppm CO with PDMS filter. Before gas exposure is in the black line. No PDMS filter with gas exposure is in the red line. With PDMS filter and with gas exposure is in the green line.

AFM Imaging of Sensors Pre and Post Exposure to NO2

To confirm that NO₂ causes a change in the doping state that results in the observed changes in transfer curves, we performed AFM phase image analysis. The phase imaging is powerful in surface characterization to detect chemical variation and reveal more detailed surface properties than the morphological image[165][·][166]. This method was applied to the mechanically exfoliated WSe₂ with and without the NO₂ exposure.

Phase lag is monitored between the signals that drive the cantilever to oscillate and the cantilever oscillation output. Electrostatic interactions between the AFM tip and the surface can be enhanced as the surface doping and carrier concentration increases[167]. A substantial decrease in the phase imaging contrast for the WSe₂ was observed by the AFM phase image after 5 ppm NO₂ exposure (Figure 2.12 (a)). This is consistent with p-doping from NO₂. In contrast, after 10 ppm H₂S exposure, phase imaging contrast increased, as showing in the highlighted circles in Figure 2.12 (b), indicative of n-doping.



Figure 2.12. AFM phase image of the WSe₂ flake before and after a) NO₂ b) H₂S exposure.

FET Characterization of Sensors to Mixture Analyte Exposure

To support that selective oils can help with selectivity in simulated operational environments, we then exposed the devices to gases with multiple analytes, including our target analyte, NO₂. The sensor device was placed in a flow-cell to simulate typical real exposure conditions. For the initial test, H₂S, an n-type dopant, and NO₂, a p-type dopant, were premixed

in a plastic bag 1:1 in a 10 L bag to create a final concentration of ~5 ppm H₂S and ~2.5 ppm NO₂. Since H₂S results in the n-doping of WSe₂ while NO₂ results in the p-doping of WSe₂, we expect the NO₂ signal to be suppressed in the presence of H₂S. Mixture gases in the bag were transferred into the falcon tube flow cell containing the WSe₂ for 40 mins. After this time period, transfer curves were acquired from the device both with and without the PDMS coating. The two-analyte mixtures all demonstrated transfer curves indicative of the p-doping shift; this indicates that WSe₂ already has a preferential absorption to NO₂ versus H₂S, and thus already confers a degree of selectivity, Figure 2.13 (a). Once the PDMS coating is applied to the channel, the V_{th} change is more than with no PDMS filter used in Figure 2.13 (b) as the indication of PDMS oil filtering H₂S, further enhancing selectivity.



Figure 2.13. Transfer characteristics of the WSe₂ sensors with exposure to a) mixture gases of the 5 ppm H₂S and 2.5 ppm NO₂ b) mixture gases of the 5 ppm H₂S and 2.5 ppm NO₂ with PDMS filter. No PDMS filter with gas exposure is in the red line. With PDMS filter and with gas exposure is in the green line.

Additional analytes were then added to the mixture and tested for sensor response. When 10 ppm H_2S , 5 ppm NO_2 is mixed with 50 ppm CO (p-doping), and 5000 ppm CO_2 in a 10L bag, only a transfer curve indicating p-doping from NO_2 is observed as shown (Figure 2.14). Interestingly, the transfer curves appear similar when CO is present with or without the PDMS coating (Figure 2.13).



Figure 2.14. Transfer characteristics of the WSe₂ sensors with exposure to a) mixture gases of the 5 ppm H₂S, 25 ppm CO, and 2.5 ppm NO₂ in 5000 ppm CO₂ b) mixture gases of the 5 ppm H₂S 25 ppm CO and 2.5 ppm NO₂ in 5000 ppm CO₂ with PDMS filter. No PDMS filter with gas exposure is in the red line. With PDMS filter and with gas exposure is in the green line.

To quantitatively compare WSe₂ sensor response to various gases and gas mixtures, the sensitivity of the WSe₂ sensors was calculated as the change of current at -20V before and after gas exposure. We reported the change in current per ppm to represent sensor sensitivity, both with and without the PDMS coating.

Equation 2.1

Sensitivity(S) =
$$\frac{\% \text{ Current change}}{ppm}$$

= $\frac{I_{After} - I_{Before}}{I_{Before}} \times \frac{100\%}{ppm}$

Equation 2.2

Normalized Sensitivity(NS)^{nofilter} =
$$\frac{S_{mixture gas}^{nofilter}}{S_{NO_2 Only}^{nofilter}}$$

Equation 2.3

$$NS^{PDMS} = \frac{S^{PDMS}_{mixture\ gas}}{S^{PDMS}_{NO_2\ Only}}$$

As expected single analytes had reduced sensitivity with the PDMS coating for all analytes tested, including the target NO₂ analyte (\sim 50 % reduction in sensitivity, Figure 2.15 (a)); we

hypothesize in-part due to the diffusion process of the gas molecules through the PDMS layer, a potential drawback that is the consequence of placing a semi-selective barrier over the sensor.

To determine sensor performance's selectivity, the response was normalized based on the ppm response to the NO₂ analyte alone (Figure 2.15 (a)). While the sensitivity was lower for all sensors with the PDMS coating, in all cases, the selectivity, as determined by the normalized ratio more than doubled, demonstrating the improved performance of the device in complex mixtures in a simulated environment.



Figure 2.15. a) Percentage current increase per ppm at -20V Vbg before and after single gases exposure to WSe2 gas sensors (Sensitivity). b) The ratio of mixture gases to NO2 of the percentage current increase per ppm at -20V Vbg before and after mixture gases exposure to WSe2 gas sensors (Normalized Sensitivity). The solid bar indicates the response of WSe2 without PDMS coating and the shaded bar for those with PDMS coating instead. Single gases NO2, H₂S, CO, and NH₃, are labeled in black, red, green, and blue, respectively. Inert gases (at STP), CO2, and CH4 are labeled in cyan and pink, respectively. Mixture gases, H₂S-NO₂, H₂S-CO-NO₂-(CO₂), and H₂S-CO-NO₂-(CH₄), are marked in purple, olive, and navy, respectively.

As a complementary way to evaluate the data, the V_{th} shift of the WSe₂ gas sensor exposed to various analytes, both with and without the PDMS filter, was reported (Figure 2.16). After coating with the PDMS oil, both p-doping from analytes such as CO and n-doping from analytes such as H₂S and NH₃ were dramatically reduced as indicated by the almost zero V_{th} change after the coating PDMS layer. The less reactive analytes CO₂ and CH₄ are labeled in cyan and pink, respectively. Surprisingly, WSe₂ devices demonstrate slight p-doping for both CO₂ and CH₄. However, PDMS oil effectively filters out the CO₂ and CH₄ analytes, reducing the observed V_{th} shift. We then tested the performance with and without the PDMS coating for analyte mixtures. The V_{th} change for these three analyte mixtures increased for the PDMS coated device compared to the intrinsic WSe₂ device. The increased V_{th} shift supports that while the bare device might have higher sensitivity for single analyte detection, the PDMS device is likely to have higher sensitivity in real-world applications with complex analyte mixtures containing common interfering agents H₂S, CO, and/or CO₂. It also demonstrates that future gas sensors using TMDs that measure the V_{th} shift are likely preferred to those that measure current as a function of a specific voltage.



Figure 2.16.The V_{th} shift of WSe₂ gas sensor with single gases (NO₂, H₂S, CO, and NH₃), inert gases (CO₂ and CH₄), and mixture gases (H₂S-NO₂, H₂S-CO-NO₂-(CO₂) and H₂S-CO-NO₂-(CH₄)). Filled symbols show the V_{th} shift without PDMS oil. Open symbols show the V_{th} shift with PDMS oil. Single gases NO₂, H₂S, CO, and NH₃ are labeled in black, red, green, and blue, respectively. Inert gases CO₂ and CH₄ are marked in cyan and pink, respectively. Mixture gases, H₂S-NO₂, H₂S-CO-NO₂-(CO₂), and H₂S-CO-NO₂-(CH₄) are labeled in purple, olive, and navy, respectively.

Figure 2.17 shows a comparison of NO₂ sensing response with and without PDMS filter with others' work[148], [168]–[170]. To fairly compare with works of literature, the gas sensor response is defined as *Response* (%) = $\frac{R_a - R_g}{R_g}$, where R_g and R_a are the sensor resistance under the exposure of NO₂ and air ambient, respectively. The WSe₂ sensor response to 5 ppm NO₂ at room temperature is 99.5% and 89.9% with the PDMS filter. Both types of WSe₂ sensor presented here is competitive with the most efficient WSe₂ sensor for room temperature and elevated temperature.



Figure 2.17. The response comparisons of NO₂ gas sensor (Black) and NO₂ gas sensor with PDMS filter (Red) with other WSe₂ based NO₂ gas sensors.

2.3.4 Conclusion

Novel 2D TMD materials are expected to play key roles in high-performance sensor applications. While sensor responses from the bare materials often exhibit low selectivity, virtually responding to any adsorbing gases, this work coating 2D TMD materials with non-volatile oils provides a useful, modular, and straightforward solution that is compatible with atomic thin layer sensing FETs. In this manuscript, we demonstrated the efficacy of this approach by creating a selective NO₂ sensor using a WSe₂ FET with a PDMS oil coating. The PDMS coating is used to filter out both polar gases such as H₂S and NH₃ and non-polar gases such as CO while allowing the target gas NO₂ to pass through. As demonstrated in the flow cell, the PDMS did act as a diffusion barrier, reducing the sensitivity by ~50% during active flow conditions. However, the

improvement in selectivity, as demonstrated by observing the V_{th} changes as a function of analyst exposure (Figure 2.16), more than offsets the loss in sensitivity and enables deployment in complex mixtures. Future work will identify polymeric oils that confer selectivity of the TMDs to other gases of interest, such as CO, H₂S, and NH₃, as well as to create a device architecture that can confine the oil while allowing sufficient gas flow to the surface, enabling deployment in wearable platforms.

2.4 Depleted Semiconductor Oxide Semiconductor (TMDs) Photodetector

Part of the material in this section of the chapter is in manuscript drafting, "Transition Metal Dichalcogenides-Insulator-Semiconductor Junction for Hybrid Photodetection Modalities ", Suki Naifang Zhang, Isaac Ruiz, Michael Goldflam and Zhihong Chen

2.4.1 Introduction

Photodetectors are critical components in many optoelectronic devices. It converts optical signals into electrical information and is widely used in sensing, displays, optical communication, and photonic applications[171]. Traditional commercial photodetectors are based on III–V semiconductors experiencing challenges as high cost, lattice mismatch, and high thermal budget as III–V devices on silicon electronics[172]–[174]. Even though photodetectors have reached a mature technology, to tackle challenges and surpass existing limitations, new device architectures and material systems are needed for low-cost fabrication and high sensitivity performance[171].

Common types of photodetectors include photodiodes, photoconductors, and photo-fieldeffect transistors (photoFETs). Photodiodes typically form a p-n junction or a Schottky junction. The junction leads to charge carrier separation after excitation, and carriers drift in different directions with the built-in electric field by diffusion[171], [174], or [175]. Photoconductors consists of semiconductor in contact with the source and drain contacts. Photoexcited charge carriers are separated by an applied drain bias and induce carrier density and device conductivity changes [171]. A promising device architecture that provides both low dark current and high gain is photoFETs. PhotoFETs performance can be tuned with gate modulation and favor the device performance to have low switch off dark current. Additional channel conductance changes can be activated by photoexcitation[171], [176]. For high-performance

photoFETs, the channel material ideally possesses high carrier mobility, a moderately large direct bandgap, and a thin profile channel[171].

For photoFETs, semiconducting channels in charge of both electronic transport and photon absorption performance. The thin channel favors large on/off and ultralow dark current since the device can be operated in full depletion, but light absorption may need to be sacrificed. On the other hand, bulk channels benefit from the thick profile but suffer from the reduced on/off ratio as the channel cannot be switched off entirely. There is always a tradeoff between efficient electronic transport or strong optical responsivity[105], [171].

These challenges can be disentangled as the 2D channel in charge of the electronic transport while using the substrate to control the light absorption. Photogenerated carriers in the substrate can modulate the electric field at the 2D channel through the capacitive coupling effect[99], [105], [177]–[180]. Unlike the graphene with no bandgap, 2D TMDs such as MoS₂ and WSe₂, and PtSe₂ are semiconductors bandgaps ranging from 1.57 to 2 eV more suitable photodetectors applications as the channel of PhotoFETs [150], [181]–[183].

In this work, we combine lightly doped silicon and MoS₂ and WSe₂ and PtSe₂ to form a depleted semiconductor-oxide-semiconductor (TMDs) photodetector. The TMDs photodetector detects optical signals via a photo-interfacial gating mechanism. As the lightly doped silicon substrate absorbs the laser power, the photogenerated carriers would gate the TMDs and change TMDs' electrical conductivity.

2.4.2 Methods

The TMDs PhotoFETs are fabricated on low doped n-type and p-type Si substrates using both e-beam lithography and optical lithography. The schematic of the device structure is shown in Figure 2.18 (a). Two kinds of channels are used in the PhotoFETs fabrication, include full area CVD monolayer TMDs and CVD monolayer triangle TMDs flakes (Figure 2.18 (b) and (c)).



Figure 2.18. a) The schematics of the device structure. The optical image of b) CVD monolayer TMDs devices fabricated using optical lithography with different channel length and channel width and c) CVD monolayer triangle TMDs flakes

Full area CVD monolayer TMDs are fabricated using optical lithography follows the sequence of 1. Substrate Cleaning, 2. Alignment Mark Fabrication, 3. TMDs Wet Transfer, 4. TMDs Etching 5. Contact Metal Fabrication, and 6. Device Passivation with a) Hexagonal Boron Nitride (hBN) or b) Hafnium dioxide (HfO₂).

CVD monolayer triangle TMDs flakes are fabricated using e-beam lithography with the same process flow as the optical lithography except step 4. TMDs etching. No channel isolation is needed for TMD flakes. Overnight 400°K vacuum annealing in the probe station is performed

before step 5. Contact Metal Fabrication and step 6. Device Passivation to reduce device hysteresis. Electrical characterization is taken before and after device passivation.

Step 1: Substrate Cleaning

As-received silicon (Si) substrates from Sandia National Lab are coated with photoresist for protection during shipment. These substrates are cleaned with the remover PG, the toluene, the acetone, the isopropanol alcohol (IPA) sequentially for 5 mins sonication before device fabrication. After the cleaning, the substrate is dried by nitrogen blowing.

Step 2: Alignment Mark Fabrication

The alignment marks are fabricated on the pre-cleaned substrate, either using the optical lithography with a hard mask or the e-beam lithography.

Step 3: TMDs Wet Transfer

Polystyrene (PS) assisted wet transfer is a commonly used method to transfer the CVD grown TMDs on SiO₂/Si substrate onto another substrate. Full area CVD monolayer TMDs and monolayer triangle TMDs flakes on SiO₂/Si substrate are purchased from 2D Layer or 2D Semiconductor. PS solution is drop-cast onto the TMD on SiO₂/Si substrate. After PS is dried in the air, use a tweezer to scrape PS off the edge of the sample. The sample is baked at 90 °C for 5 mins on a hotplate to remove the solvent in the PS coating. After baking, the sample is soaked in water in a Patri dish. The PS layer can be peeled off from the SiO₂/Si substrate at the water and air interface. Use the substrate with the alignment mark to pick up the PS layer. After the PS layer is dried in the air overnight, PS can be removed using toluene soaking and follows with Acetone, IPA cleaning, and nitrogen blow dry. TMD is transferred from the SiO₂/Si substrate to the target substrate with the alignment mark.

Step 4: TMDs Etching

The channel of full area CVD monolayer TMDs is patterned using optical lithography. HMDS and AZ5214 are spin-coated onto the pre-cleaned substrate with 4000 rpm for 60 sec. The photoresist is baked at 110 °C for 1 min on a hotplate. Devices are then patterned with an optical hard mark using MJB 2 with light exposure of 8s. After the light exposure, the sample is postbaked on a hotplate at 110 °C 45 sec for the image reversal. The sample is followed by the flood exposure of UV light for 60 sec using MJB 2. The sample is developed in the MF-26A developer for 30 sec, followed by 2 mins water soaking to avoid MF-26A residual. After that, the patterned sample is cleaned with water and dried by nitrogen blowing. The sample is etched with SF₆/Ar for 10s or Cl_2/O_2 for 15s using Panasonic E620 Etcher. After the etch, the sample is soaked in acetone overnight to remove the optical resist. After the lift-off process, the sample is cleaned with IPA and dried with a nitrogen gun.

Step 5: Contact Metal Fabrication

Source and drain contacts were patterned using either optical lithography or e-beam lithography. The fabrication process is the same as listed in session 2. Alignment Mark Fabrication. 100 nm Ni as contact metal is deposited onto the patterned sample at the rate of 1A/s using PVD E-Beam Evaporator. Pd contact metal with Ti/Pd/Au (1 nm/20 nm/40 nm) is deposited onto the patterned sample at the rate of 1A/s using CHA e-Beam Evaporator. After the metal deposition, the sample is soaked in acetone overnight. After the contact metal lift-off, the sample is cleaned with IPA and dried using a nitrogen gun.

Step 6: Device Passivation

The TMDs PhotoFETs can be passivated either with hBN coating or ALD HfO₂ layer after 400K vacuum annealing in the probe station overnight.

hBN Passivation

CVD monolayer hBN on SiO₂/Si substrate is purchased from Graphene Supermarket. PS solution is drop-casted onto the hBN on SiO₂/Si substrate. After PS is dried in the air, use a tweezer to scrape PS off the edge of the sample. The sample is baked at 90 °C for 5mins on a hotplate to remove the solvent in the PS coating. After baking, the sample is soaked in water in a Patri dish. The PS layer can be peeled off from the SiO₂/Si substrate at the water and air interface. Use the substrate with the alignment mark to pick up the PS layer. After the PS layer is dried in the air overnight, PS can be removed using toluene soaking and follows with Acetone, IPA cleaning, and nitrogen blow dry. hBN is transferred from the SiO₂/Si substrate to the devices for Passivation.

HfO₂ Passivation

A window for ALD deposition on the devices is patterned using e-beam lithography. PMMA is spin-coated onto the pre-cleaned substrate with 6000 rpm for 60 sec. PMMA is baked at 180 °C for 5 mins on a hotplate to remove the solvent. The deposition windows are patterned using Raith nanofabrication instrumentation. The post-exposed e-beam resists were developed in 75% isopropanol for 1 min. 1nm Al seeding layer is deposited onto the sample at the rate of 0.1A/s using PVD E-Beam Evaporator. The seeding layer would be oxidized in the air for one hour before putting the sample into the ALD chamber for the ALD deposition. 90 °C ALD deposition recipe is used to grow 10nm HfO₂ on the sample using Cambridge Nanotech Fiji ALD. The 60-sec purging time is chosen between each pulse of H₂O and trimethylaluminum (TMA) deposition during the ALD growth. After the ALD growth, the sample is soaked in acetone overnight for the lift-off process. After the ALD passivation lift-off process, the sample is cleaned with IPA and dried using a nitrogen gun.

Optical lithography Process

Hexamethyldisilane (HMDS) adhesion promoter and AZ5214 photoresist are spin-coated onto the pre-cleaned substrate with 4000 rpm for 60 sec. The photoresist is baked at 110 °C for 1min on a hotplate. Devices are patterned with an optical hard mark using Suss MJB 2 UV400 Mask Aligner with 405 nm UV light exposure of 18 sec. After the light exposure, the sample is developed in MF-26A developer for 30 sec, follow with 2 mins water soaking to avoid MF-26A residual. After that, the patterned sample is cleaned with water and dried by nitrogen blowing. 100 nm Ni as the alignment mark metal is deposited onto the patterned sample at the rate of 1A/s using PVD E-Beam Evaporator. The sample is soaked in remover PG for 2 hours for the lift-off process. After the alignment mark lift-off, the sample is cleaned with Acetone, IPA and follows with nitrogen blow dry.

e-beam lithography Process

PMMA A4 950 e-beam resist is spin-coated onto the pre-cleaned substrate with 6000 rpm for 60 sec. e-beam resist is baked at 180 °C for 5 mins on a hotplate. Devices are patterned using Raith nanofabrication instrumentation. The post exposed e-beam resists were developed in 75% isopropanol for 1 min, followed by e-beam metal evaporation of 20 nm Ti and 100 nm Au as

alignment mark metal using CHA E-Beam Evaporator. The sample is soaked in the remover PG for 2 hours for the lift-off process. After the alignment mark lift-off, the sample is cleaned IPA and follows with nitrogen blow dry.

Electrical Characterization

The initial electrical characterization on the TMDs photoFETs, both dark and illuminated conditions, would be examined using an HP 4156C semiconductor parameter analyzer at Purdue Lab for prescreen device performance. The selected samples would be shipped out to Sandia National for optical characterization. Before testing the optical response of the TMDs photoFETs, the transfer characteristics of the TMD FETs for both dark and illuminated conditions are taking using an HP 4155B semiconductor parametric analyzer (SPA) at Sandia National Laboratory. LabVIEW was utilized to record the source and drain currents as a function of applied back gate bias. All electronic measurements were taken at room temperature in a Signatone probe station located inside an optically dark box that is shielded from electromagnetic interference.

Optical Characterization

The optoelectronic characteristics of the TMDs photoFETs are characterized in this work. The 514 nm laser would deliver light to the TMDs photoFETs on the probe station. The laser intensity is controlled using neutral density filters.

2.4.3 **Results and Discussion**

Optoelectronic Response of TMDs PhotoFETs

The Capacitance-voltage (C-V) measurements on both low doped n-Si substrate and low doped p-Si substrates in the MOS capacitors structure are shown in Figure 2.19. The C-V measurements were taken on an HP 4284A Precision LCR meter. The MOS devices were initially held under a depletion bias then swept into accumulation. The C-V measurements help us understand the operation state of the TMDs PhotoFETs under illumination. The Si substrate is responsive to the light absorption, and the induced carrier changes due to light absorption would gate the TMDs and change the TMDs' conductivity.



Figure 2.19. a) The C-V measurements on the low doped n-Si substrate and b) The C-V measurements on the low doped p-Si substrates, reprint from Ruiz, Isaac, et al. ACS Applied Nano Materials (2019).

The optoelectronic characteristics of the MoS_2 photodetector were measured in terms of the gate bias and different laser illumination powers are shown in Figure 2.20 (a). The MoS_2 is on the low-doped n-Si substrate. The cyan curves the transfer characteristics of MoS_2 as it is in dark. As the laser power increases from 10nW to 250 nW, the drain current increased substantially compared to that in the dark condition when the device is biased beyond 5V gate bias. The optoelectrical characteristics of MoS_2 photoFETs as a function of time and optical powers are shown in Figure 2.20 (b). The device is biased from accumulation, depletion, and back to the accumulation, as shown in Figure 2.20 (b). As the laser power increases, drain currents increases which is an indication of photogenerated carriers increases. Besides, the response is faster compare with dark current or low power current. At the fixed gate bias, the size of the depletion well is fixed due to the electric field applied to the device is fixed. With increasing laser power, more carriers filled into the depletion well show up the light response faster.



Figure 2.20. a) The optoelectrical characteristics of MoS₂ photoFETs from dark to 250nW illumination. b) The optoelectrical characteristics of MoS₂ photoFETs as a function of time and optical power(dark to 250nW). The device is biased from accumulation, depletion, and back to the accumulation.

To understand what happens to the TMDs device as the laser shining on, three regions of the optoelectronic characteristics are taken into consideration. At region I, the flatband voltage (V_{FB}^{Si}) of Si is at -0.5 V according to the C-V in Figure 2.19 (a). By applying -0.5 V gate bias to Si is equivalent to apply 0.5V gate bias to the MoS₂. The threshold voltage (V_T^{TMD}) of MoS₂ is at 2.5 V. At region I, Si is in the accumulation state as the applied gate bias smaller than 0.5V to MoS₂. At the same time, the MoS₂ device is still in the off state. As the low doped Si substrate absorbs the laser power, majority carriers are generated, no carrier change would be observed on the MoS₂ devices. At region II, the threshold voltage (V_T^{Si}) of Si is at -1.5V (Figure 2.19 (a)), which equivalent to 1.5V gate bias to MoS₂. In between 1.5V and 2.5 V gate bias to MoS₂, Si starts to be depleted, and the depletion well is created due to the applied electric field from the gate bias. Photogenerated electron and hole pairs are created as the Si substrate absorbs laser power Figure 2.21 (b). The majority carrier would diffuse to the bulk and leave the minority carriers trapped at the interface of Si/Dielectric Figure 2.21 (c). The trapped minority carriers would induce opposite charges to the interface of MoS₂/Si and modify the channel conductivity of MoS₂(Figure 2.21 (d)). However, at gate bias between 1.5V and 2.5 V, as the Si depleted, MoS₂ is still in the off state. Photogenerated minority carriers would be hard to gate the off state MoS₂. No differentiable photoresponse would be observed as increasing laser powers. The desired operation state would
be at region III, in which Si is in the deep depletion state while MoS_2 is at the subthreshold region or on-state, at the gate bias larger than 2.5V. As the Si substrate absorbs the laser power, trapped minority carriers at the interface of Si/Dielectric would gate the MoS_2 channel and modify MoS_2 conductivity.



Figure 2.21. Operation states of the MoS₂ photoFETs as a function of gate bias

Figure 2.22 shows the response of the TMDs in terms of illumination. In Figure 2.22 (a), The TMDs photoFET is in the dark. In Figure 2.22 (b), the laser shine on the TMDs photoFET and the electron-hole pair are created due to the Si's light absorption. In Figure 2.22 (c), after the electron-hole pair is created, the majority carriers diffuse to the bulk while the minority carriers got trapped at the Si/Dielectric interface. In Figure 2.22 (d), the trapped minority carrier induces opposite charges to the interface of TMD/Dielectric and changes the conductivity of TMDs.



Figure 2.22. Response of the TMDs in terms of illumination. a) The TMDs photoFET is in the dark. b) Laser shines on the TMDs photoFET, the electron-hole pair is created by the Si's light absorption. c)Majority carriers diffuse to the bulk and leave the minority carrier at the Si/Dielectric interface. d)The trapped minority carrier induces opposite charges to the interface of TMD/Dielectric.

Photogenerated current is proportional to the channel mobility, minority carriers number trapped at the depletion well, and the applied electric field ($I_{ph} \propto u \Delta pn E$). We desire to improve the interface (Si/Dielectric, Dielectric/TMD, and TMD/Air) quality by reducing the trap state and trap charges and passivate the TMDs photoFETs after device fabrication. Any trap states and impurities would decrease the photogenerated current as mobility (u) and minority carrier number $\Delta pn E$ suffers. The scattering happens as the carriers meet the impurities and reduce the channel mobility. If the trap state locates the interface, recombination events occur and the photogenerated minority carrier number would be reduced. As the increasing electric field is applied to the TMD channel, a more profound depletion well can trap more photogenerated minority carriers and induce more significant current change in the TMD device performance.

Annealing Effect on TMDs Photodetector

Due to the water and solvent molecules may be introduced to the interfaces and channel during the fabrication process, annealing steps in different stages of the device fabrication and testing process are added to remove excess water and solvent molecules. Figure 2.23 shows a transfer characteristic of the WSe2 device after device fabrication with large hysteresis. After probe station annealing as described in session 2.4.2, hysteresis reduced, and a more profound light response is observed compared with dark. Compare with no post-annealing, half order of current change due to the light exposure increases to 2 orders of magnitude of current change at 3V gate bias.



Figure 2.23. The annealing Effect to WSe₂ PhotoFETs fabricated using optical lithography

hBN Passivation to TMDs Photodetector

To preserve the channel from the impurities and moisture after the fabrication and annealing process, the hBN coatings are transferred onto the TMDs photoFETs. Figure 2.24 presents the WSe₂ transfer characteristics before and after hBN passivation. WSe₂ photoFETs are fabricated on the low doped p-Si substrate. WSe₂ shows the ambipolar characteristics with both electron and hole conduction. To bias the p-Si substrate into a deep depletion state, WSe₂ is chosen explicitly for pFETs purpose. By putting the hBN coating on top of the WSe₂ photoFETs, the p-branch on current increases while the hysteresis gets reduced for both the e-beam lithography fabricated devices and optical lithography fabricated devices.



Figure 2.24. The hBN passivation to WSe₂ PhotoFETs fabricated using both e-beam and optical lithography. a) and c) The transfer characteristic of WSe₂ devices before the hBN passivation. b) and d) The transfer characteristic of WSe₂ devices after the hBN passivation. a) and b) WSe₂ device is fabricated using the e-beam lithography process. c) and d) WSe₂ device is fabricated using the optical lithography process.

2.4.4 Conclusion

А sensitive photodetector is presented based on а deeply depleted semiconductor(Si)/oxide/semiconductor(TMDs) junction using the TMDs as the channel materials and the Si substrate as the light absorption layer. We fabricated the MoS2, WSe2, PtSe2 photodetector using e-beam lithography and optical lithography process and understood the operation mechanism of photo interfacial gating using these TMDs photoFETs. To preserve and improve the photogenerated current by the TMDs photoFETs, annealing steps and passivation coatings (hBN and ALD coatings) are implemented.

APPENDIX A. METAL PHTHALOCYANINE (PCS) DOPING TO TMDS



Figure A.1. Transfer characteristics of a MoS₂ device before and after CuTsPc doping, and removal of the doping effect by resolubilizing the dopants in solvent.



Figure A.2. The trend of correlating V_{TH} shift after molecular doping with work functions of metal core atoms in MoS₂ devices



Figure A.3. The Effect of fluorination on Metal-phythalocyane doping of by comparing doping effect of CuTsPc and F-CuTsPc in WSe₂ devices.



Figure A.4: UV-vis spectra of metal free phythalocyanine (black), PtTsPc (red), and Na₂TsPc (blue)

APPENDIX B. SELECTIVE ELECTRONIC NO₂ SENSORS USING POLYDIMETHYLSILOXANE FILTER ON WSE₂ DEVICES



Figure B.1. Thickness of WSe₂ is confirmed by AFM.



Figure B.2. Transfer characteristics of the WSe₂ sensors with exposure to a) 5000 ppm of CO₂ for 10min b) 5000 ppm of CO₂ for 10min with PDMS filter. c) 25000 ppm of CH₄ for 10min d) 25000 ppm of CH₄ for 10min with PDMS filter. No PDMS filter with gas exposure is in the red line. With PDMS filter and with gas exposure is in the green line.



Figure B.3. a)Current change per ppm at V_{gs}=-10V for single gas exposure and carrier gas exposure. Open squares show statistics of devices with PDMS filter. b) Current change per ppm at V_{gs}=-10V for mixture gas exposure. Single gases NO₂, H₂S, CO, and NH₃, are labeled in black, red, green, and blue, respectively. Carrier gases CO₂ and CH₄ are marked in cyan and pink, respectively. Mixture gases, H₂S-NO₂, H₂S-CO-NO₂-(CO₂), and H₂S-CO-NO₂-(CH₄) are labeled in purple, olive, and navy respectively.

Figure B.4 shows the transfer characteristics of WSe₂ devices after gas exposure as time passes. For 1000 ppm NO₂, WSe₂ devices reach maximum doping level immediately (labeled in the red circle in Figure S4 (a)) after gas exposure and start reducing the doping level to saturation limit after 12 mins (marked in a black circle in Figure B.4 (a)). It is suspected that the entire WSe₂ channel is initially are physiosorbed and chemisorbed by the large quantity of NO₂ molecules. Due to the crowding of NO₂ molecules, some of the physiosorbed NO₂ molecules may lose contact with the WSe₂ channel and start to evaporate to air and leave the chemisorbed on the WSe₂ channel with stable doping level.

For 5 ppm NO₂, WSe₂ devices reach a maximum doping level immediately (labeled in a black circle in Figure B.4 (b)). It is suspected that at the low level of NO₂, only a partial WSe₂ channel is in contact with NO₂ molecules, and the channel can quickly grab all the absorbed NO₂ molecules, which the doping level remains the same as time passes.

For 5 ppm NO_2 with PDMS coating, PDMS serve as diffusion barriers for NO_2 molecules. Most of the NO_2 are in contact with WSe_2 immediately after gas exposure. However, some NO_2 molecules may be delayed due to the diffusion process. The on-current of the WSe2 devices

slightly increases and reaches the saturation doping level after 4mins of gas exposure (labeled in a black circle in Figure B.4 (c)).



Figure B.4. Adsorption kinetics of WSe₂ devices with exposed to a) 1000 ppm NO₂, b) 5 ppm NO₂, and c) 5 ppm NO₂ With PDMS coating as time passes after gas exposure.



Figure B.5. Output characteristics of WSe₂ devices of a) device 1 and b) device 2.

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VITA

Suki Zhang was born and raised in Shenzhen, China. She moved to the United States with her family and settled down in the bay area when she was in high school.

She received a Bachelor's degree in Materials Engineering from the University of California, Los Angeles, in 2013. Her undergraduate research focused on improving polymer composites performance with different nanoparticles in Professor Qibing Pei's soft materials lab.

She obtained a Master's degree in Materials Science Engineering from Cornell University in 2015.Her master research aimed to improve the dopant activation and extend InGaAs' damage threshold using the laser spike annealing method in Prof. Michael Thompson's transient thermal process lab. She has done extensive Raman mapping on InGaAs to understand how laser spike annealing is different from conventional annealing methods.

She started her Ph.D. study in the Electrical Computer Engineering department at Purdue University in 2015 and expects to graduate in May 2021. Her Ph.D. study focused on "Electronic Application of Two Dimensional Materials" in Professor Zhihong Chen's group. In automotive industry applications, she used different kinds of graphene coating to reduce the friction of the electrical terminal and prevent corrosion from happening on the terminals' surface. She also improved the piezoelectric composite cells performance with reduced graphene oxide for energy harvesting application. Besides graphene applications, she also had extensive device fabrications and characterizations using transitional metal dichalcogenides (TMDs). She explored various chemical doping strategies to achieve high-performance TMDs devices. She also utilized TMDs as a selective NO₂ gas sensor application with a Polydimethylsiloxane filter. Last but not least, she studied photo interfacial gating mechanism on TMDs oxide semiconductor stack as photodetector application.

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