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TECHNICAL REPORT

Radiation Effects in 2D Heterostructure Devices

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RADIATION EFFECTS IN 2D HETEROSTRUCTURE DEVICES

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1. INTRODUCTION

The overall objective of this project was to develop a fundamental understanding of radiation-induced defects in heterostructure devices fabricated using 2D materials (graphene, h-BN, Mo/W S₂/Se₂), including the atomic-scale nature and location of defects in the heterostructures, the impact of these defects on operation for both lateral and vertical electronic transport, and the potential of these devices in a high radiation environment. Due to the strong impact of interfaces and passivation on the radiation responses of 2D materials, radiation effects in heterostructures are expected to be complex. The PIs combined experience in 2D materials synthesis and characterization, device fabrication and characterization, radiation and reliability effects, and density-functional-theory (DFT) calculations to develop a fundamental understanding of radiation-induced defects in these devices.

This report first lists the personnel supported (Section 2) and the theses, publications and presentations (Section 3) resulting from the project. A comprehensive report of the significant accomplishment and findings is then described (Section 4). The impact of radiation on the lateral electronic transport in graphene (Section 4.1) and MoS₂ (Section 4.2) with various overlayers is first described. Section 4.3 describes the fabrication of two-terminal vertical heterostructures from MoS₂ synthesized directly onto gold without requiring any transfer steps. Section 4.4 describes the impact of metal-MoS₂ Fermi level pinning on the resultant vertical heterostructure electronic properties. Section 4.5 describes the radiation response of MoS₂-based vertical heterostructure devices where electronic transport is out-of-the-plane.

2. PERSONNEL SUPPORTED

2.1 Principal Investigators

- Prof. Eric M. Vogel, Georgia Institute of Technology, School of Materials Science and Engineering
- Prof. Dan. Fleetwood, Vanderbilt University, Department of Electrical Engineering and Computer Science
- Prof. Sokrates Pantelides, Vanderbilt University, Department of Physics and Astronomy
- Dr. Enxia Zhang, Vanderbilt University, Department of Electrical Engineering and Computer Science

2.2 Post-doctoral Researchers

- Dr. Andrew O'Hara, Vanderbilt University, Department of Physics and Astronomy

2.3 PhD Students

- Christopher Perini, Georgia Institute of Technology, School of Materials Science and Engineering
- Pan Wang, Vanderbilt University, Department of Electrical Engineering and Computer Science

3. PROJECT THESES, PUBLICATIONS AND PRESENTATIONS

3.1. Theses

- Chris Perini, Georgia Institute of Technology, PhD in Materials Science and Engineering, May 2019, “Impact of As-synthesized and Radiation-induced Defects in Two-dimensional Heterostructures”
<https://smartech.gatech.edu/bitstream/handle/1853/61255/PERINI-DISSERTATION-2019.pdf?sequence=1&isAllowed=y>
- Pan Wang, Vanderbilt University, PhD in Electrical Engineering, August, 2019, “Radiation Effects and Low Frequency Noise of Microelectronic Devices Based on Two-Dimensional Materials”
<https://etd.library.vanderbilt.edu/available/etd-07192019-104923/unrestricted/Wang.pdf>

3.2. Publications

- P. Wang, C. J. Perini, A. O’Hara, H. Gong, P. Wang, E. X. Zhang, M. W. McCurdy, D. M. Fleetwood, R. D. Schrimpf, S. T. Pantelides, and E. M. Vogel, "Total Ionizing Dose Effects and Proton-Induced Displacement Damage on MoS₂-Interlayer-MoS₂ Tunneling Junctions," *IEEE Transactions on Nuclear Science* **66**, 420 (2019).
- P. Wang, H. Kalita, A. Krishnaprasad, D. Dev, A. O’Hara, R. Jiang, E. Zhang, D. M. Fleetwood, R. D. Schrimpf, S. T. Pantelides, and T. Roy, "Total-Ionizing-Dose Response of MoS₂ Transistors With ZrO₂ and h-BN Gate Dielectrics," *IEEE Transactions on Nuclear Science*, vol. 66, pp. 1584-1591, 2019.

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- P. Wang, C. Perini, A. O'Hara, B. R. Tuttle, E. X. Zhang, H. Gong, L. Dong, C. Liang, R. Jiang, W. Liao, D. M. Fleetwood, R. D. Schrimpf, E. M. Vogel, and S. T. Pantelides, "Radiation-induced charge trapping and low-frequency noise of graphene transistors," *IEEE Transactions on Nuclear Science* **65**, 156-163 (2018).

- P. Campbell, J. K. Smith, W. J. Ready, and E. M. Vogel, “Material Constraints and Scaling of 2-D Vertical Heterostructure Interlayer Tunnel Field-Effect Transistors,” *IEEE Transactions on Electron Devices* **64**, 2714-2720 (2017).

3.3. Presentations

- P. Wang, K. Hirokijyoti, A. Krishnaprasad, D. Dev, A. OHara, R. Jiang, E. Zhang, D. Fleetwood, R. Schrimpf, S. Pantelides and T. Roy, “Total-Ionizing-Dose Response of MoS₂ Transistors with ZrO₂ and h-BN Gate Dielectrics” 2018 18th *European Conference on Radiation and Its Effects on Components and Systems (RADECS)*, Gothenburg, Sweden, September 16-21, 2018.
- P. Wang, A. O’Hara, H. Gong, P. F. Wang, E. X. Zhang, D. M. Fleetwood, R. D. Schrimpf, S. T. Pantelides, C. J. Perini, and E. M. Vogel, “Radiation Response of MoS₂-Interlayer-MoS₂ Tunnel Junctions,” IEEE Nuclear and Space Radiation Effects Conference, Kona, HI, July 16-20, 2018.
- E. M. Vogel (invited), “Large Area Synthesis, Characterization and Application of 2D Materials,” AVS Appalachian Regional Microscopy Society Meeting, Knoxville, TN, Oct. 5, 2018.
- E. M. Vogel (invited), “Two-dimensional Materials for Vertical Heterostructures,” US-EU Workshop on Two-dimensional Materials, San Sebastian, Spain, September 14, 2018.
- E. M. Vogel (invited), “Application and Synthesis of Large-area 2D Materials,” TMS Meeting, Phoenix, AZ, March 13th, 2018.
- E. M. Vogel (invited), “2D Vertical Heterostructures for Novel Tunneling Device Applications,” GOMACTech, Reno, NV, March 22, 2017.

- E. M. Vogel (invited), “2D Materials for Tunnel Diodes,” Materials and Manufacturing Processes Technical Interchange Meeting (TIM), Dayton, OH, March 28, 2017.
- C. J. Perini, M. J. Muller, E. M. Vogel, “Plasma-Assisted Sulfurization of Thin Molybdenum-Containing Films for MoS₂ Synthesis,” Semiconductor Interface Specialists Conference, San Diego, CA, December 6-9, 2017.
- D. M. Fleetwood (short course), “Evolution of total ionizing dose effects in MOS devices with Moore’s Law scaling,” European Conference on Radiation Effects on Components and Systems (RADECS), Geneva, Switzerland, Oct. 2, 2017.
- A. O’Hara, P. Wang, C. J. Perini, D. M. Fleetwood, E. M. Vogel, S. T. Pantelides, “Passivation and Depassivation of Defects in Graphene-based field-effect transistors,” American Physical Society Meeting, New Orleans, LA, March 13-17, 2017.
- P. M. Campbell, J. Chiu, E. Snyder, A. Gupta, H. Ray, H. Chen, K. Wenzel, B. Wagner, J. Ready and E. Vogel, “Lower Temperature 2D MoS₂ Deposition Utilizing Plasma Processing,” MRS Spring Meeting, Phoenix, AZ, April 17-21, 2017.
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4. ACCOMPLISHMENTS AND FINDINGS

4.1 Impact of h-BN and Al₂O₃ Over-layers on Radiation Response of Graphene [1]

In this section, the role of overlayers in the radiation response of graphene field effect transistors (FETs) was studied. Graphene FET devices were fabricated onto a 300 nm SiO₂/Si substrate and cleaned. Two different passivation materials were chosen to reside on top of the graphene devices: Al₂O₃ and hexagonal boron nitride (hBN). Al₂O₃ was deposited using atomic layer deposition (ALD), yielding two separate samples with 4 and 19 nm thick Al₂O₃ overlayers. 40 nm hBN was transferred on top of the graphene FETs using a standard wet transfer technique [2]. An additional set of devices was left unpassivated to act as a control group.

The graphene FETs were irradiated with 10 keV X-rays at a dose rate of 30 krad(SiO₂)/min at room temperature while grounding the source and drain contacts and applying a gate bias of +5, 0, or -5 V. Baking was performed in ambient conditions at temperatures up to 400 K. When low-frequency noise is caused by random thermally activated processes with broad energy distributions relative to kT , the frequency and temperature dependences of the noise are correlated by the Dutta-Horn model, which can be used to relate defect energy to temperature and frequency through the simple expression [3, 4]

$$E_0 \approx -kT \ln(\omega \tau_0) \quad (1)$$

where $\omega = 2(\pi)(f)$ and τ_0 is the transport scattering time. For eq. (1) to successfully be used, the noise must be accurately described by the full Dutta-Horn model. Low-frequency (1/f) noise measurements were performed on the graphene FETs at temperatures ranging from 85 to 400 K. V_{ds} was held at 0.02 V, with a fixed gate bias of -20 V from the Dirac point, where the current is at a minimum. Figure 1 shows the noise frequency dependence of the graphene transistors with 19

nm Al_2O_3 compared to predicted values using the full Dutta-Horn model. The agreement between the measured and calculated dependences implied that eq. (1) can be used to infer defect energies from $1/f$ noise measurements.

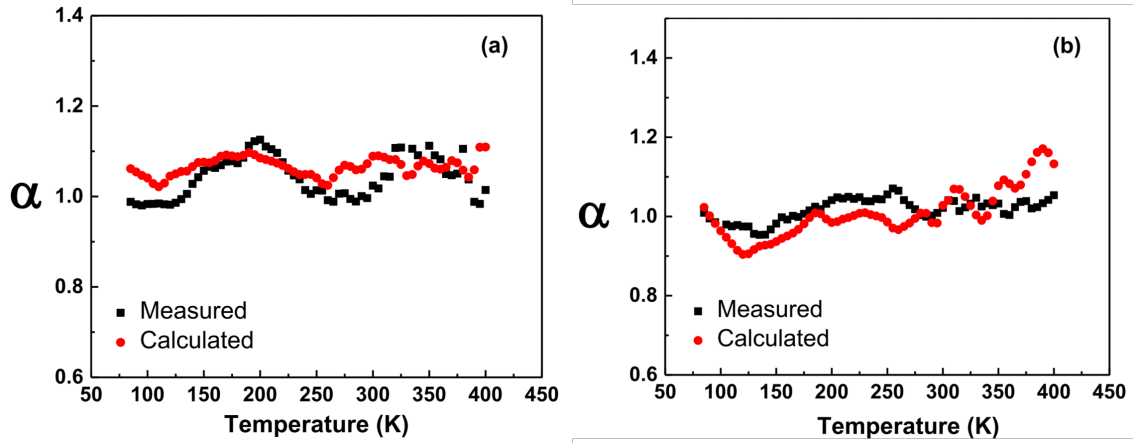


Figure 1. Comparison of measured and predicted noise frequency dependence of the 19 nm Al_2O_3 passivated graphene FETs before (a) and after (b) baking at 400 K for 24 hours.

To obtain a baseline for the performance of the graphene FETs, the effects of room-temperature aging and high-temperature baking were explored. Figure 2 shows I_d - V_g characteristics for a 19 nm Al_2O_3 passivated FET before and after it was baked at 400 K. After an initial 24 hour bake at 400 K, the charge neutrality point (CNP) shifts approximately 10 V closer to 0, before shifting to its original value when stored in ambient conditions for 48 hours. A subsequent bake successfully reduces the voltage value of the CNP, indicating that the regeneration process is reversible.

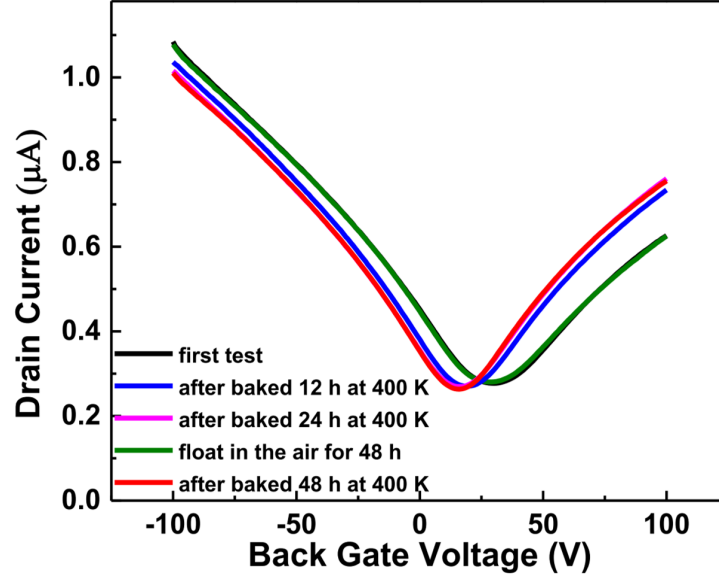


Figure 2. I_d - V_g curves with $V_d = 0.02$ V for a 19 nm Al_2O_3 passivated graphene FET before and after devices were baked at 400 K. The Dirac point shifts closer to 0 V when baked, and returns to its initial value when re-exposed to atmosphere.

To understand what defects and impurities may lead to the observed changes when exposed to baking, normalized $1/f$ noise measurements were taken on the 19 nm Al_2O_3 passivated FETs. Figure 3 shows the normalized low-frequency noise magnitude $S_v f/T$ from 85 to 400 K for the different baking conditions. The top axis of Figure 3 represents the effective defect energy, obtained from eq. (1). For these defect-energy distribution estimates, the value of τ_0 was set at 1×10^{-13} seconds for graphene [5]. The magnitude of the low-frequency noise decreases after the device is baked at 400 K, and returns to its original level after exposure to air for 49 hours. The reduction in trapped-negative charge density (CNP shift towards negative values) observed in Figure 2 and decrease in noise observed in Figure 3 are likely due to outgassing and desorption of water-related mobile impurities in through the graphene passivation layer [6, 7] and/or defect passivation due to hydrogen motion within the dielectric layers [8]. A noticeable peak is visible in

Figure 3 at $\sim 200\text{-}225$ K, corresponding to effective defect energies of 0.4 to 0.5 eV (upper x-axis). The breadth of the effective defect energy distribution implies that there is not a single defect type that dominates the response; in contrast, various hydrogen/water complexes are likely responsible for the shifts in CNP and increased noise.

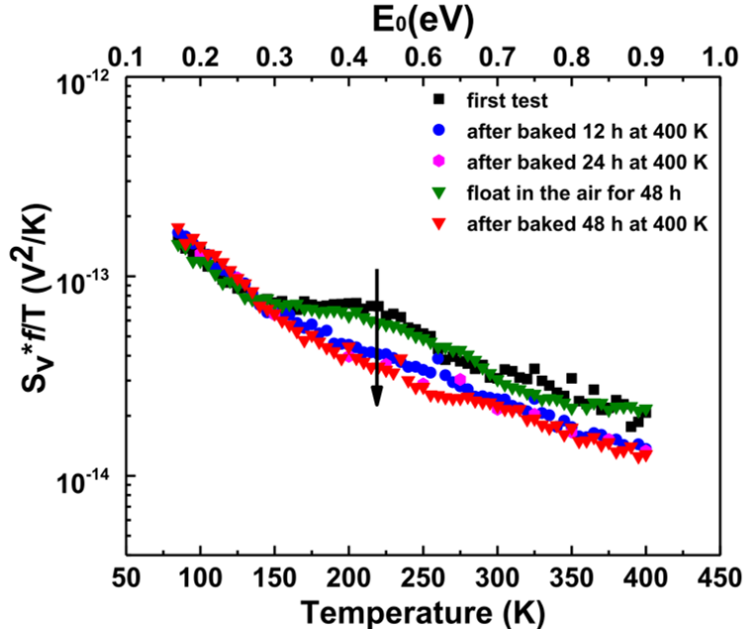


Figure 3. Normalized low-frequency noise magnitude $S_V f/T$ at $f = 10$ Hz for the device shown in Figure 2 as a function of temperature for different baking conditions. Devices were measured at $V_g - V_{CNP} = -20$ V.

Now that a baseline for the graphene FET performance is established, including defect and impurity effects that are intrinsic to the device structure, an understanding of the impact of radiation can be obtained. Figure 4 shows $I_d - V_g$ characteristics as a function of dose rate at room temperature for graphene FETs passivated with 19 nm Al_2O_3 . Prior to irradiation, the FETs exhibit the characteristic electron conduction under positive gate biases and hole conduction at negative gate biases [9]. The deviation from 0 V of the CNP is primarily due to process-related charging at

the graphene/insulator interfaces, which can be both positive or negative. For devices irradiated under a +5 and 0 V applied gate bias, the CNP shifts negatively (Figure 4 (a,b)), whereas the devices irradiated under a -5 V applied gate bias shifts positively (Figure 4 (c)).

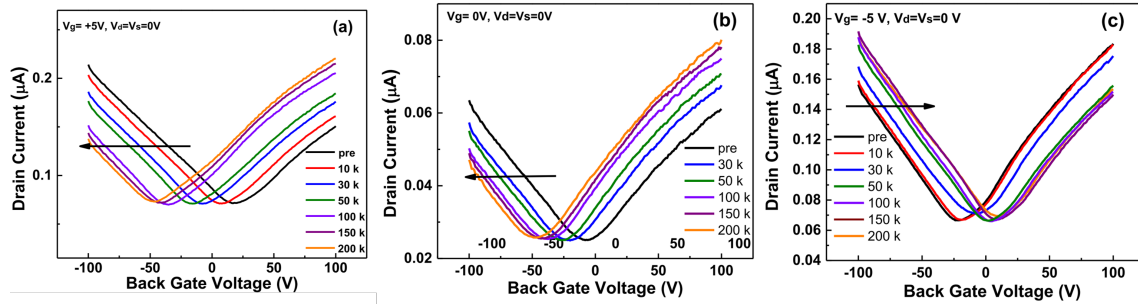


Figure 4. I_d - V_g curves as a function of total ionizing dose for graphene FETs passivated with 19 nm Al_2O_3 for applied gate biases of +5 (a), 0 (b), and -5 V (c). Devices were irradiated with 10 keV X-rays at a dose rate of 30 krad(SiO_2)/s with -5 V bias applied to the gate.

To this point, only the 19 nm Al_2O_3 passivated FETs have been discussed. The effects of the three different overlayers (4 nm Al_2O_3 , 19 nm Al_2O_3 , and 40 nm hBN) on each sample's resulting CNP shift is summarized in Figure 5 for devices irradiated under +5, 0, and -5 V applied gate biases. For all passivation layers, the CNP shift is strongly bias dependent; all CNP shifts are negative under +5 and 0 V applied biases during irradiation and positive under -5 V applied bias during irradiation. This response is qualitatively similar to previous studies on radiation response of graphene transistors [10-12]. Additionally, a significant effect of the passivation layer on the resulting radiation response is observed. The unpassivated graphene devices exhibit the smallest CNP shifts when exposed to X-rays for all bias conditions. The radiation response of the unpassivated devices are similar to those observed by Zhang et al., and can be ascribed to radiation-induced electron trapping caused by oxygen atoms adsorbed on the graphene surface. Although

the response of the hBN passivated devices are considerably larger in magnitude than the response reported by Zhang et al. [12], the amount of trapped charge is weaker than both Al_2O_3 passivated devices; when factoring in the relative thicknesses of the passivation layers, it is clear that the hBN exhibits the least amount of charge trapping. The devices passivated with 19 nm Al_2O_3 exhibits the largest CNP shifts, indicating that they experience the strongest doping due to a high density of trapped charge. Whereas dehydrogenation during baking is expected to primarily occur at the over-layer graphene interface, radiation induced charge trapping should occur at both interfaces above and below the graphene. The negative CNP shifts for +5 and 0 V biases are likely due to radiation-induced hole trapping in either the underlying SiO_2 or overlying Al_2O_3 . Conversely, the positive shifts under -5 V biases are likely due to electron trapping that occurs at either interface.

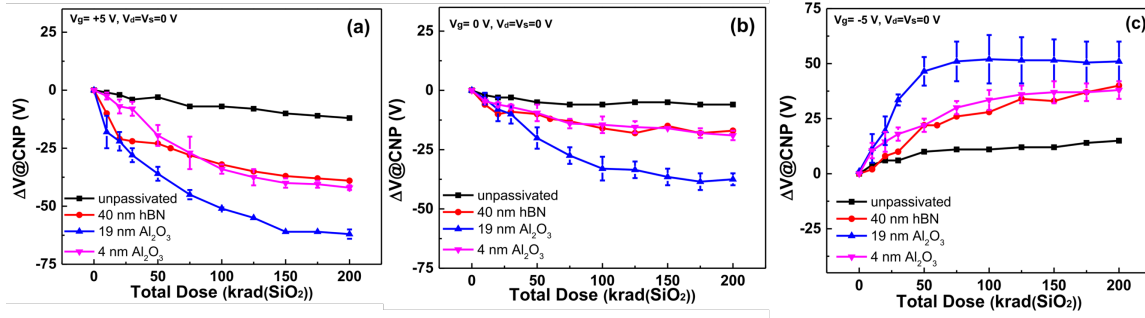


Figure 5. CNP shifts as a function of X-ray dose for devices irradiated under applied gate biases of +5 (a), 0 (b), and -5 (c) V. Error bars shows device to device variations on a given sample.

To learn the specific defect types and energies and are responsible for the Al_2O_3 devices observed behavior in Figure 5, $1/f$ noise measurements of each sample were performed. Figure 6 shows the low-frequency noise measurements for the 4 nm and 19 nm Al_2O_3 passivated graphene FETs, as well as an unpassivated control FET, as a function of temperature. For all devices, peaks at defect energies of ~ 0.4 and ~ 0.7 eV are observed after 100 krad(SiO_2) irradiation. The

unpassivated devices shown in Figure 6(c) exhibit an additional increase in noise magnitude at low temperatures. Of note, these noise peaks are not commonly observed when Si-based MOS devices are X-ray irradiated [3, 13], suggesting that the observed peaks correspond to defects associated specifically with graphene and its interfaces, as opposed to bulk SiO₂.

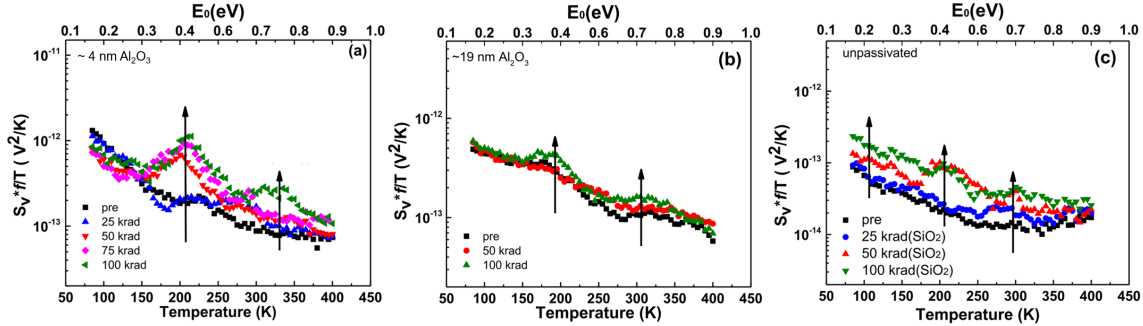


Figure 6. Normalized low-frequency noise from 85 to 400 K at $f=10$ Hz under various irradiation doses under -5 V applied gate bias. Devices with 4 nm and 19 nm Al₂O₃ are shown in (a) and (b), respectively. (c) corresponds to an unpassivated device. Black arrows note the position of defect-induced peaks in the noise with increasing dose. Devices were biased at $V_g - V_{CNP} = -20$ V during noise measurements.

To provide insight into defects and impurities that contribute to the irradiation and/or baking-induced charge in these devices, density functional theory (DFT) calculations were performed by Dr. Andy O'Hara, from Dr. Sokrates Pantelides' group at Vanderbilt University using the Vienna *Ab initio* Simulation Package (VASP) code [14, 15]. We employed the Perdew, Burke, and Ernzerhof generalized gradient approximation to calculate the exchange-correlation [16], applied a Van der Waals interaction correction [17], and used projector-augmented wave pseudopotentials [18] for the computations. A 400 eV plane wave cutoff energy was employed. A $3 \times 3 \times 1$ k-point grid was used for Brillouin zone integrations (and an increased density grid for density of states plots). Atoms were relaxed until all forces were less than 0.01 eV/Å [15]. The

surface oxide model was created from a bulk amorphous SiO₂ model that was previously generated [19] and optimized with the current DFT method. The resulting surface oxide model was interfaced to a 72 atom graphene sheet. The disorder of the amorphous surface results in variations in the calculated defect energetics and defect levels.

Figure 7 shows the atomic structure and electron density of states for relevant oxide-graphene environments. For a pristine (charge free) oxide-graphene interface, as shown in Figure 7 (a), the graphene has electrons completely filling the valence bands and the CNP is at a gate voltage of zero. Excess hydroxyl (OH⁻) groups can bind to silicon atoms, as shown in Figure 7 (b), resulting in 5-fold coordinated silicon atoms. Such configurations have previously been found for surfaces in *ab initio* and molecular dynamics studies [19, 20]. If the hydroxyl defect is neutral, an electron can transfer from graphene to the oxide defect. Graphene with hydroxyl defects consists of negatively charged hydroxyls and positively charged graphene with the CNP shifted to positive gate voltages. Due to wave-function symmetry of the oxygen *p*-orbitals, two defect levels occur for this single defect complex. For the hydroxyl defects studied here, we find defect levels are ~ 0.3 eV and ~ 0.7 eV below the graphene Fermi level. An extra hydrogen at the pristine interface results in an OH⁺ bond (where the oxygen remains as a bridging atom), as illustrated in Figure 7 (c). The hydrogen defect level is above the graphene Fermi level, so the hydrogen donates an electron to graphene. Graphene with hydrogen defects consists of positively charged hydrogen bonds and negatively charged graphene with the CNP shifted to negative gate voltages. Hence, of positively charged hydrogen bonds and negatively charged graphene with the CNP shifted to negative gate voltages. Hence, oxide OH⁻(H⁺) defects result in positive (negative) CNP gate voltage shifts.

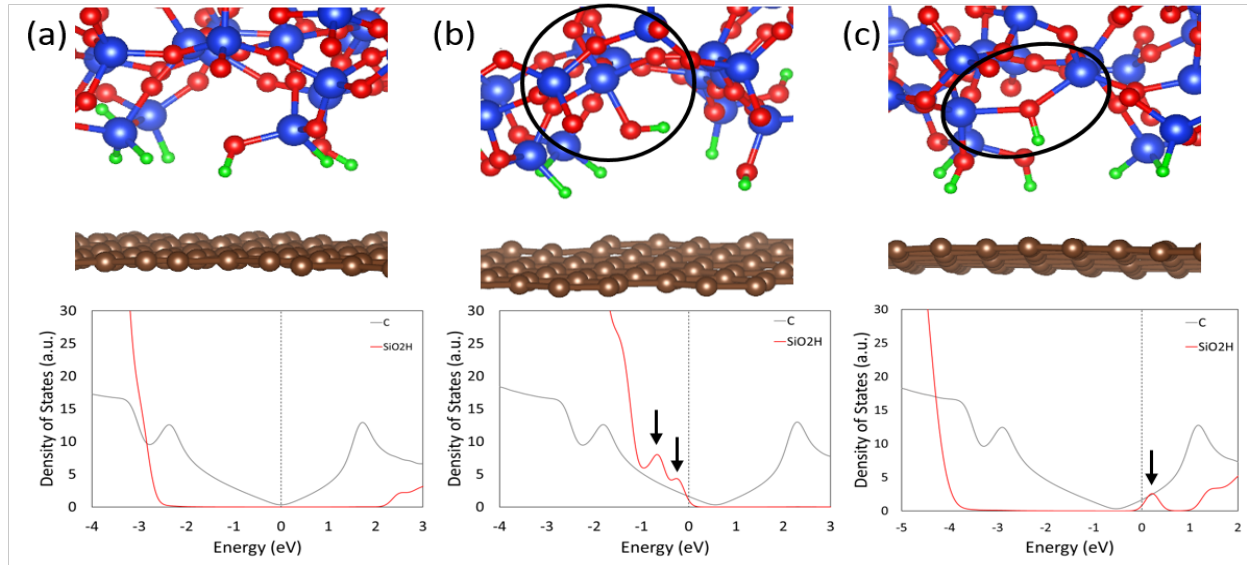


Figure 7. Atomistic models of the (a) passivated SiO₂/graphene interface, (b) dehydrogenated oxygen site, and (c) dehydrogenated silicon site. For (b) and (c), the black arrow indicates the dehydrogenation site; illustrative defect alignments are shown relative to the graphene Dirac point. Red arrows in (c) indicate the energy range for these levels. Carbon is brown, silicon is dark blue, oxygen is red, and hydrogen is green.

It is known that hydroxyl radicals bind with a broad distribution on energy levels that are sensitive to microstructure in alumina [21]. Additionally, DFT studies in the literature have shown that adsorbed water at the graphene/Al₂O₃ interface traps negative charge from the graphene layer [22]. The CNP shifts positively after baking, which corresponds to a reduction of OH⁻ ion density near the graphene/dielectric interfaces when exposed to high temperatures. Atmospheric exposure allows hydroxyls to return to that interface, restoring the doping density to the original value. Moreover, the DFT calculations suggest that the presence of depassivated oxygen and oxygen vacancies can contribute to CNP shifts when exposed to X-ray radiation. As such, it is likely that both oxygen and hydrogen/water related defects are important in determining the radiation response and low-frequency noise in graphene transistors.

Conclusions

Graphene FETs were fabricated and subsequently passivated with hBN and Al₂O₃. Current-voltage and low-frequency noise measurements provide insights into the energy distribution of defects in graphene transistors. Charge trapping at the graphene/insulator interfaces results in CNP shifts, positively for negative bias irradiation and negatively for positive bias irradiation. The noise of these devices is described well by the Dutta-Horn model, consistent with a wide range of other microelectronic material systems. Both hydrogen-related impurities and oxygen defect complexes lead to significant changes in device behavior, indicating their relevance in performance, reliability, and radiation response of graphene-based heterostructure devices. In particular, the 2D/insulator interface was found to significantly influence device performance.

4.2 Impact of h-BN and ZrO₂ Over-layers on Radiation Response of MoS₂ [23]

In this section, the effects of 10-keV X-ray irradiation of multiple layer MoS₂ transistors with ZrO₂ or h-BN gate dielectrics under different bias conditions will be investigated. Significant radiation-induced charge trapping is observed in all cases. For devices with ZrO₂ dielectrics, greater threshold voltage shifts and peak transconductance degradation are observed for devices irradiated under negative and grounded gate bias conditions than for positive bias irradiation. h-BN passivated devices exhibit positive threshold voltage shifts under negative bias irradiation. We attribute the variations in the observed response to different kinds of defects in MoS₂ and surrounding dielectric layers.

Devices used in this work are multi-layer MoS₂ transistors, which were constructed on a bulk Si with wafer with 260 thermally-grown SiO₂. These samples were fabricated by Dr. Tania Roy's group at the University of Central Florida, Orlando. The perspective view of a multilayer MoS₂ FET with a top gate structure is shown in Figure 8. For each device, thickness of MoS₂ is between 3-10 layers, which were mechanically exfoliated on SiO₂. The gate dielectric was either 9 nm ZrO₂ deposited by ALD at 250 °C using Tetrakis(ethylmethyamido)zirconium and H₂O precursors or 2D h-BN added by layer transfer [24]. Prior to depositing ZrO₂, 1.5 nm of SiO_x was deposited by electron beam evaporation to serve as the seeding layer for ALD. Source, drain, and gate metal electrodes were patterned using e-beam lithography, followed by e-beam evaporation of Ni (50 nm). Due to variations in MoS₂ layer thickness, transistors exhibit different pre-irradiation electrical performance (e.g., variations in drive current).

MoS₂ transistors were irradiated with 10-keV X-rays at a dose rate of 30.3 krad(SiO₂)/min at 295 K with applied top gate biases of +1 V, 0 V, or -1 V and all other terminals grounded, including the back gate. I_D - V_G characteristics were monitored using a HP 4156A Semiconductor

Parameter Analyzer. To characterize the defects created during irradiation, low frequency noise measurements were performed before and after irradiation from 85 K to 400 K. At least two devices of each type were measured under the same conditions with similar results.

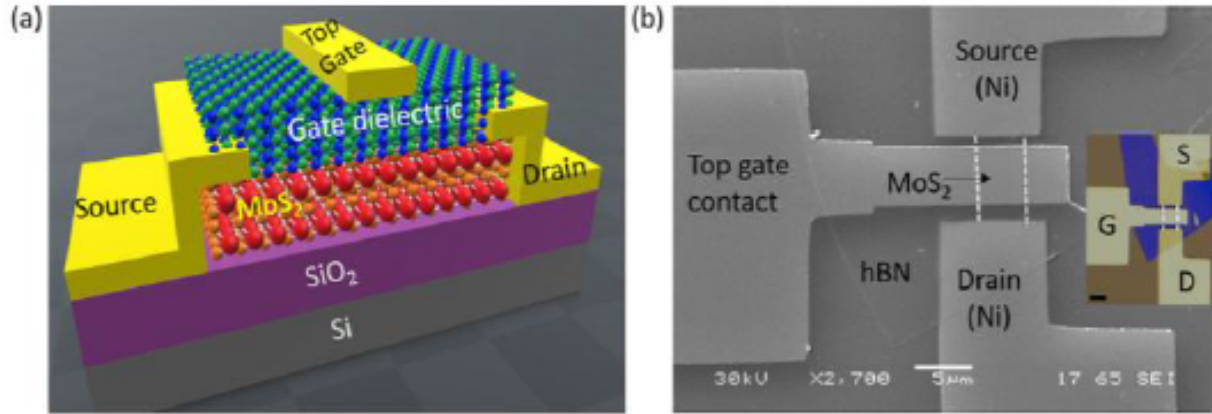


Figure 8. Device schematic—the channel is underlapped by the gate (not drawn to scale). (b) SEM image of a representative MoS₂ FET with the h-BN dielectric. (Inset) Optical microscopy image; scale bar: 4.75 µm [23, 24].

Figure 9 shows typical device characteristics for MoS₂ transistors with ZrO₂ dielectric layer. Figure 9(a) shows drain current as a function of gate voltage for drain voltages of 0.05 V and 1 V and Figure 9(b) shows output characteristics for drain voltages ranging from 0 V to 2.0 V and gate voltages from 0 V to 0.8 V with a step of 0.2 V. Figure 10 shows typical device characteristics for MoS₂ transistors with h-BN dielectric layer. Figure 10 (a) shows drain current as a function of gate voltage for drain voltages of 0.05 V and 1 V and Figure 10 (b) shows output characteristics for drain voltages ranging from 0 V to 2.0 V and gate voltages from -3 V to 1.5 V with a step of 0.5 V.

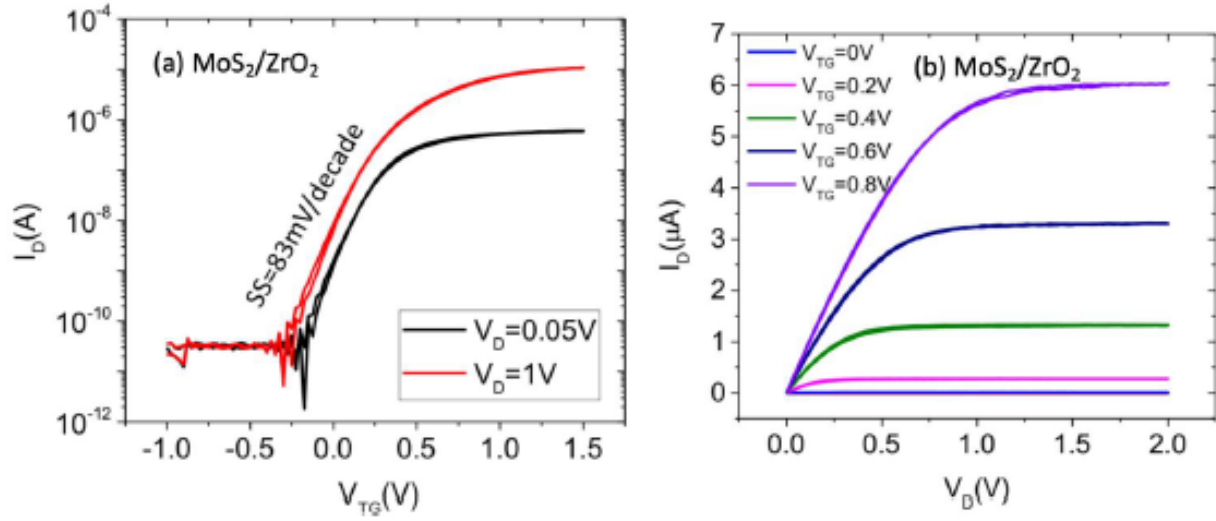


Figure 9. Typical characteristics of MoS₂ transistors with ZrO₂ dielectric layer: (a) I_D - V_G curves for drain voltages of 0.05 V and 1 V, and (b) I_D - V_D curves at gate voltages from 0 V to 0.8 V with a step of 0.2 V.

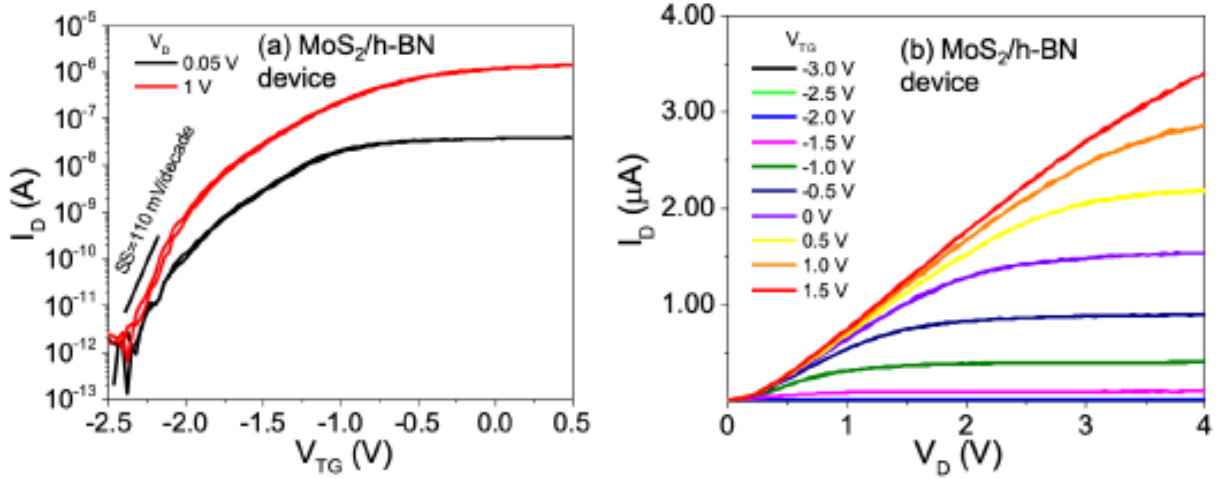


Figure 10. Typical characteristics of MoS₂ FETs with h-BN dielectric layer: (a) I_D - V_G curves for drain voltages of 0.05 V and 1 V, and (b) I_D - V_D curves at top gate voltages from -3.0 V to 1.5 V with a step of 0.5 V.

For both ZrO_2 and h-BN samples, devices respond as a typical n-type FET [25, 26], with an as-processed on/off ratio greater than 10^4 . Figure 11 shows the drain current versus top gate voltage with varying SiO_2 back gate bias, illustrating the strong effects of back-gate bias on device characteristics. For both ZrO_2 and h-BN-encapsulated MoS_2 devices, when the applied back-gate voltage increases from -10 V to 10 V, the peak transconductance G_M and on-state current increase, while the top-gate threshold voltage shifts negatively, as a result of strongly increasing back-channel conduction [27]. If not otherwise specified, the back-gated terminal is grounded in this work. The stability of the devices with applied bias is illustrated in Figure 12. No measurable shifts of the I_D - V_G curves are observed for electrical stress without irradiation for similar times used for irradiation.

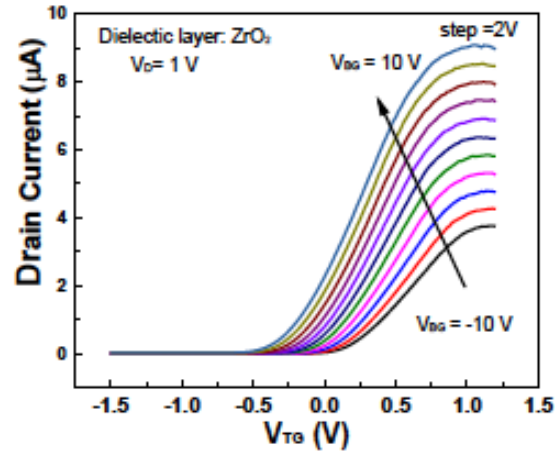


Figure 11. I_D - V_G curves with applied back-gate voltage stepped from -10 V to 10 V.

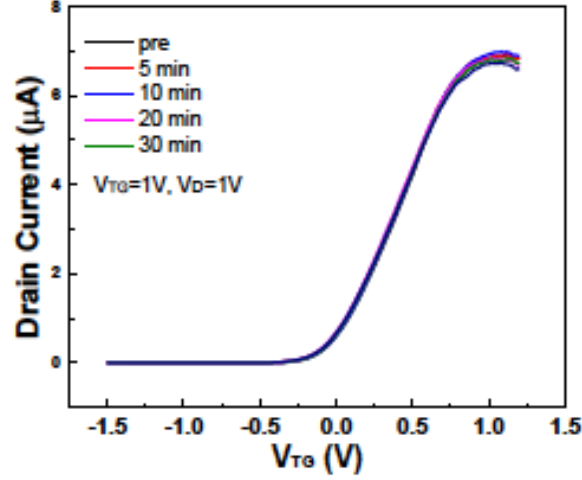


Figure 12. Drain current as a function of gate voltage and time with applied top gate bias of +1 V.

Figure 13 and Figure 14 shows the drain current versus top-gate voltage and G_M vs. $V_{gs}-V_{th}$ as a function of total dose at room temperature, for MoS₂ transistors with a 9 nm ZrO₂ dielectric, when biased at $V_{TG}=1V$ and $V_{TG}=-1V$ respectively. Figure 13(a) shows that the drain current increases for irradiation under positive top-gate bias, while G_M first decreases and then increases as a function of dose, as shown in Figure 13 (b). The shapes of the G_M -voltage curves show little change with dose, indicating that increases in peak G_M are due to decreases in scattering rate, and not an artifact of V_{th} shifts [28].

Figure 14 shows that, when devices are biased at -1 V top-gate voltage during irradiation, I_D - V_G characteristics shift negatively, and the drain current decreases significantly. Values of G_M decrease with increasing dose. These results differ from previous results on back-gated MoS₂ devices with no passivation layer, which show large positive V_{th} shifts for both positive and negative bias irradiation [29]. V_{th} shifts and normalized peak G_M degradation are plotted as functions of dose in Figure 15 for MoS₂ devices with a 9 nm ZrO₂ top-gate dielectric. Much larger V_{th} shifts are observed for irradiation under negative and grounded-bias than under positive bias. This occurs primarily because these bias conditions favor trapping of radiation-induced holes in

the thick SiO₂ that underlies the MoS₂. This in turn leads to a significant negative shift in V_{th} , analogous to the response shown in Figure 11, when positive back-gate bias is applied [30]. For positive top-gate bias, holes in the SiO₂ are trapped more closely to the distant (bottom) Si/SiO₂ interface, and have much less effect on conduction in the MoS₂.

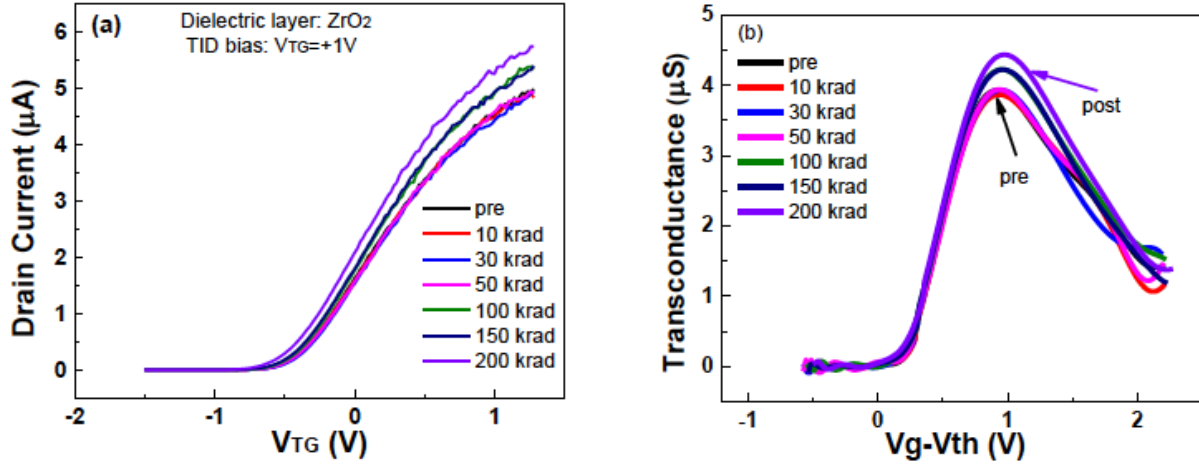


Figure 13. (a) I_D - V_G curves and (b) G_M vs. V_{gs} - V_{th} as a function of dose for MoS₂ transistors with ~ 9 nm ZrO₂ dielectrics for applied top-gate biases +1 V. $V_D = 1$ V during measurement of the I_D - V_G characteristics. The back gate was grounded during irradiation and measurement.

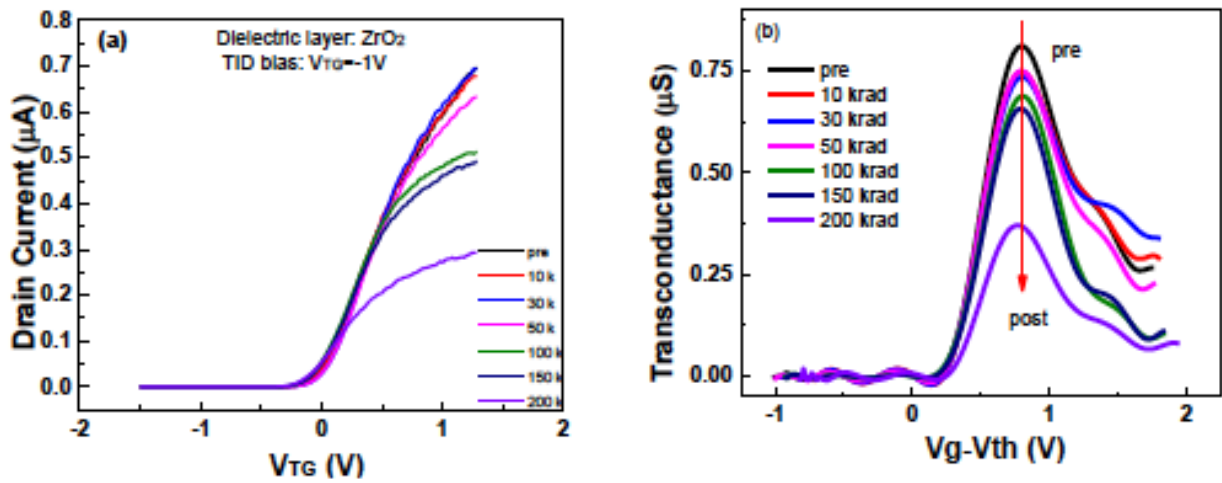


Figure 14. (a) I_D - V_G curves and (b) G_M vs. V_{gs} - V_{th} as a function of dose for MoS₂ transistors with ~ 9 nm ZrO₂ dielectrics for applied top-gate biases -1 V. $V_D = 1$ V during measurement of the I_D - V_G characteristics. The back gate was grounded during irradiation and measurement.

Figure 15(b) plots normalized peak G_M as a function of dose and irradiation bias. Significant G_M degradation is observed for -1 V and grounded-bias conditions, with post-irradiation peak G_M decreasing to $\sim 30\%$ of its pre-irradiation value. Such large degradation in G_M is consistent with the presence of high densities of radiation-induced trapped-positive charge in the underlying SiO_2 , quite near the MoS_2 . These defects act as Coulomb scattering centers and degrade carrier mobility [29]. The resulting degradation is similar to that observed in other 2D devices after X-ray irradiation, e.g., black phosphorus [31], graphene [1], and unpassivated MoS_2 [29]. For positive bias during irradiation, $\sim 10\%$ increase in the peak transconductance can be observed after 200 krad(SiO_2) irradiation, which is due most likely to radiation-induced neutralization [32] of process-induced charge associated with the e-beam deposition of the top contacts [33].

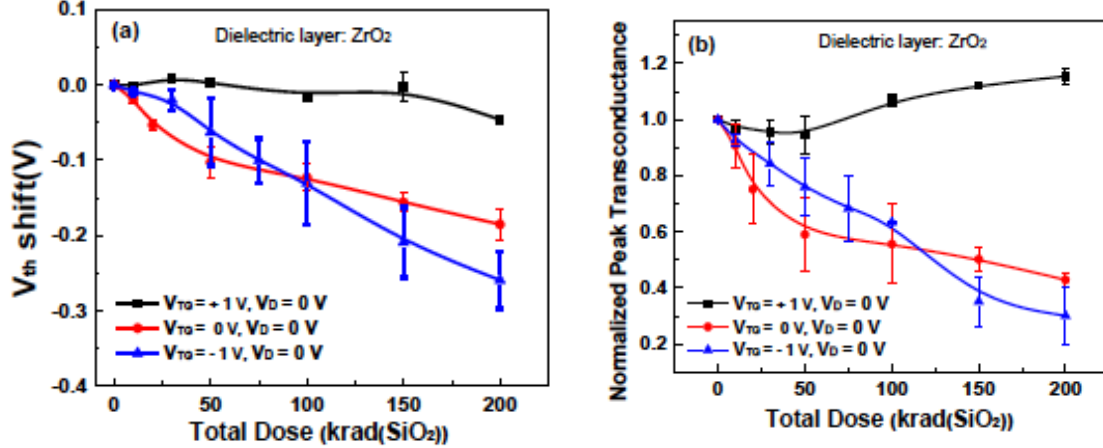


Figure 15. (a) Threshold voltage shift and (b) normalized peak transconductance as a function of total ionizing dose for MoS_2 transistors with ~ 9 nm ZrO_2 dielectrics for applied top-gate biases of +1 V, 0 V and -1 V during irradiation. $V_D = 1$ V during the measurement of the I_D - V_G curves. Error bars represent the ranges of responses of three samples.

Figure 16 compares effects of X-ray irradiation on MoS₂ transistors with different dielectrics and/or fabrication processes. The V_{th} shifts in Figure 16 (a) indicate that devices with h-BN dielectrics exhibit a net increase in charged electron trap density [11, 29], whereas devices with ALD-grown ZrO₂ exhibit a net increase in radiation-induced trapped-positive charge density when irradiated under similar bias conditions. Values of peak G_M degrade similarly in all cases, showing that h-BN devices show small V_{th} shifts because of nearly offsetting electron and hole trapping, and not because of reduced radiation-induced charge trapping [29]. The presence of dose enhancement in the devices with ZrO₂ dielectrics (higher Z), but not in devices with h-BN dielectrics (lower Z), may affect the relative comparisons in Figure 16 [30, 34]. However, the qualitative differences in results in Figure 16(a) shows that differences in defect type and densities plays a larger role in these differences in response.

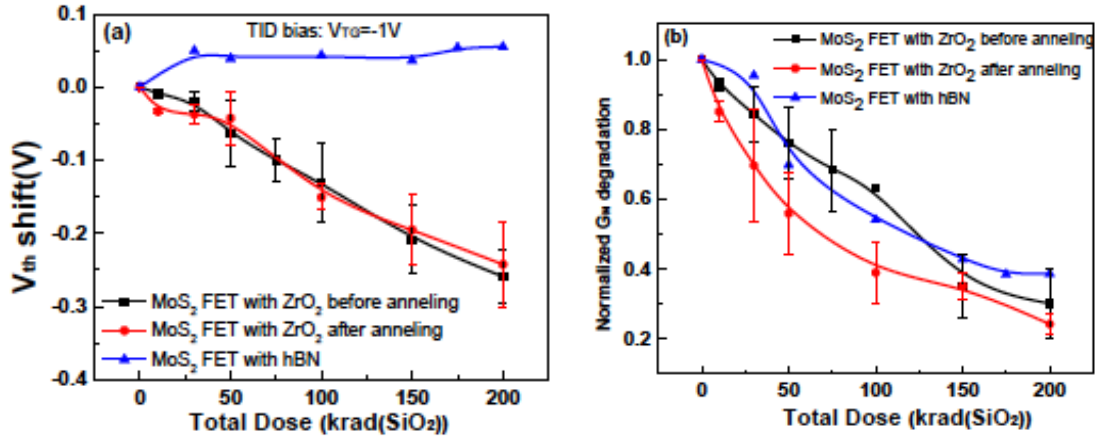


Figure 16. (a) V_{th} shift and (b) G_M as a function of total ionizing dose for samples with different process for applied gate bias of -1V. $V_D = 1V$ during the measurement of the IV characteristics. For devices with ZrO₂ dielectrics, similar shifts were observed for devices with or without a forming gas anneal during fabrication.

To further investigate the carrier mobility of MoS₂ FETs during X-ray irradiation, a 4-probe resistance measurement of a MoS₂ Hall bar structure is performed, as illustrated

schematically in Figure 17. A constant current flows through the length of the sample through probes 1 and 4. The voltage drop between probes 2 and 3 is monitored by a HP 4156 A parametric analyzer. The resistance of the sample between probes 2 and 3 is due to the ratio of the voltage drop between probes 2 and 3 and the value of the output current of the power supply. Before the start of the irradiation, the resistance increases with increasing time, most likely due to oxygen adsorption and reaction with the surface of this unpassivated structure [29, 35]. When the X-ray beam turns on, the resistance of the hall bar structure decreases significantly, because X-ray induced photocurrent increases the effective carrier density. After X-ray exposure, the resistance of the MoS₂ hall bar structure increases significantly, confirming that the mobility of the carriers in the MoS₂ structures decreases further as a result of the increased scattering from radiation-induced defects at or near the MoS₂ interface [29].

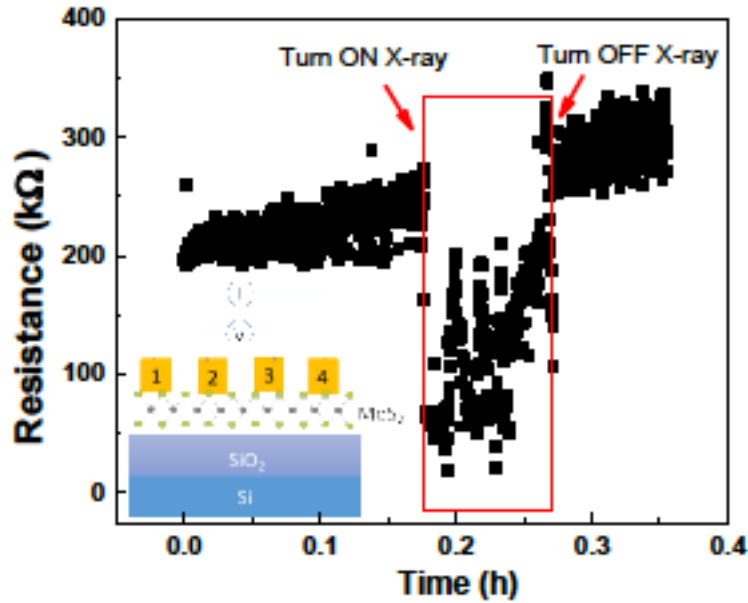


Figure 17. Resistance as a function of time before and after X-ray irradiation for a MoS₂ Hall bar structure. The inset figure is a schematic illustration of the four-terminal Hall bar structure.

Figure 18 shows an example of the excess drain-voltage noise power spectral density S_{Vd} (corrected for background noise) as functions of temperature and frequency for unirradiated MoS₂ FET with ZrO₂ as gate dielectric. The bias voltages are chosen to ensure the noise originates from the gated portion of the channel, with an approximately constant channel resistance [3, 28, 36]. The noise varies approximately inversely with frequency in Figure 18. The frequency exponent of low frequency noise is defined as $\alpha = -\partial \ln SV / \partial \ln f$. At room temperature, $\alpha = 1.10 \pm 0.05$ for the devices of Figure 18, which is typical of values observed in previous studies of MOSFETs made on 2D materials [1, 35]. The noise magnitude and frequency dependences change with temperature, suggesting a thermally activated process is responsible for the observed noise [3, 4].

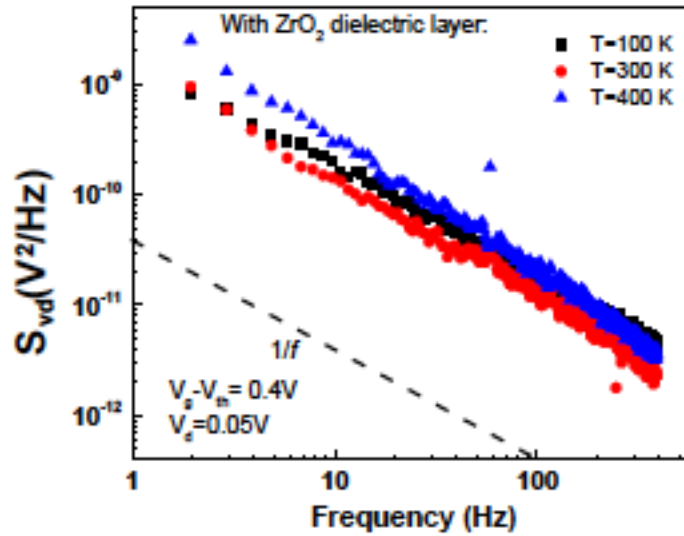


Figure 18. S_{Vd} vs. f for as-processed devices with ZrO₂ dielectrics at 100 K, 300 K, and 400 K. Devices were biased at $V_g - V_{th} = 0.4$ V and $V_d = 0.05$ V during noise measurements.

Figure 19 shows the frequency exponent of the noise-power spectral density α as a function of temperature T for MoS₂ FETs with ZrO₂ dielectrics before and after 10-keV X-ray irradiation. Over the entire range of temperatures, both before and after X-ray irradiation, the experimental frequency exponent and the prediction based on the temperature dependence of the noise

magnitude agree well with each other, as shown in Figure 19. This enables us to estimate the defect-energy distribution from the temperature dependence of low frequency data.

Figure 20 shows normalized noise magnitudes from 85 K to 400 K for MoS₂ FETs with ZrO₂ layer irradiated under (a) positive or (b) negative top-gate bias. The top x-axis represents the corresponding range in activation energy E_o , 0.2 eV to 1 eV. Here the value of τ_o was set at $\sim 1.81 \times 10^{-15}$ to be consistent with previous studies of low-frequency noise in MOSFETs [3, 13]. Because of the logarithm, the inferred energy scale changes only modestly with changes in τ_o [13]. The y-axis is proportional to the defect-energy distribution.

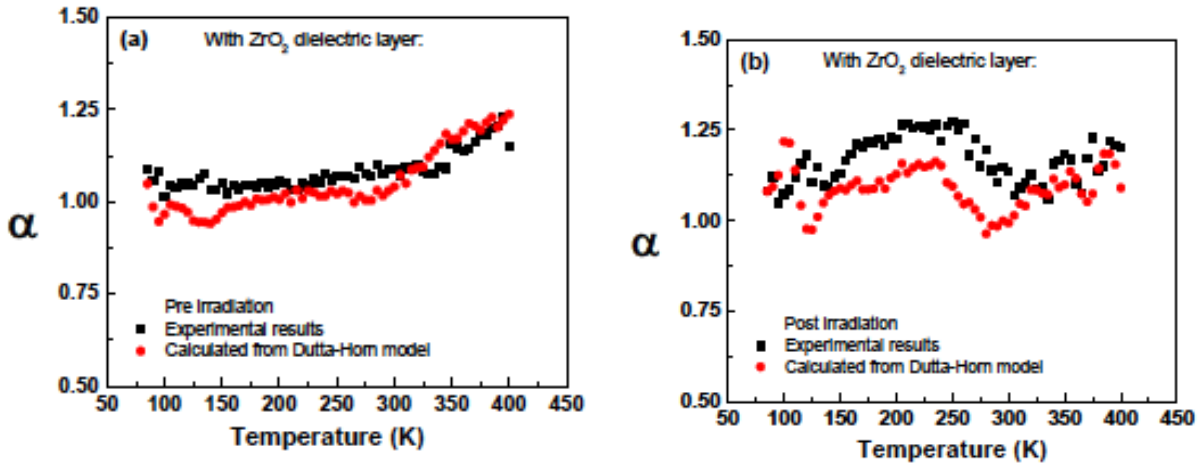


Figure 19. Experimental and calculated frequency exponents of noise power spectral density as a function of temperature from 85 K to 400 K for devices with ZrO₂ top dielectric layers (a) before irradiation and (b) after 200 krad(SiO₂) X-ray irradiation.

For MoS₂ FETs with a ZrO₂ dielectric layer, when biased at $V_g = +1$ V during irradiation (Figure 20(a)), after irradiation to 200 krad(SiO₂), the normalized low-frequency noise magnitude increases significantly over a broad range of temperatures around 250 K, corresponding to an activation energy of ~ 0.6 eV. For devices biased under -1 V during irradiation (Figure 20(b)), small,

broad peaks at energies of ~ 0.5 eV and ~ 0.8 eV are observed. These broad ranges of energies suggest the possible generation or activation of multiple defects during irradiation.

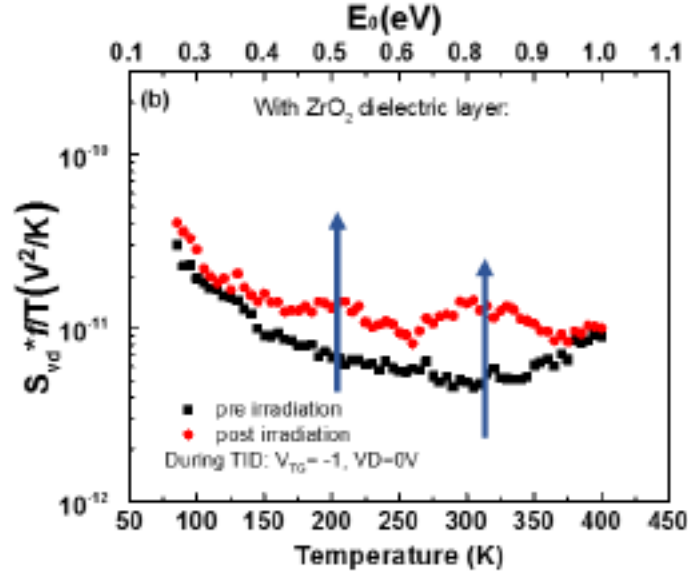


Figure 20. Normalized low-frequency noise from 85 K to 400 K at $f = 10$ Hz for MoS₂ transistors with ZrO₂ dielectric layers irradiated under (a) +1 V bias and (b) -1 V bias. Devices were biased at $V_g - V_{th} = 0.4$ V and $V_d = 0.05$ V during the noise measurements.

In order to gain insight into the microscopic nature of the defects responsible for the observed changes in threshold voltage and transconductance, DFT calculations (Figure 21) were performed by Dr. Andy O'Hara using the VASP code [14, 15]. For interface structure atomic models (e.g., MoS₂/h-BN and MoS₂/ZrO₂), the exchange-correlation functional was calculated using the Perdew, Burke, and Ernzerhof generalized gradient approximation [16] with a van der Waals interaction correction [17]. Calculations were performed using projector-augmented-wave pseudopotentials [18] with a 550-eV plane-wave-cutoff energy and Brillouin-zone integration was performed using a k-point. Calculations of the oxygen vacancy levels in ZrO₂ were performed

using the HSE06 range-separated hybrid functional for the exchange correlation potential [37] with experimental lattice constants as this approach is known for related oxides to give an improved description of the defect levels [38]. In this case, a supercell of the primitive cell of ZrO_2 with the Brillouin zone sampled on a k-point grid and an energy cutoff of 400 eV were employed with electrostatic potential corrections [39]. Calculations of charged-defect transition levels in the heterostructure slabs were performed using the method of Ref. [40].

Band alignments were calculated by constructing heterostructures between bilayer MoS_2 and either ~ 1 nm of [100] oriented monoclinic ZrO_2 or four layers of h-BN. The calculated ~ 1.3 eV band gap for bilayer MoS_2 , while a slight underestimation, is consistent with the band gap for few-layer MoS_2 [41, 42], as in the present devices. Figure 21 shows valence band offsets of 1.80 eV for $\text{MoS}_2/\text{ZrO}_2$ and 0.51 eV for $\text{MoS}_2/\text{h-BN}$. Within the HSE06 exchange-functional parameterization, we obtain a bandgap of 5.31 eV, in good agreement with other calculations and experimental reports [43], which yields a conduction band offset of 2.20 eV. Although the band gap for h-BN is underestimated, a common issue in DFT with known methods for compensation when necessary [15], our $\text{MoS}_2/\text{h-BN}$ model reproduces the expected type-I band alignment with a large (>2.35 eV) conduction band offset.

In ZrO_2 , there are two types of O vacancies: one where the vacant oxygen atom is originally 4-fold coordinated ($\text{V}_{4\text{O}}$) and one where it is originally 3-fold coordinated ($\text{V}_{3\text{O}}$). When O vacancies become de-passivated due to transporting hydrogen released during X-ray irradiation, they introduce defect levels that can trap one or two holes if the system Fermi energy is below the defect-energy levels. These trap levels are shown in Figure 21(a) as $+/-0$ and $++/+$. The corresponding energy levels are at 0.05 eV and 0.46 eV above the MoS_2 conduction band for the $\text{V}_{4\text{O}}$ defect and 0.41 eV and 0.95 eV for the $\text{V}_{3\text{O}}$ defect. The 0.4 eV to 0.5 eV energy levels

for the $+/0$ V_{4O} and $+/\!+\!+$ V_{3O} defects in Figure 21(a) are similar to the lower defect peak in the low-frequency noise measurements in Figure 20(b). Moreover, the $+/0$ V_{3O} defect level is similar to the higher measured defect peak for devices in Figure 20(b). These results suggest that O vacancies likely play an important role in the radiation response and low-frequency noise of these devices. The charge density projection of the defect wave functions (lower middle and right panels of Figure 21(a)) for ZrO_2 oxygen vacancies indicate that these defects are highly localized and that their relative positions are controlled primarily by the local Zr coordination.

During the fabrication of the ZrO_2 -based devices, deposition of the SiO_x nucleation layer for ALD growth can introduce silicon-based defects on the surface of MoS_2 in the form of substitutional silicon (Si_S). This defect can trap up to two electrons, with the $0/-$ and $-/--$ levels at 1.1 eV and 0.65 eV below the MoS_2 CBM, respectively, as shown in Figure 21(a). The lower value is similar to the peak in low-frequency noise shown in Figure 20(a) for devices irradiated with positive top-gate bias. However, the defect wave function for a Si_S defect (shown in the lower panel of Figure 21(a)) extends towards the interfacial oxide. Therefore, the energy levels of such peaks are sensitive to the nature of the surrounding material, which can shift the level in energy by up to several tenths of an eV. This dependence on local microstructure effectively broadens the observed peak. Such a defect is therefore also likely to affect the low-frequency noise and radiation response of these devices. The trapped negative charge in this defect can partially or fully compensate trapped-positive charge in the upper or lower dielectric layers, consistent with the radiation response observed under positive bias for these devices in Figure 15(a), for example.

For MoS_2/h -BN devices, several common defects are known to occur, including sulfur vacancies (V_S), boron vacancies (V_B), nitrogen vacancies (V_N), and carbon substitutional impurities (C_N or C_B). In previous work on graphene/ h -BN devices, for example, C_N and C_B defects

were identified as the primary h-BN defects responsible for electron and hole trapping [29]. Figure 21(b) shows defect transition energy levels for each of these defects in MoS₂/h-BN. V_S, V_B, and C_N defects introduce electron trap (0/-) levels at 0.18 eV, 1.07 eV, and 0.19 eV below the MoS₂ CBM, respectively.

For the V_S, there is also a fairly shallow second level (-/--) 0.08 eV below the MoS₂ CBM, which at most temperatures will be unoccupied due to thermal ionization. Although the V_B defect can nominally trap up to three electrons depending upon the Fermi energy, the -/-- and 2-/3- levels are not accessible in the present devices. As shown in the charge density projections in Figure 21(b), these defects are localized to the defect host material layer with the V_B and C_N defects slightly delocalized in plane. The V_N and C_B defects introduce a hole trap level (+/0) at 0.13 eV and 0.10 eV above the MoS₂ CBM, respectively. Furthermore, their wave functions indicate a small amount of coupling with the MoS₂ conduction bands. The net effect of these defects is some electron trapping at the interface consistent with the slight positive shift in V_{th} (Figure 16(a)) and a degradation in the transconductance (Figure 16(b)). These defects appear to be mostly too high or too low to affect the low-frequency noise of MoS₂/h-BN devices significantly, which is a useful topic for future work.

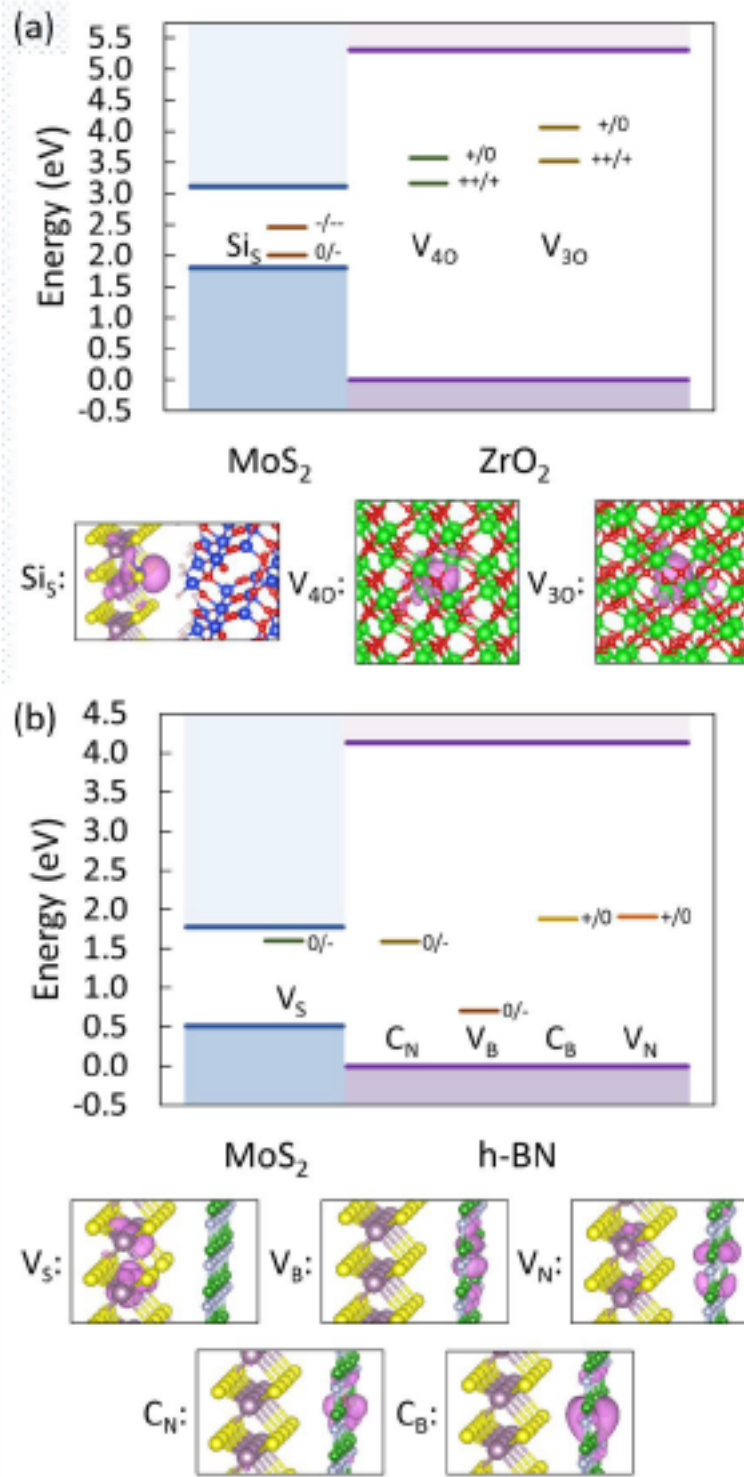


Figure 21. Band alignment, defect energies, and charge density projections for the relevant defects in the (a) MoS₂/ZrO₂ and (b) MoS₂/h-BN models for the current devices.

Conclusions

The electrical properties of ZrO_2 and h-BN encapsulated dual-gate MoS_2 transistors are reported before and after 10-keV X-ray irradiation. Significant radiation-induced charge trapping is observed in all cases. For devices with ZrO_2 dielectrics, greater threshold voltage shifts and peak transconductance degradation are observed for devices irradiated under negative and grounded top-gate bias than for positive top-gate bias irradiation. This occurs primarily because of radiation-induced hole trapping in the SiO_2 that underlies the MoS_2 . Electron trapping under negative top-gate bias at Si_S defects also likely contributes to the radiation response and low-frequency noise of these devices. h-BN devices exhibit positive threshold voltage shifts under negative bias irradiation because boron vacancies and substitutional carbon (C_B) in the h-BN serve as additional electron traps in these structures. Similar transconductance degradation is observed in both ZrO_2 and h-BN passivated devices, as a result of both negative and positive charge trapping at the surface of the MoS_2 , and/or in nearby oxides.

4.3 Low-temperature Synthesis of MoS₂ on Metals for Vertical Heterostructures [44]

One significant benefit of achieving low-temperature MoS₂ synthesis is that MoS₂ films can be synthesized on substrates that cannot withstand traditional synthesis temperatures. As such, MoS₂ can be synthesized directly onto substrates, such as plastics or metals, that otherwise would require transfer steps to yield MoS₂ placement. In the case of vertical heterostructures, synthesizing MoS₂ directly onto a contact metal is required. Because gold is one of the more commonly used contact metals in microelectronics and 2D materials research, this chapter will focus on synthesizing MoS₂ onto gold substrates and fabricating devices without any transfer steps.

Optimization of MoS₂ Synthesis on Gold

To explore MoS₂ synthesis on gold, samples were prepared for synthesis by e-beam evaporating 100 nm of gold onto 300 nm SiO₂/Si substrates. These substrates were cleaned using a standard acetone/isopropyl alcohol solvent clean, then loaded into the MBE chamber. Synthesis was performed using a cyclic process. The temperature of the substrate was raised to 400 °C, and a 15-minute H₂S plasma pre-anneal was performed to further clean the sample surface. Once H₂S plasma annealed, three Mo sputter/H₂S plasma soak cycles were performed in an attempt to yield 3-layer MoS₂. At the conclusion of the final sputter/soak cycle, the sample is cooled to 200 °C under vacuum, then moved to the load lock and cooled to room temperature under nitrogen.

The Raman response of the initial attempt at MoS₂ synthesis on gold is shown in Figure 22. The two characteristic phonon peaks are visible at ~405 cm⁻¹ for the A_{1g} and ~380 for the E_{2g}¹, indicating that some MoS₂ exists in its characteristic hexagonal structure. However, the signal-to-noise ratio of the spectrum is extremely small, where the intensity of both peaks is barely above the background noise. Although metal substrates do provide a significantly larger Raman

background signal and reduce the signal-to-noise ratio than insulating substrates, the resulting MoS₂ signal is significantly lower than other reported Raman spectra of MoS₂ on gold [45]. Therefore, MoS₂ film corresponding to the Raman spectrum in Figure 22 is likely of rather low quality, and the synthesis process must be optimized for synthesis on gold.

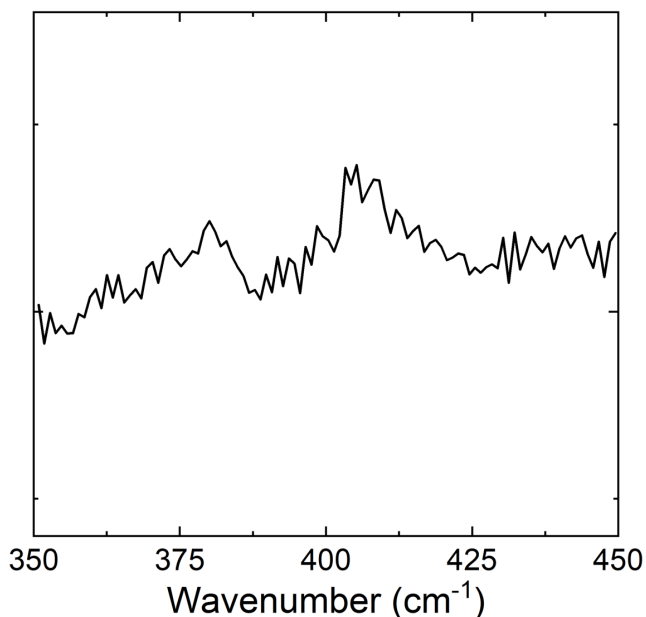


Figure 22. Raman response of a 3-cycle 400 °C metallic-Mo MoS₂ synthesis process on a gold substrate. The y-axis is shown in arbitrary units. Faint A_{1g} and E_{2g}¹ peaks can be seen at 405 and 380 cm⁻¹, respectively.

One possible explanation for the poor film quality is that sulfur reacts favorably with gold [46], yielding two competing sulfurization reactions between the gold substrate and deposited Mo films. Oxidizing each deposited Mo layer to MoO_x should promote the sulfurization reaction, as MoO_x thermodynamically reacts more favorably with sulfur than metallic Mo. Therefore, the reactive sulfur species may be more likely to react with the oxidized molybdenum film as opposed

to the gold substrate. In an attempt to improve the quality of MoS₂ films synthesized on gold, each Mo sputter step was moved to the load lock and oxidized.

Figure 23(a) shows that Raman response for MoS₂ synthesized on gold using metallic and oxidized initial Mo films. The spectrum corresponding to the metallic Mo film is the same shown in Figure 22. It is immediately apparent that oxidized MoO_x initial films result in significantly higher quality resulting MoS₂ based on the improved signal-to-noise ratio of the spectrum. The peak separation of both spectra are similar, indicating that the resulting film thickness synthesized on gold is independent of initial Mo film composition. However, the Raman peak widths for MoS₂ synthesized on gold using MoO_x initial films are slightly larger than equivalent synthesized films on SiO₂ substrates, indicating that the quality of material synthesized on gold is slightly lower than material synthesized on SiO₂.

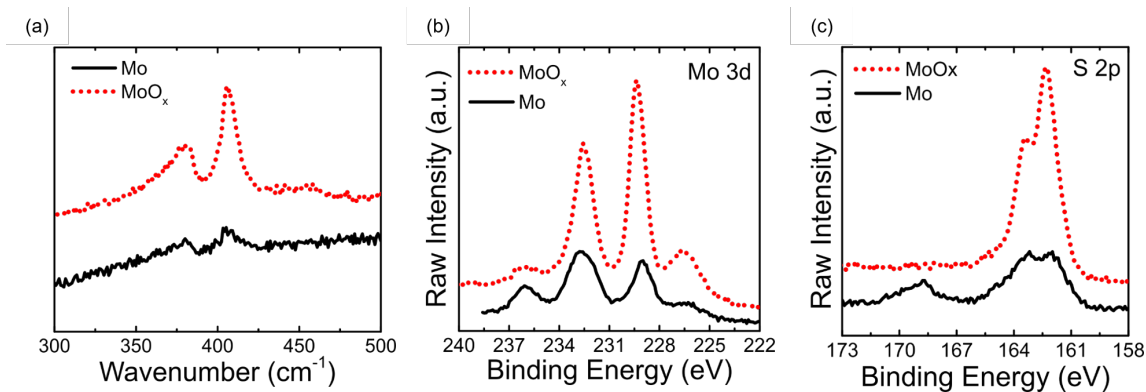


Figure 23. **(a)** Raman response of MoS₂ synthesized on gold substrates using metallic (Mo) and oxidized (MoO_x) initial Mo films. XPS Mo 3d **(b)** and S 2p **(c)** spectra for MoS₂ synthesized on gold using metallic (Mo) and oxidized (MoO_x) initial Mo films.

Figure 23 (b) shows the Mo 3d XPS spectra for MoS₂ synthesized on gold from the two different initial Mo films. The spectrum corresponding to the MoS₂ synthesized from MoO_x initial

films is dominated by the doublet of peaks at 230 and 232 eV corresponding to MoS₂. In addition, the spectrum exhibits a small MoO₃ contribution, suggesting that the MoO_x sulfurized to near completion. Conversely, the spectrum corresponding to the metallic Mo initial film exhibits strong MoO₃ peak intensities at 233 and 236 eV. Moreover, the S 2s peak at 226 eV is not present in the metallic Mo spectrum, whereas it is not only present in the MoO_x initial film spectrum, but also exhibits a relative intensity that is consistent with MoS₂. The absence of sulfur in the metallic Mo initial film sample is confirmed by the S 2p XPS spectra shown in Figure 23(c). The S 2p spectrum corresponding to the metallic Mo initial film synthesis is weak in relative intensity compared to the C 1s spectrum (not shown), indicating that there is not a large amount of sulfur present in the film. In contrast, the S 2p spectrum corresponding to the MoO_x initial film synthesis exhibits a strong signal corresponding to sulfur in the MoS₂ chemical state.

The stoichiometry of both MoS₂ films can also be calculated using the Mo 3d and S 2p spectra shown in Figure 23 (b,c). The calculated atomic ratio of MoS₂ synthesized on gold from metallic Mo initial films is only 1:1.02, indicating that the molybdenum initial film significantly under-reacted with the H₂S plasma. This is corroborated by the large MoO₃ percentage of the Mo 3d spectrum, where MoO₃ accounts for 51% of the molybdenum spectrum. In contrast, the atomic ratio between Mo and S in the MoO_x initial film sample is 1:1.94, indicating that the molybdenum reacted with the H₂S plasma nearly in full. These results confirm the hypothesis that oxidizing the initial Mo film will promote the sulfurization reaction, which is necessary for successfully MoS₂ synthesis on gold substrates.

Heterostructure Devices from MoS₂ Synthesized on Gold

Because MoS₂ synthesis on gold is now possible, transfer-free MoS₂ heterostructure can be fabricated by directly synthesizing MoS₂ onto bottom gold contacts. Because the metal/TMD/metal heterostructure is one of the simplest heterostructure architectures, in addition to their recent interest as memory select devices [47, 48], it is an obvious choice for initial heterostructure experiments. In addition, the purely vertical structures contain no in-plane conduction, implying that the variable range hopping limitation is no longer relevant to device operation and the material constraint is therefore mitigated. Tri-layer MoS₂ was synthesized on gold substrates, and top gold contacts were e-beam evaporated to yield a gold/MoS₂/gold device structure.

The device behavior of the gold/MoS₂/gold heterostructure devices is shown in Figure 24. Interestingly, the heterostructure devices exhibit resistive switching behavior, where the resistance of the device switches between a high and low resistance state as the source/drain voltage is swept. This switching behavior is highlighted by the arrows showing the voltage sweep direction, and the colors representing the high and low resistance state. The inset of Figure 24 shows the switching behavior on a linear scale, which breaks down the switching into four segments. As the source-drain bias is increased from 0 to positive biases, the device begins in a high resistance state (i). At around 0.5 V, the device begins to switch to a low resistance state and the current density increases significantly before hitting the set compliance value of 0.08 A. When the bias is reduced, the current decreases linearly, but this time at a higher current density than during the positive voltage sweep (ii). Further decreasing the bias to negative values continues the linear I_d - V_d behavior, until approximately -0.75 V where the device switches back to a high resistance state (iii). Sweeping

the bias back from -1 to 0 V brings the device state back to the initial point while maintaining the high resistance state (iv).

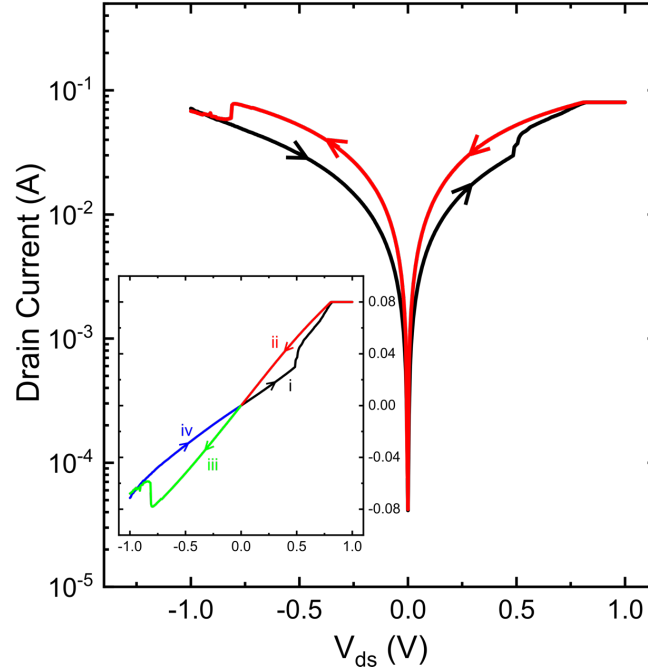


Figure 24. Device behavior of the gold/MoS₂/gold heterostructures. Switching is highlighted by the arrows and colors, which indicate the sweep direction and resistance state. The inset shows the same data on a linear scale, where the four switching regimes are indicated as (i) – (iv).

This switching behavior has traditionally been investigated in oxide materials systems[49], although recently switching has been observed in MoS₂ devices [50]. In this case, MoS₂ is synthesized using a traditional CVD process to yield individual flakes that do not fully coalesce into a single film. Although the grains do not fully coalesce, a number of grains impinge on one another, resulting in a grain boundary between two single-crystal grains. Sangwan et al. then fabricated a device over this two-grain MoS₂ flake, where the source and drain contacts are located on opposite grains such that the grain boundary is located between them. When V_{ds} is swept, the

resistivity through the film switches due to the motion of the grain boundary, which is confirmed through AFM [50]. In addition, the resistivity of the device can also be modulated by an applied back gate, as the device architecture is the same as a standard FET.

Although the switching demonstrated by Sangwan et al. [50] and shown in Figure 24 are both observed in MoS₂ systems, it is likely that the mechanisms that dictate the switching behavior are different. The switching observed by Sangwan et al. is based on lateral grain motion in the direction of the applied bias. However, because the heterostructure device operates based on out-of-plane carrier conduction, it is unlikely that applying a bias across the device will physically alter the position of the grain boundaries. Reports in literature have shown filamentary switching in hBN systems, where metal ions diffusion through hBN interlayers to form a volatile low-resistance filament before diffusing back out of the interlayer [51]. It is possible that the switching behavior observed in Figure 24 is due to metal filament formation, although the resistance state of the gold/MoS₂/gold heterostructure appears to be non-volatile, as the resistance state is stored for more than 24 hours, which is in contrast to the observed behavior in the hBN filamentary systems. As such, further investigation is necessary to determine the cause for the switching behavior. Nevertheless, although the switching window of the devices shown in Figure 24 is small, where the on-off ratio is less than an order of magnitude, the switching window is comparable to the devices demonstrated by Sangwan et al. [50] despite the likely difference in switching mechanism.

While the gold/MoS₂/gold heterostructures do demonstrate switching behavior, they are ohmic in nature. The previous device characteristics indicate that an insulating interlayer is likely needed in order to induce tunneling across the structures. Therefore, to induce tunneling behavior in the transfer-free, directly synthesized low-temperature MoS₂ devices, tunnel heterojunctions were fabricated using a high-k interlayer as a tunnel barrier. Tri-layer MoS₂ was again synthesized

directly onto gold substrates using the previously discussed method, after which 2.78 nm of Al_2O_3 or 2.71 nm of HfO_2 were ALD deposited onto the bottom layer MoS_2 . After the high-k interlayer was deposited, the tri-layer MoS_2 was synthesized directly onto the dielectric and was capped with a top gold contact deposited via e-beam evaporation. A resulting vertical structure of gold/ MoS_2 /interlayer/ MoS_2 /gold is therefore achieved, notably without requiring any transfer steps, implying that each interface is pristine.

The device I_d - V_d behavior of the Al_2O_3 interlayer device is shown in Figure 25 (a). A clean non-linearity is observed, indicating that the device is non-ohmic and that the device characteristics are dictated by tunneling. Figure 25(b) re-plots the behavior in a Fowler-Nordheim (FN) plot, which shows the voltage threshold for the transition between direct tunneling (DT) and FN tunneling. In addition, (b) shows the evolution of the band structure from direct tunneling to FN tunneling. Extracting the FN tunneling threshold voltage from the FN plot enables showing the threshold voltages on (a) as dotted red lines. HfO_2 interlayer structures exhibit similar behavior (not shown).

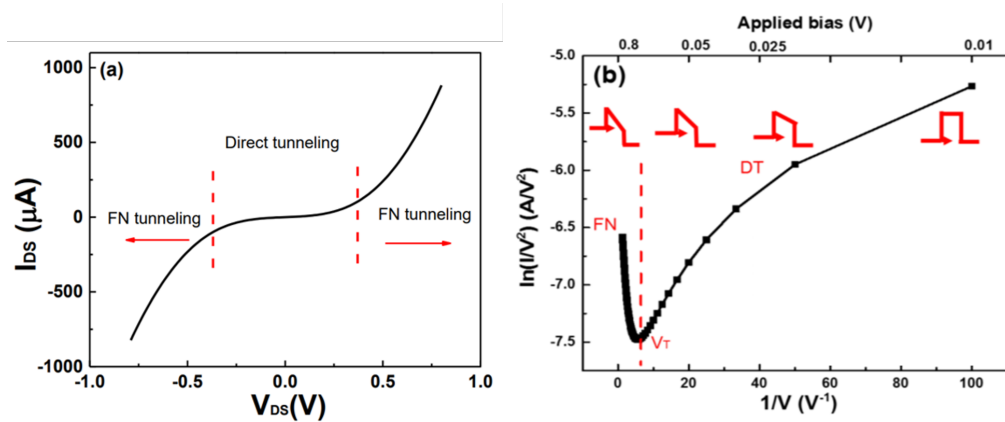


Figure 25. Device characteristics for an Al_2O_3 interlayer MoS_2 tunnel junction. (a) shows the device behavior in a normal scale, highlighting the different tunneling regimes occurring at different voltages. (b) re-plots the device data from (a) in a FN plot, and shows the band structure leading to FN tunneling with increasing bias.

Because the heterostructures are symmetric, they theoretically are a plausible fit for negative differential resistance (NDR) tunneling applications. However, it is apparent that the devices do not exhibit any NDR behavior. The lack of NDR behavior is likely due to the fact that the material quality is relatively low, where disorder induces inhomogeneity in the electronic structure of the films and mitigates any NDR effects [52]. As such, further electrical characterization of these heterostructures as-fabricated likely will not yield any additional information.

Conclusions

In this section, low-temperature synthesis of MoS₂ on gold substrates was successfully achieved. In contrast to previous results, where metallic Mo initial films yield higher quality resulting MoS₂, thin film reaction synthesis of MoS₂ on gold requires oxidizing each deposited molybdenum film to MoO_x prior to sulfurization. Because sulfur reacts with gold much more favorably than with SiO₂, the sulfur-gold interaction competes with the sulfur-molybdenum interaction, preventing complete sulfurization of metallic molybdenum films. By oxidizing the molybdenum film, the sulfur-MoO_x interaction thermodynamics improve the favorability of the sulfurization reaction, resulting in successful MoS₂ synthesis. However, MoS₂ films synthesized on gold substrates still exhibit lower quality than equivalent synthesis on SiO₂ substrates, indicating that further optimization is required for synthesis on gold.

Two-terminal vertical heterostructures were fabricated from MoS₂ synthesized directly onto gold without requiring any transfer steps. Gold/few-layer-MoS₂/gold heterostructures displayed ohmic behavior, and exhibited memristive non-volatile switching. Although the switching window was small, the behavior mirrored switching characteristics in other MoS₂ device

systems [50]. Placing a high-k dielectric interlayer between tri-layer MoS₂ films induced tunneling behavior, yield symmetric tunnel junctions. NDR was not observed, suggesting that the film quality is too poor to exhibit the well-defined homogenous electronic structure needed for resonant tunneling, indicating further optimization of low-temperature synthesis on gold is required. Nevertheless, these results demonstrate that directly synthesizing MoS₂ onto metallic substrates can be utilized to fabricate vertical heterostructures without requiring transfer steps.

4.4 Impact of Metal-MoS₂ Fermi Level Pinning on Heterostructure Electronic Properties [53]

An important consideration for all heterostructure devices is the influence of Fermi level pinning at the metal/semiconductor interface. The pinning studies found in the literature discussed previously explored defect effects on pinning strength, and demonstrated atomic scale inhomogeneities in the effective barrier height between the MoS₂ and metal contact. However, little work has been conducted to investigate the effect of wafer-scale MoS₂ quality (i.e., quality differences on a scale larger than 10 μm) on pinning and the resulting device behavior. This work explores the impact of wafer-scale MoS₂ quality on Fermi level pinning. MoS₂ of varying qualities are synthesized and subsequently characterized using Raman spectroscopy and XPS. Symmetric and asymmetric purely vertical heterostructure devices are fabricated from both film qualities, and their electrical characteristics are measured and modeled to determine the dominant injection mechanism. Ultraviolet Photoelectron Spectroscopy (UPS) is used to probe the work function of the metal/MoS₂ interfaces, which show consistency with the electrical measurements by revealing lower effective work functions of metal in contact with low-quality MoS₂. Whereas the previous chapters focused on material synthesized at low temperature, this chapter will explore Fermi level pinning effects in MoS₂ films synthesized at higher temperatures. As Fermi level pinning is a subtler mechanism, high temperature synthesized films are used in order to mitigate any effects unrelated to pinning.

Purely Vertical Heterostructure Device Operation

The device architecture utilized for this pinning study is the simple two-terminal metal/TMD/metal heterostructure, shown in Figure 26 (a) for the case of MoS₂. As stated earlier, current flow through this device is purely vertical and out-of-plane; no lateral current transport

occurs through the MoS₂. The three injection mechanisms (Direct tunneling, thermionic emission (TE), and Fowler-Nordheim (FN) injection) are represented by the band diagram of the heterostructure device shown in Figure 26 (b). With sufficient MoS₂ thickness (greater than ~5 nm), direct tunneling is mitigated and carrier injection is limited to TE and FN injection. Both of these injection mechanisms strongly depend on the Schottky barrier height, which in turn can be influenced by pinning effects. Therefore, different levels of pinning strength should yield different injection behavior, and therefore different device characteristics.

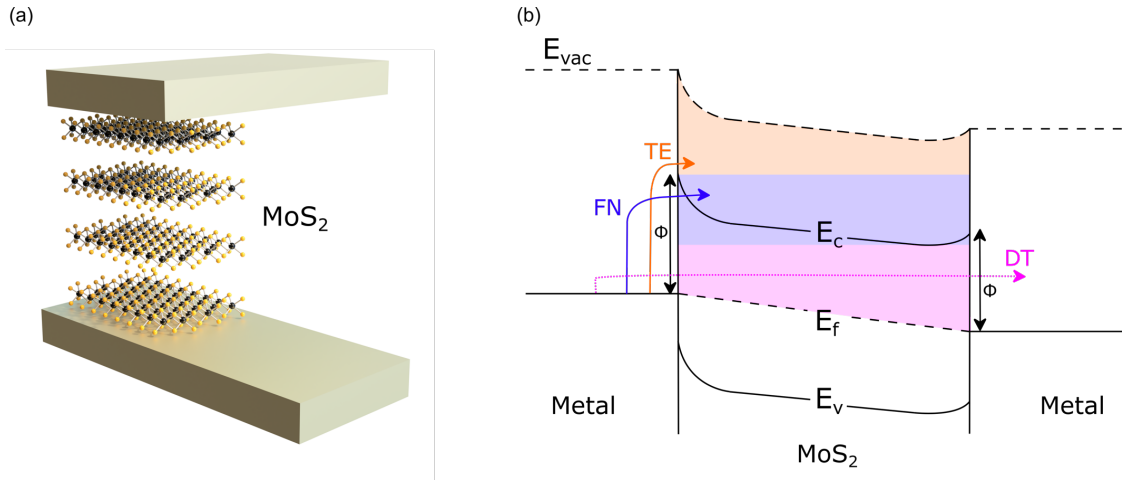


Figure 26. (a) Schematic of a metal/TMD/metal purely vertical heterostructure, with MoS₂ as the TMD. The associated band structure of the device is shown in (b). The three forms of carrier injection are shown via colored arrows along with their associated energy levels. The three injection mechanisms are TE, FN tunneling, and DT.

Synthesis of Varying Quality MoS₂ Films

To generate MoS₂ films of various qualities, MoS₂ synthesis was performed at “low” (700 °C) and “high” (900 °C) temperatures [54]. Molybdenum (1 nm) was evaporated onto a thermally grown SiO₂ by electron beam evaporation. The thin film was placed in a tube furnace along with a quartz crucible with 50 mg of sulfur powder (sigma-Aldrich). The furnace was evacuated to a

base pressure of 10^{-6} Torr and then backfilled with argon to 5 Torr. The chamber was then sealed, and the temperature was increased to the desired synthesis temperature (700 and 900 °C), whereupon temperature was held for 1 hour before cooling under argon.

Representative Raman spectra for each synthesis are shown in Figure 27 (a). The peak separation between the out-of-plane A_{1g} phonon node and the in-plane E^{1}_{2g} phonon node yields film thickness information [55]. Both the high and low temperature synthesized MoS_2 yield spectra with a peak separation of 23.4 cm^{-1} , consistent with three-layer MoS_2 . Minor variation over the full $2 \times 2 \text{ in}^2$ wafer was observed, with an inhomogeneity of only ± 0.2 layers measured. The FWHM of both peaks also yields qualitative information about the physical structure of the film, with sharper peaks indicating higher quality material [56, 57]. As noted in Figure 27 (a), the 900 °C MoS_2 's A_{1g} and E^{1}_{2g} FWHMs are both sharper and closer to values obtained from exfoliated geological MoS_2 crystals than the 700 °C synthesized film, indicating that the 900 °C film is of higher quality [54].

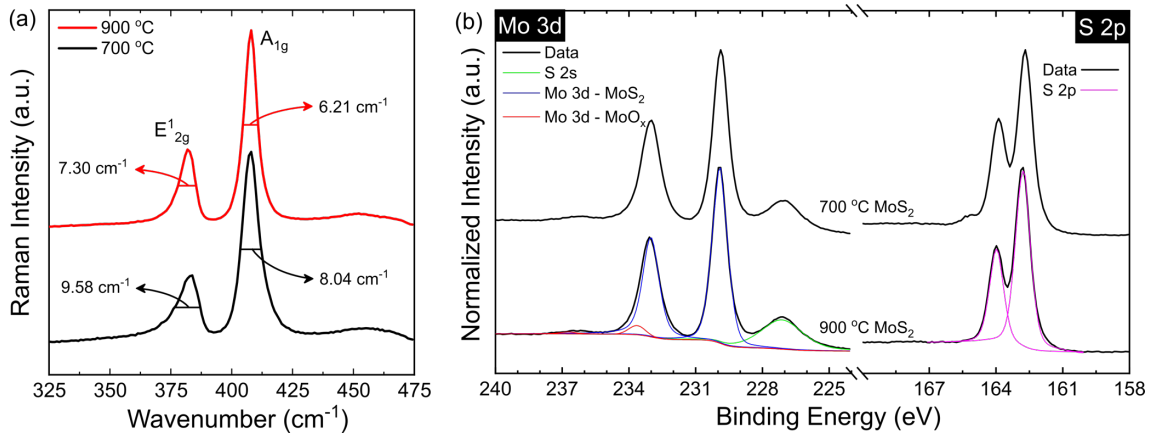


Figure 27. (a) Raman spectra for the 900 and 700 °C synthesized MoS_2 . Peak widths for the A_{1g} and E^{1}_{2g} peaks are shown, with uncertainty on the order of $\pm 0.04 \text{ cm}^{-1}$. (b) XPS Mo 3d and S 2p spectra for the 900 and 700 °C synthesized MoS_2 , including the peak fits for the 900 °C synthesis. The Mo 3d spectrum includes the S 2s contribution as well as the MoS_2 and MoO_3 Mo 3d doublets. The S 2p is fit with a single S 2p doublet.

To determine the stoichiometry of the MoS₂, XPS was performed on the synthesized films. Figure 27 (b) shows the Mo 3d and S 2p XPS spectra for the 900 and 700 °C synthesized MoS₂, as well as the fit for the 900 °C spectra. To fit the Mo 3d spectrum, five standard peaks are used: The S 2s found at approximately 227 eV, a Mo 3d doublet corresponding to the MoS₂ Mo 3d^{5/2} and 3d^{3/2} peaks, and a second Mo 3d doublet corresponding to the MoO₃ Mo 3d^{5/2} and 3d^{3/2} peaks [58]. The peak separation of each Mo 3d doublet between Mo 3d^{5/2} and 3d^{3/2} is held constant at 3.1 eV, and the area ratio between the peaks is fixed at 1.5:1. Additionally, the peak widths of all four Mo 3d peaks are constrained to be the same. The position of each doublet relative to the other, as well as the S 2p peak, is allowed to change. All parameters corresponding to the S 2p peaks were unconstrained. Similarly, the S 2p spectrum is fit with a single doublet corresponding to the S 2p^{3/2} and 2p^{1/2} peaks, with the peak separation fixed at 1.18 eV, the peak widths constrained to be the same, and the area ratio between the S 2p^{3/2} and 2p^{1/2} fixed at 2:1. Both the Mo spectrum and S spectrum are consistent with the position and peak shapes of the semiconducting 2H phase of MoS₂[59].

The stoichiometry calculation was performed by normalizing the area of the MoS₂ Mo 3d doublet by molybdenum's sensitivity factor (2.75), by normalizing the area of the S 2p doublet by sulfur's sensitivity factor (0.54) [60] and taking the ratio of the normalized peak areas. Doing so for 900 °C MoS₂ yields a stoichiometry of 1.99:1, nearly at the perfectly stoichiometric 2:1 Ratio. The Mo 3d and S 2p spectra for 700 °C MoS₂ are nearly identical in peak shapes, positions, and relative intensities, and the stoichiometry calculation from the fitted spectra yield an atomic ratio of 1.98:1.

The difference in Raman peak widths and similarity in stoichiometries between the 700 °C and 900 °C MoS₂ indicates that the primary difference in quality between the two films involves atomic structure and grain size [56]. The 700 °C film therefore has a higher density of grain boundaries, which typically are Mo-terminated and are high-energy sites [61, 62].

Symmetric Heterostructure Device Behavior

To study the effects of Fermi level pinning in metal/MoS₂/metal heterostructure devices, purely vertical two-terminal heterostructures were fabricated in a cross-point architecture, shown optically in Figure 28 (a). Each set of 8 cross-bars (4 bottom and 4 top) yield 16 devices per array, with a single device located at the intersection of each cross-bar. Each cross-bar has a width of 10 μm , resulting in an active device area of 100 μm^2 . Planar, three-layer MoS₂ was repeatedly transferred using a standard wet transfer method [2] to yield approximately 6 nm of MoS₂ encapsulated between top and bottom 80 nm gold contacts. Each intersection of cross-bars results in the same device structures shown in Figure 26 (a), which consists of van der Waals MoS₂ stacked vertically between symmetric gold contacts.

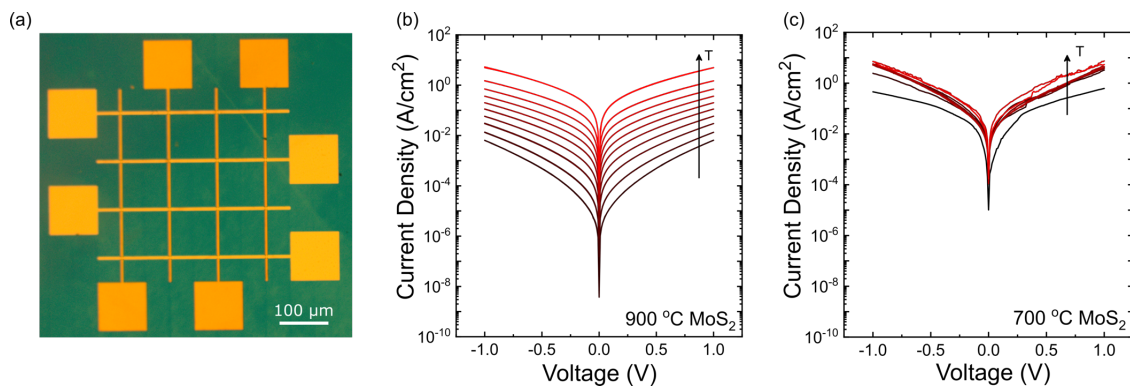


Figure 28. (a) Optical image of a cross-point array of purely vertical heterostructures. Each intersection between cross-bars is a single active device. Temperature dependence of I–V

measurements for the 900 (b) and 700 °C (c) MoS₂ vertical structures. Measurements were conducted at temperatures ranging from 100 K (black curves) to 400 K (red curves) in increments of 30 K.

As discussed previously, the current through the vertical heterostructures is due to a combination of FN and TE injection. FN injection is a process that follows an exponential tunneling form

$$I_{FN} \propto \frac{V^2}{\Phi} \exp\left(-\frac{8d(2m)^{1/2}\Phi^{3/2}}{3\hbar qV}\right) \quad (2)$$

where V is the applied bias, m is the carrier effective mass, $\hbar$ is the Plank constant, d is the Schottky barrier width, and Φ is the Schottky barrier height (SBH) [48, 63-67]. Because the FN tunnel current is dependent on the integral of the difference in Fermi functions in the metal and MoS₂, FN tunnel current can be regarded as temperature-independent. Therefore, FN injection should contribute equally to current density across all measurement temperatures [68]. In contrast, TE injection is a temperature-dependent process and is of the form

$$I_{TE} = A^* T^2 e^{-q\Phi/kT} (e^{qV/kT} - 1) \quad (3)$$

where A^* is the Richardson constant, T is the temperature, and k is the Boltzmann constant [65, 69, 70]. Both FN and TE injection mechanisms are dependent on the effective barrier height at the metal/MoS₂ interface, and therefore any changes in the barrier height due to Fermi level pinning should influence both injection mechanisms.

The temperature dependence of the current-voltage relationship is shown for both high- and low-temperature MoS₂ devices in Figure 28 (b,c). The 900 °C MoS₂ devices exhibit a strong temperature dependence across the temperature range of 100-400 K. Conversely, the 700 °C MoS₂ exhibits essentially no temperature dependence. Additionally, the current density at all temperatures for the 700 °C MoS₂ is similar in magnitude to that for the 900 °C MoS₂ at high measurement temperatures (i.e., >340 K).

An alternative way to view the I - V data shown in Figure 28 is in an FN plot. By viewing the I - V data in a $\ln(I/V^2)$ versus $1/V$ form, the transition between FN tunneling and TE injection can be observed as the minimum in the $\ln(I/V^2)$ curve [48, 71]. The temperature dependence of the 900 °C MoS₂ devices is shown in Figure 29 (a). From inspection, two distinct features immediately visible in the data. First, the strong temperature dependence is again visible, with increasing temperature giving rise to larger current densities. The second feature is subtler: the FN threshold voltage shifts to higher voltages with increasing temperature, as highlighted by the blue triangle. Alternatively, this phenomenon can be described as the FN threshold voltage shifting to lower voltage values with decreasing temperature. This shift agrees with the conventional understanding of carrier injection; by decreasing the temperature, TE injection is mitigated and less FN tunnel current is required to dominate the I - V relationship [72, 73]. The I - V characteristics of the 700 °C MoS₂ devices are shown in Figure 29 (b). In contrast to the 900 °C MoS₂ devices, the 700 °C devices not only exhibit minimal temperature dependence, but the FN threshold voltage also does not exhibit the same shift to higher voltage values with increasing temperature. The lack of FN threshold dependence on measurement temperature exhibited by the 700 °C MoS₂ devices as well as the strong FN threshold temperature dependence exhibited by the 900 °C MoS₂ devices is shown in Figure 29 (c). For the 900 °C devices, the voltage required to shift from TE injection to FN

injection increases from 0.2 V to nearly 0.7 V from 130 to 400 K. Conversely, the 700 °C devices show no apparent temperature dependence, where the FN threshold voltage maintains a constant average value of approximately 0.4 V.

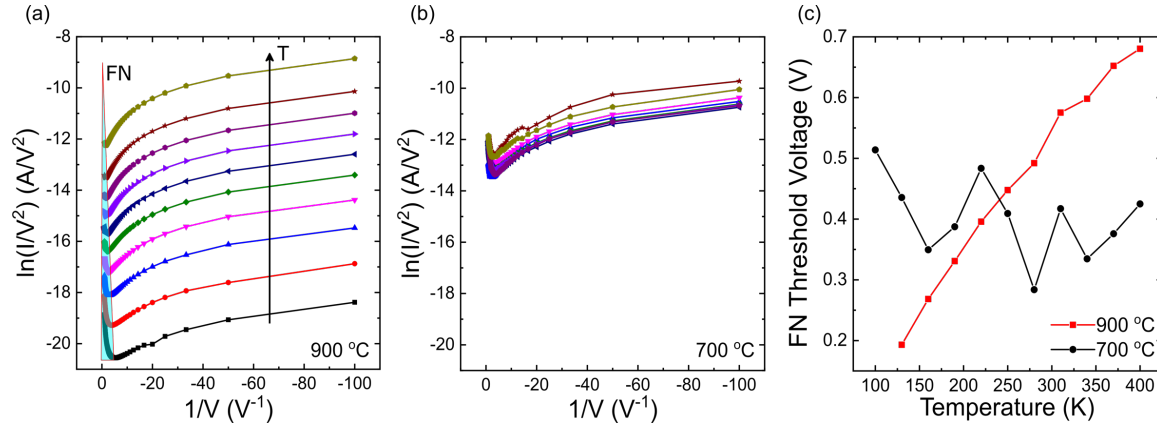


Figure 29. FN plots of the temperature dependence of the I – V relationship for 900 (a) and 700 °C (b) devices. The FN injection regime is highlighted in (a) by the blue triangle. The temperature dependence in (b) is essentially nonexistent. The FN threshold voltage at each temperature for both MoS₂ films is shown in (c). Error bars are smaller than the shown data points.

The disparity in temperature dependence between the high- and low-quality MoS₂ devices suggests that the low-quality MoS₂ devices are dominated by a temperature-independent mechanism, whereas the high-quality MoS₂ devices have contributions from both temperature-independent and -dependent mechanisms. To verify that these two mechanisms of injection are consistent with the observed behaviors of the 900 and 700 °C MoS₂ devices, device modeling was performed to fit the measured I – V data.

From eq. (2), the barrier height at the gold/MoS₂ interface can be extracted using the slope of the high voltage FN regime of the $\ln(I/V^2)$ versus $1/V$ trendline. Rewriting eq. (2) yields

where d is the FN barrier width. From the slope of the linear portion of the trendline in the low $1/V$

$$q\Phi = \left(\frac{(\text{slope})(3hq)}{8\pi d\sqrt{2m^*}} \right)^{2/3} \quad (4)$$

regime, an effective barrier height can be extracted, given an effective electron mass and Schottky barrier width. An effective mass ratio of $0.18m^*/m_o$ is used, as per the results of Zhu et al. [48]. This specific value is chosen because the effective mass was calculated specifically in the out-of-plane direction, corresponding to the orientation of current flow in these purely vertical heterostructures. An effective barrier width of 0.3 nm is used, as per the study by Ahmed et al. [64]. Ahmed et al. utilized 14 nm-thick MoS₂ flakes in their experiments, a thickness that produced interface characteristics analogous to “bulk” MoS₂ contacted with metal. Similarly, this work uses relatively thick MoS₂ films, so values corresponding to the interaction between “bulk” MoS₂ and metal are essential. By taking the slope of the linear portion of the trendline in the low $1/V$ regime, using the out-of-plane effective mass for MoS₂ calculated by Zhu et al. [48] and the barrier width determined by Ahmed et al. [64], the effective barrier height can be extracted for the gold/MoS₂ interface for both the high- and low-quality MoS₂ devices. Specifically, a barrier height of 0.44 eV is extracted for the high-quality MoS₂/gold interface, whereas a height of 0.18 eV is extracted for the low-quality MoS₂ interface.

Using the extracted effective barrier heights determined from the FN injection portion of the I - V characteristics, contributions from both FN and TE injections can be modeled and compared to the measured device data using eqs. (2) and (3), respectively. Figure 30 (a) shows the

experimental device characteristics of the 900 °C MoS₂ devices measured at 130 and 500 K in a FN plot form. The single FN contribution and the two temperature-dependent TE contributions are superimposed, where TE injection dominates at low voltages (high $1/V$ values) and FN injection dominates at high voltages (low $1/V$). the modeled FN injection follows the description of the FN tunnel current well: a linear regime at high biases followed by a levelling off at low biases. Similarly, the modeled TE contributions align well with the experimental data, dominating injection behavior at low biases before being overtaken by FN injection at larger biases. The modeled device characteristics agree well with the measured behavior, indicating that FN and TE injections are the mechanisms that dictate device behavior. In addition, the effective SBH of 0.44 eV extracted from eq. (2) is in good agreement with both the measured behavior as well as previously studied injection barrier heights [48].

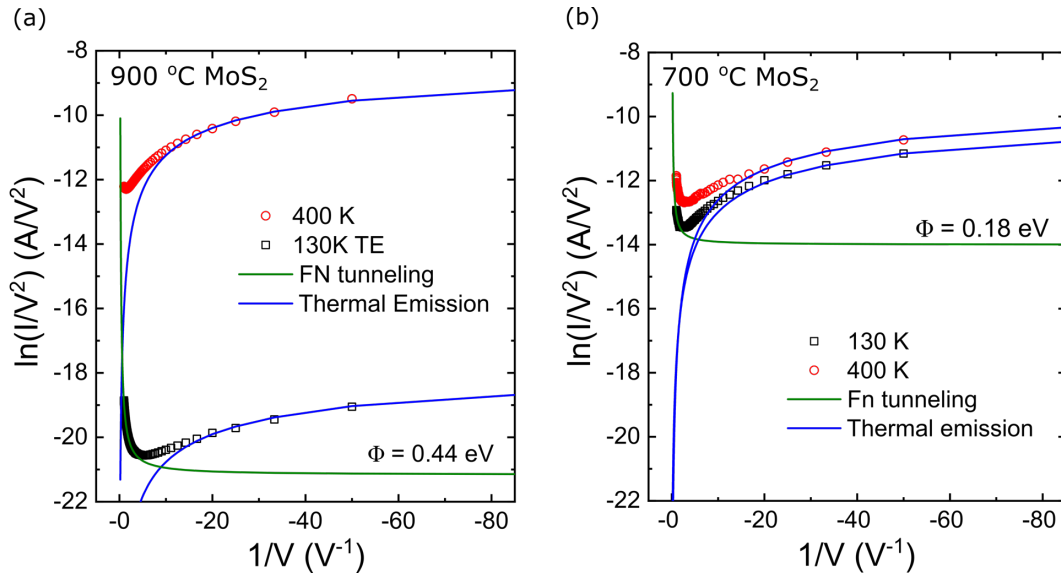


Figure 30. Modeled I–V characteristics of the 900 (a) and 700 °C (b) MoS₂. Measurement temperatures of 130 and 400 K are denoted by black squares and red circles, respectively. The FN and TE contributions are plotted in green and blue, respectively. Two TE curves are plotted in (a,b) because of the temperature dependence of the TE contribution.

The device characteristics measured at 130 and 400 K, as well as the FN and TE modeled contributions, for the 700 °C MoS₂ devices are shown in Figure 30 (b). Notably, both high-and low-temperature measurements exhibit similar current magnitudes, which falls in agreement with the overall larger FN contribution across all biases. In addition, the TE contribution loses some of its temperature dependence, where TE contributions at both 130 and 400 K exhibit similar current densities. The combination of increased FN injection along with mitigation of TE temperature dependence can be explained by the reduced effective SBH, which dropped significantly to 0.18 eV. The FN contribution in the low-voltage regime saturates at a larger value for a smaller barrier height, which is consistent with the findings from Zhu et al. [48]. Additionally, these results demonstrate that a decrease in the effective barrier height leads to a smaller difference in TE contributions between two temperatures, evidenced by the similar current magnitudes for the 130 K and 400 K measurements at the low bias regimes shown in Figure 30 (a,b).

The significant reduction in the barrier height in the 700 °C MoS₂ sample suggests that gold is susceptible to strong Fermi level pinning effects that arise from material quality effects. The increase in interaction may be due to an increase in the defect density and grain boundary edges in the MoS₂, which can act as sites for gold to interact more strongly with the adjacent MoS₂. The increased interaction leads to stronger electrostatic coupling between the layers, pinning the gold's work function and effectively reduced the SBH at the interface.

This observed change in SBH at the MoS₂/gold interface, observed experimentally and verified theoretically, is due to a change in the gold's effective work function. It appears that because the lower quality MoS₂ has an overall higher defect density (primarily due to grain boundaries), the MoS₂ pins the gold's work function at a higher energy level [74]. The reduction of the gold's effective work function reduces the barrier height at the interface and enables a larger

FN tunneling current density at a given applied bias. In contrast, the high-quality MoS₂ does not pin the gold's work function as strongly, resulting in a larger SBH and a lower overall FN tunnel current density. Because the SBH is larger, a larger applied bias is required to induce significant FN injection, and at higher temperatures, TE provides a larger injection current than FN tunneling at low-to-moderate biases. A band diagram schematic showing the differences between the high- and low-quality MoS₂ devices is shown in Figure 31 (a,b) respectively. In the case of low-quality MoS₂, the effective barrier height at the gold/MoS₂ interface is reduced because of a strong interaction between defect states in the MoS₂ and the adjacent gold. We also note that the 900 °C MoS₂ case is not absent from pinning effects, as metal-induced gap states (MIGS) can exist in the absence of defects [75]; these results simply imply that defect effects strongly influence the pinning strength between the high and low MoS₂ film qualities when in contact with gold.

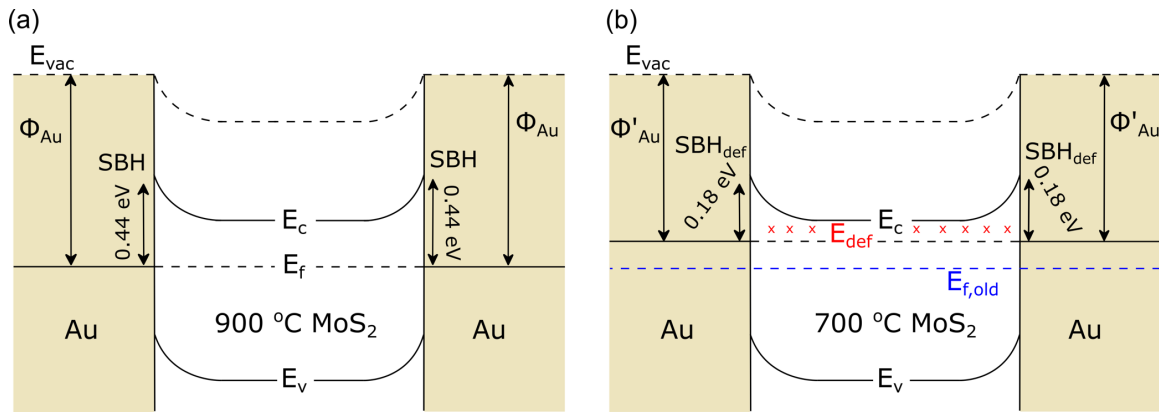


Figure 31. Band diagrams for the symmetric Au structures are shown in (a,b) for the 900 and 700 °C MoS₂, respectively. In (b), shallow conduction band defects are denoted by the red x, the work function of the Au when pinned is given by Φ'_{Au} , and the defect-induced reduced effective SBH height is labeled as SBH_{def}. $E_{f,old}$ in (b) corresponds to the E_f and Au band edge when in contact with high quality MoS₂, where weaker pinning effects are assumed. Drawings are not to scale.

Asymmetric Heterostructure Device Behavior

Because the injection behavior at the MoS₂/metal interface is dependent on the contact metal's work function, choosing a metal with a different work function should significantly change the I - V behavior. As such, the role of material quality on fermi level pinning can be further explored. Therefore, a second set of heterostructure devices was fabricated, this time using platinum as the bottom contact metal. Platinum has a larger work function than gold and should yield asymmetric injection in the forward and reverse bias regimes because of offering SBHs at each interface [76, 77]. Specifically, the SBH of the MoS₂/gold interfaces is expected to be significantly lower than that of the MoS₂/platinum interface, and therefore injection into MoS₂ from gold (positive biases) is expected to be more favorable than injection from platinum (negative biases).

Room temperature I - V characteristics for the 700 and 900 °C asymmetric MoS₂ devices are shown in Figure 32(a). the positive and negative bias regimes are highlighted as injection from gold and platinum, respectively, by the metal's corresponding color. Interestingly, the high-quality MoS₂ synthesized at 900 °C yields device characteristics that are symmetric, opposed to initial expectations. This result suggests that gold and platinum are pinned to a similar energy level when in contact with the 900 °C MoS₂/ leading to similar barrier heights at both interfaces. However, the 700 °C MoS₂ does result in asymmetric device characteristics, with approximately 2 times larger current densities in the gold injection regime. This implies that the barrier height at the gold/MoS₂ interface is smaller than that at the platinum/MoS₂ interface, leading to preferential injection from the gold.

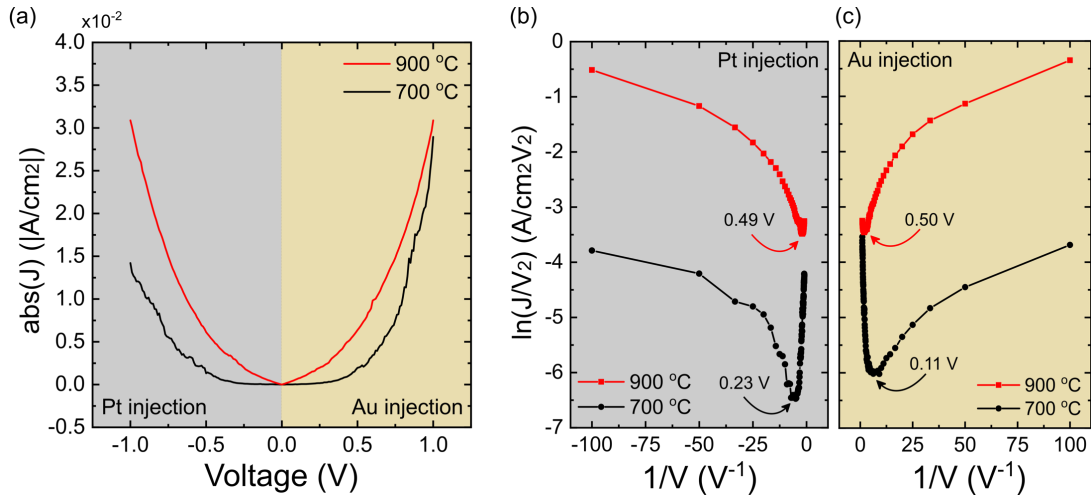


Figure 32. (a) Absolute value of the I - V relationship for the 900 and 700 °C MoS₂ asymmetric Au/Pt devices measured at room temperature. The positive bias regime corresponds to injecting electrons from the Au into MoS₂, whereas the negative bias regime corresponds to injecting electrons from the Pt into MoS₂. (b,c) show the same data plotted in (a) but presented in FN plots for the Pt and Au injection regimes, respectively. The FN threshold voltage is noted for each curve, given by the voltage value at each minimum.

The I - V characteristics are replotted in FN plot form in Figure 32 (b,c) for platinum and gold injections, respectively. The FN threshold voltage is given for each interface for both MoS₂ qualities. The FN threshold voltage for the 900 °C MoS₂ asymmetric structure is nearly identical for both injection regimes; TE is overtaken in the current density at near 0.5 V in both directions. The 700 °C asymmetric structure yields a noticeable different upon observation of the FN plots. The FN threshold voltage is larger at the Pt injection interface compared to that at the gold injection interface. The discrepancy between the two threshold voltages suggests that the gold's work function is pinned to a higher energy value than the platinum's work function, reducing the barrier height at the gold/MoS₂ interface more drastically than the platinum/MoS₂ interface. The reduction in the effective barrier height leads to an increased FN tunnel current, shifting the FN threshold voltage to lower values.

As performed for the symmetric gold/MoS₂/gold heterostructures, the effective barrier height can be extracted for both high-and low-quality MoS₂/platinum interfaces using eq. (4). Doing so yields an effective barrier height of 0.46 eV for the 900 °C MoS₂/platinum interface and a barrier height of 0.33 eV for the 700 °C MoS₂/platinum interface. The modeled behavior for the high- and low-quality MoS₂ devices is shown in Figure 33 compared to their respective experimental data.

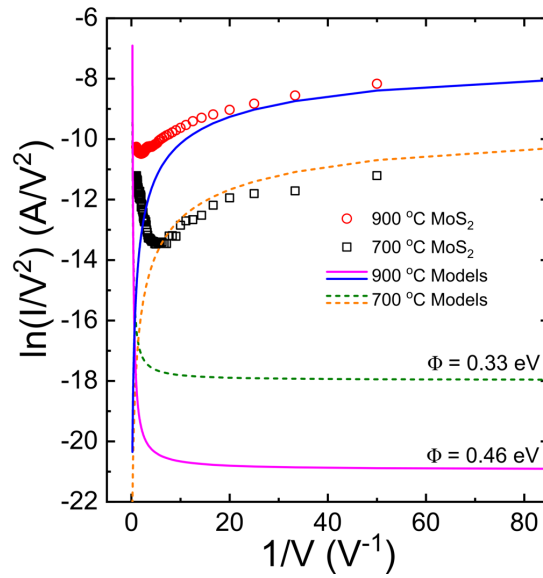


Figure 33. Modeled I–V characteristics of the 900 and 700 °C MoS₂ asymmetric heterostructures measured at room temperature. The FN and TE contributions are plotted as solid and dashed lines for the 900 and 700 °C devices, respectively.

Physically Characterizing the MoS₂/Metal Interface

To concretely probe the work function of the metal/MoS₂ interface, UPS was used to explicitly calculate the work function of a measured sample using the following equation

$$\phi = h\nu - (E_{SEE} - E_f) \quad (5)$$

Where $h\nu$ is the incoming photon energy, E_{SEE} is the secondary electron edge (SEE) energy, and E_f is the Fermi energy. Because the incoming photon energy is a known value and both the E_{SEE} and E_f can be extracted from the UPS spectrum, the work function can be explicitly calculated. Previous studies have used UPS to examine the effective work function of metals deposited onto MoS₂ as a function of the metal thickness [78], but to our knowledge, no studies have been performed on the effect of macroscopic MoS₂ quality on Fermi level pinning and the resulting metal work function.

Figure 34 (a) shows the UPS spectra for the as-grown 900 °C and 700 °C MoS₂ films. The SEE and E_f are highlighted on the 900 °C spectrum. Figure 34 (b,c) shows the UPS spectra for the bulk control gold and platinum surfaces, respectively. The statistical calculation of each surface's work function is shown in Figure 34 (d) using a standard box and whisker plot, and is consistent with the literature values of each surface's work function [76-78]. Notably, the 700 °C MoS₂ has a larger variance of the calculated work function compared to the 900 °C film, which can be attributed to the broader SEE the 700 °C film exhibits, seen by the increased width of the shaded region. The larger variance in the calculated work function can be attributed to increased inhomogeneity in the film because of the higher defect density and additional disorder. The calculated work functions of the control metals shown minimal variance.

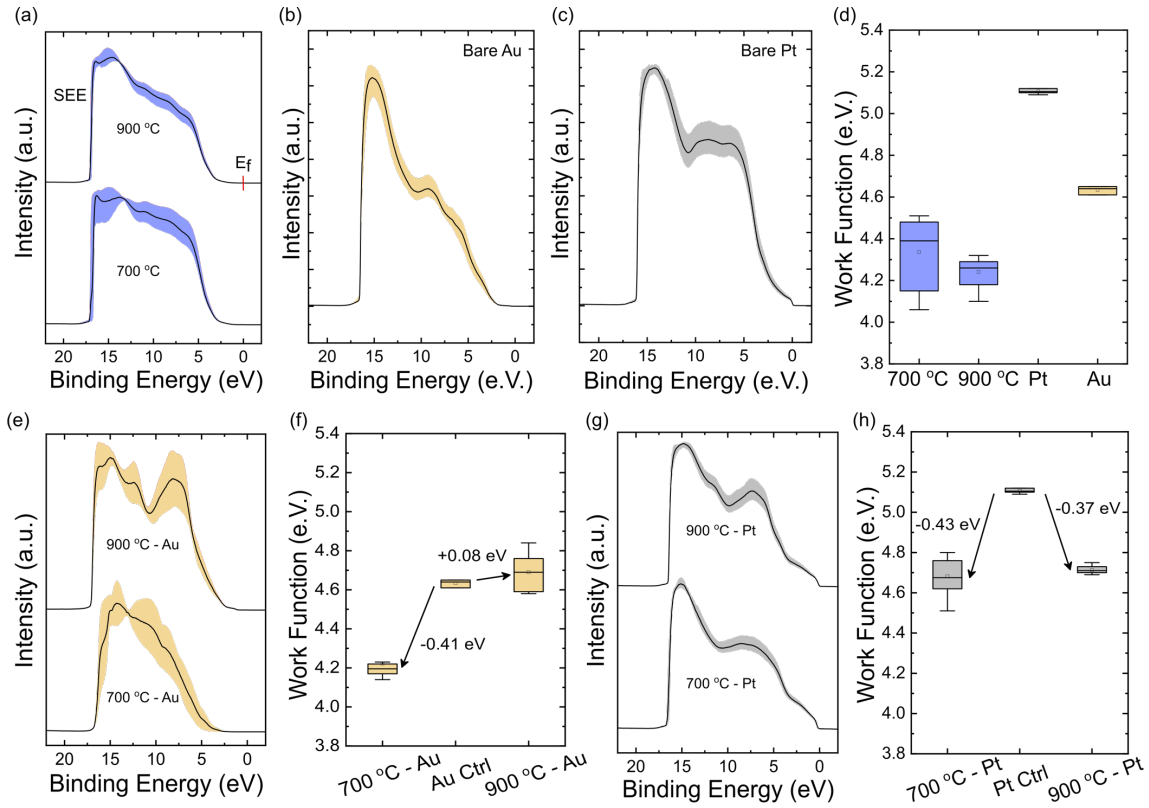


Figure 34. UPS spectra of MoS₂/metal interfaces. The UPS spectra for as-grown 900 and 700 °C MoS₂ are shown in (a). The secondary electron edge and E_f are shown on the 900 °C spectrum in (a). (b,c) show the control UPS measurements for bulk Au and Pt control surfaces, whereas (d) contains the statistics of the calculated work functions for each spectrum in (a–c). The measured UPS spectra for Au in contact with both high- and low-quality MoS₂ are plotted in (e), and the calculated work functions for both are compared to a bulk Au control’s work function in (f). Similarly, (g) shows the UPS spectra for Pt in contact with high- and low-quality MoS₂ and (h) shows the calculated work functions compared to a bulk Pt control. For all spectra, the shaded region represents the area between the maximum and minimum spectra measured for each sample, and the solid black trendline represents the average of all spectra taken.

To determine the work function of the MoS₂/metal interface, samples were prepared where a thin metal layer was evaporated onto the high- and low-quality MoS₂. The thickness of the metal is strictly limited by the measurement depth of the UPS technique, and therefore depositing thicker metal films would skew the work function determination by introducing the “bulk” metal [78].

Therefore, 0.5 nm of gold and platinum were deposited on both MoS₂ qualities via e-beam evaporation at a rate of 0.01 nm/s.

The UPS spectra for the 0.5 nm gold/MoS₂ interfaces are shown in Figure 34(e), and the calculated work functions of each interface are shown in Figure 34 (f), along with the control gold work function. Noticeably, the work function of the gold in contact with the low-quality MoS₂ is drastically reduced, suggesting strong pinning toward the MoS₂ conduction band edge. Additionally, the 0.41 eV gold work function reduction is consistent with the extracted effective SBH reduction shown in Figure 30. The agreement between the modeled reduction in SBH from electrical results and measured work function change using UPS further supports the strong Fermi level pinning seen at the 700 °C MoS₂ gold interface. Conversely, the high-quality MoS₂ does not appear to strongly modify the gold work function, as the work function of the 900 °C MoS₂/gold interface exhibits a negligible shift from the control gold work function. Figure 34 (g,h) shows similar data pertaining to the platinum/MoS₂ interfaces. The work function calculations for the platinum interfaces yield interesting results. The 900 °C MoS₂ appears to pin the work function of the platinum to a similar value as the gold work function. the similar energy level that both metals are pinned to is consistent with the symmetric I - V relationship observed in Figure 32 and the similar extracted barrier heights in Figure 33. Gong et al. have shown theoretically that MIGS can occur in MoS₂ metal interfaces, leading to pinning effect that do not require a large defect density [75]. When observing gold's and platinum's work functions when in contact with the 700 °C MoS₂, a clear different of approximately 0.5 V is observed. The definitive difference in the interface work function at the gold/MoS₂ and platinum/MoS₂ interfaces corroborates the asymmetric I - V behavior and the different in the FN threshold voltage for each interface shown in Figure 32.

From the calculated work functions of each MoS₂/metal interface, a new set of representative band diagrams can be drawn. Band diagrams for the 900 and 700 °C MoS₂ asymmetric gold/platinum devices are shown in Figure 35 (a,b), respectively. Unexpectedly, the 900 °C MoS₂ asymmetric structure results in a relatively symmetric band diagram, where the difference between the platinum and gold work functions is only 0.03 eV. Conversely, the 700 °C MoS₂ asymmetric structure results in an asymmetric band structure, where the difference between the platinum and gold work functions is 0.47 eV. The effective barrier heights extracted from Figure 33 are also included, showing similar barrier heights at each interface for the 900 °C MoS₂ and asymmetric barrier heights at each interface for the 700 °C MoS₂.

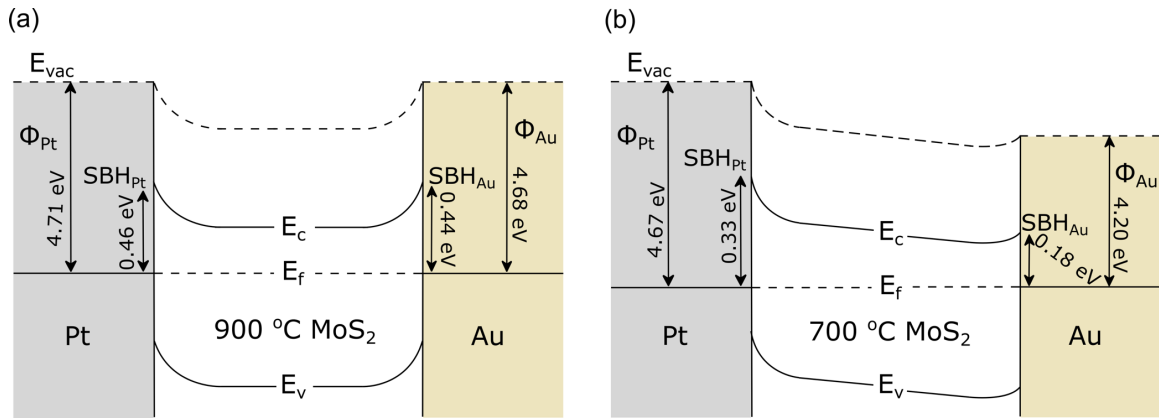


Figure 35. Band diagrams for the 900 (a) and 700 °C (b) MoS₂ asymmetric Pt/MoS₂/Au vertical heterostructures, calculated using the extracted barrier heights and the calculated work functions. Drawings are not to scale.

To understand the reason behind the significant difference in pinning between the high- and low-quality MoS₂ asymmetric structures, XPS was performed on each MoS₂/metal interface sample. By investigating shifts in the core levels, potential bonding and interactions can be determined between MoS₂ and the metal. Figure 36 shows XPS spectra for the different samples,

with each spectrum normalized to the C 1s peak's position. The Mo 3d core level spectrum for the as-grown high- and low-quality MoS₂ films, in addition to the gold thin film interface samples, is shown in Figure 36 (a). A clear shift of 0.29 eV is observed in the 700 °C gold/MoS₂ spectrum, whereas both the as-grown films as well as the 900 °C MoS₂/gold spectra exhibit degenerate peak positions. Prior work has shown that a shift to lower binding energies in the Mo 3d spectrum indicates a partially covalent metal/MoS₂ interface [79]. A similar shift is observed in the 700 °C MoS₂/gold sample, indicating some amount of covalent bonding between gold and MoS₂, forming a partially covalent interface (a deviation from the expected van der Waals interaction). Similarly, a shift of 0.36 eV is observed in the S 2p spectrum for the 700 °C MoS₂/gold sample, whereas the as-grown films and the 900 °C MoS₂/gold sample again exhibit degenerate peak positions, observed in Figure 36 (b). This shift has also been previously observed as a result of increased covalent interaction between gold and sulfur atoms [80]. In Figure 36 (c), the Au 4f spectra for both MoS₂/gold interface samples are shown and compared to a standard gold reference spectrum. The 700 °C MoS₂/gold interface again exhibits a noticeable shift, this time manifesting in the Au 4f doublet position. This shift can also be attributed to a transition away from a van der Waals interaction and further supports the trend of a partially covalent gold/MoS₂ interface [80, 81]. Notably, no such shifts are observed for the 900 °C MoS₂/gold interfaces for any of the Mo 3d, S 2p, or Au 4f spectra; all differences in the peak positions of each respective spectra, compared to the reference samples, are less than 0.03 eV.

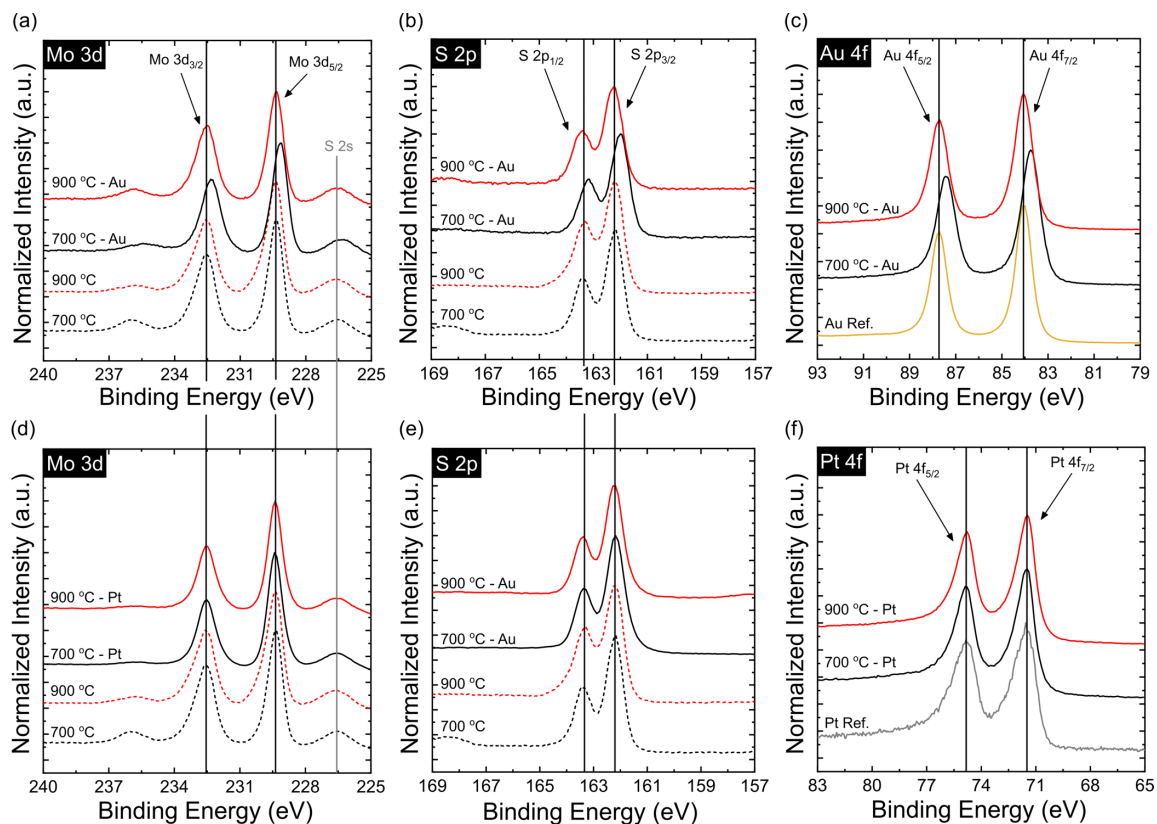


Figure 36. Mo 3d spectra for the MoS₂/Au (a) and MoS₂/Pt (d) interfaces, compared to the as-grown spectra (dashed lines). The MoS₂ Mo 3d^{3/2} and 3d^{5/2} peak positions are denoted by the black lines in (a,d), along with the S 2s peak by the gray line. (b,e) show the S 2p spectra for the MoS₂/Au and MoS₂/Pt interfaces, respectively, compared to the as-grown spectra (dashed lines). S 2p^{1/2} and 2p^{3/2} are denoted by black lines. (c) shows the Au 4f core level spectra for the MoS₂/Au interfaces, compared to the bulk Au reference spectrum. Au 4f^{5/2} and 4f^{7/2} are denoted by black lines. (f) shows the Pt 4f core level spectra for the MoS₂/Au interfaces, compared to the bulk Pt reference spectrum. Pt 4f^{5/2} and 4f^{7/2} are denoted by black lines.

The observed strong interaction between the defective MoS₂ and gold can be explained by looking at an analogous system. A large amount of literature exists on the interaction chemistry between sulfur and gold, particularly in the self-assembled monolayer (SAM) community [46, 82-85]. Specifically, in the context of SAMs, the sulfur-gold bond takes the form of a metal thiolate, which is extremely strong and yields a bond strength of approximately 44 kcal/mol [83]. Similarly,

in a defective MoS₂ film comprising a high density of point defects and grain boundaries, sulfur atoms that do not have a full valence of electronic bonds to molybdenum can interact strongly with the adjacent gold film. This chemical interaction forms a covalent bridge between the gold and MoS₂, electrically coupling the two materials more strongly than a typical van der Waals interaction.

In Figure 36 (d,e), the Mo 3d and S 2p core level spectra are shown for both as-grown MoS₂ films as well as the 700 and 900 °C MoS₂/platinum interfaces. In contrast to the 700 °C MoS₂/gold interface, platinum does not exhibit any core level shifts in either the Mo 3d or S 2p spectra, where any difference in peak position is less than 0.04 eV. The lack of any observable shift in either spectrum suggests that the interface between platinum and MoS₂, both high and low qualities, remains predominantly van der Waals. One possible explanation is simply that platinum does not interact as strongly with sulfur as gold is known to, leading to a more inert interface. Figure 36 (f) shows the Pt 4f spectra for both MoS₂/platinum interface samples as compared to a platinum bulk reference sample. As in Figure 36 (d, e), no observable peak shift is detected, further supporting the conclusion that minimal covalent interaction occurred between platinum and MoS₂ of either quality.

The lack of interaction between platinum and both qualities of MoS₂ is in noticeable contrast to the case of defective MoS₂ in contact with gold. This result can also be explained from the perspective of sulfur-based thiol SAM functionalization to platinum. Whereas the gold-sulfur interaction is strong and leads to a strong covalent interaction, sulfur thiols do not bond as strongly to platinum surfaces [86]. Specifically, sulfur-based thiols bonded to gold yield a single doublet contribution to the resulting S 2p XPS spectrum. In contrast, these thiols, when exposed to platinum surfaces, yield three different doublets in the resulting S 2p spectrum, indicating that a

significant portion of the sulfur end groups did not functionalize to the platinum surface. The reduced functionalization percentage suggest that sulfur and platinum do not interact as covalently as sulfur and gold, which is consisted with our observed interfaces between MoS₂ contacted to gold and platinum.

These XPS results are consistent with the UPS data and calculated work functions for each interface. A strong core level shift is observed in all 700 °C MoS₂/gold spectra, which is in agreement with the reduction in the work function when gold contacts 700 °C MoS₂, as seen in Figure 34. The low-quality MoS₂ contains a high level of defect states, which offer sites for covalent bonding between MoS₂ and gold, resulting in a partial covalent interface. The increased covalency between MoS₂ and gold then leads to a strong interaction between the materials, leading to strong Fermi level pinning. This pinning then reduces the work function of gold, leading to an effective reduction of the SBH. In contrast, the 900 °C MoS₂ does not result in any noticeable covalent interaction via XPS core level shifts, which is consistent with the lack of observed pinning resulting in an unchanged gold work function. Similarly, the platinum/MoS₂ interfaces exhibit no core level shifts in the XPS spectra, suggesting minimal covalent interaction at the interface. The minimal interaction leads to a fixed amount of pinning due to MIGS, resulting in comparable work functions of platinum in contact with both high- and low-quality MoS₂.

Conclusion

In this study, the effect of MoS₂ material quality on Fermi level pinning was investigated, and an understanding of the relationship between wafer-scale material quality and effective contact metal work function was established. MoS₂ films of varying qualities were synthesized, and purely

vertical heterostructure devices were fabricated using gold/gold and platinum/gold contacts. The temperature dependence of the devices was explored, and it was found that low-quality MoS₂ devices are dominated by a temperature-independent injection mechanism. FN plots revealed that the FN threshold voltage is temperature-dependent for the 900 °C MoS₂ device but independent for the 700 °C MoS₂ devices. Device modeling was performed to verify the injection mechanisms, which demonstrated good agreement between the experimental and theoretical behaviors. Additionally, effective barrier heights were extracted from the device models, which revealed that low-quality MoS₂ strongly pins gold and reduces the SBH at the interface. Pinning that results in low barrier heights leads to temperature independent injection, where FN tunneling dominates injection regardless of measurement temperature. Asymmetric devices were used to realize that high-quality MoS₂ does not result in asymmetric I - V behavior. In contrast, low-quality asymmetric MoS₂ devices do exhibit an asymmetric I - V relationship and yield different FN threshold voltages for gold and platinum injection, suggesting different barrier heights at each interface. UPS was performed to calculate the effective work function of each interface, which revealed that 700 °C MoS₂ pins the gold's work function strongly to low energy values, whereas platinum remains relatively unaffected. Additionally, the measured change in the gold's work function when in contact with the 700 °C MoS₂ showed good agreement with the extracted SBH change found from modeling the symmetric device behavior. XPS measurements confirm the increased covalency between gold and low-quality MoS₂ and show minimal covalent interaction between both MoS₂ films and the platinum metal.

This work demonstrated the relevance of MoS₂ material quality on Fermi level pinning. Using cross-point device architecture, the relationship between the macroscopic material quality and the strength of Fermi level pinning was demonstrated, and various characterization techniques

were used to investigate the physical mechanisms that lead to the increased pinning strength. These experiments shed light on the impact of material quality on a large scale in purely vertical heterostructure device performance and provide insight on material requirements for successful heterostructure device construction and operation.

4.5 Radiation Effects of MoS₂-based Vertical Heterostructure Devices [87]

The previous study on radiation effects on graphene and MoS₂ FETs yielding valuable information concerning the oxide adjacent to the 2D film. However, the previously discussed radiation experiments focused on in-plane conduction of a heterostructure device, where the overlayers simply acted to passivate the 2D film from the environment. As such, the next logical step of investigating the radiation response to 2D heterostructures involves investigating heterostructure device architectures that operate on out-of-plane carrier conduction.

To facilitate the investigation of radiation effects on out-of-plane heterostructure devices, the radiation response of the MoS₂/interlayer/MoS₂ tunnel junctions was investigated. Heterostructures were fabricated using low-temperature 400 °C synthesized MoS₂, where the interlayer consists of either Al₂O₃ or HfO₂. Notably, these structures require no transfer steps; the bottom layer MoS₂ film are synthesized directly onto the bottom gold contacts, the interlayer dielectric is deposited using ALD, and the top layer MoS₂ is synthesized directly onto the dielectric interlayer. Al₂O₃ and HfO₂ were chosen for two reasons. First, the oxidation state of the metal is different for each dielectric. The previously discussed radiation studies on graphene FETs indicated that oxygen sites play a significant role in the radiation response of the device; the passivation state and vacancy concentration of oxygen in the dielectric significantly influences the behavior when exposed to ionizing radiation. Second, the work function of the two dielectrics is different, which should therefore yield different barrier heights at the MoS₂/insulator interface and therefore yield different tunneling behavior.

To fabricate the devices, 80 wells were etched into 300 nm SiO₂ using SF₆ plasma. Bottom gold contacts were e-beam evaporated into the wells, whereupon MoS₂ was directly synthesized

onto the gold. 2.71 nm of HfO₂ and 2.78 nm of Al₂O₃ were deposited onto the bottom layer MoS₂ via ALD. Afterwards, a subsequent top MoS₂ layer was directly synthesized onto the dielectric interlayer, and top gold contacts were deposited onto the top of the heterostructure using e-beam evaporation, yielding a total structure of Au/MoS₂/interlayer/MoS₂/Au. The resulting heterostructure is purely vertical, so that current flow tunnels between the MoS₂ layers predominantly out-of-plane.

X-ray irradiation effects were first explored on the vertical tunnel junctions. Both heterostructures were irradiated with 30.3 krad(SiO₂)/min X-rays at room temperature while biasing the drain contact at 0.3 V. Figure 37(a,b) shows the I_d - V_d behavior as a function of X-ray dose for the Al₂O₃ and HfO₂ heterostructures, respectively. Markedly, no significant deviations in electrical behavior are observed with increasing dose for either sample for exposures up to 1 Mrad(SiO₂), suggesting that these heterostructures are stable and not significantly influenced by X-ray irradiation. This result is in significant contrast to the in-plane graphene FETs examined in the previous study.

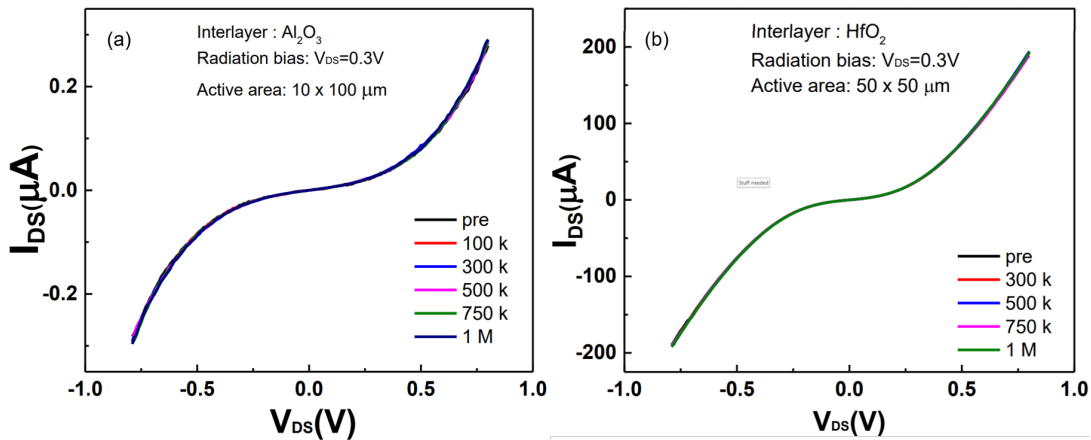


Figure 37. I_d - V_d curves as a function of X-ray total ionizing dose for MoS₂ tunnel junctions with interlayer dielectrics of Al₂O₃ (a) and HfO₂ (b). Devices were irradiated with 10 keV X-rays with 0.3 V bias applied to the drain during exposure.

As the MoS₂/insulator/MoS₂ vertical heterostructures are strongly resistant to X-ray irradiation, the next logical step is determining the tunnel junction's response to proton irradiation. The heterostructures were exposed to increasing fluences of protons, up to 10¹⁴ protons/cm². I_d - V_d device characteristics for each structure as a function of proton fluence are plotted in Figure 38. No significant changes in device behavior are observed for either structure for fluences up to 10¹³ protons/cm². Further increasing the proton fluence induces an increase in current for the Al₂O₃ interlayer devices (Figure 38 (a)), whereas the HfO₂ interlayer devices exhibit no noticeably change in device behavior with increasing fluence (Figure 38 (b)).

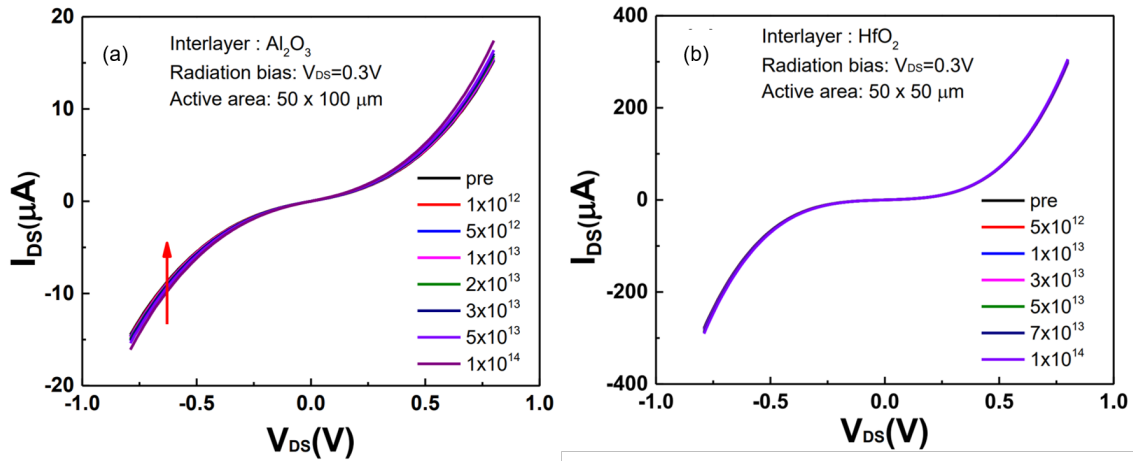


Figure 38. I_d - V_d response as a function of proton fluence for MoS₂ tunnel junctions with Al₂O₃ (a) and HfO₂ (b) interlayers. The HfO₂ devices exhibit a noticeably higher current density.

The device measurements shown in Figure 38 can be replotted in FN form, which yields information on the change in injection behavior with increasing proton fluence. Figure 39 plots the I - V data shown in Figure 38 in FN form. The inset of Figure 39 (a) shows the transition voltage between FN tunneling at high voltages (low $1/V$) and direct tunneling at low voltages (high $1/V$) for the Al_2O_3 interlayer sample. A clear shift of the FN threshold voltage is observed for the Al_2O_3 interlayer sample, decreasing from 0.54 V to 0.48 V after receiving a proton fluence of $10^{14}/\text{cm}^2$. Conversely, the HfO_2 interlayer devices exhibited no change in FN threshold voltage. The fact that the Al_2O_3 devices exhibit a FN threshold voltage shift with increasing proton fluence while the HfO_2 interlayer devices do not strongly suggests that the changes in device behavior are defect related, and not due the indirect-to-direct band gap transition in MoS_2 structures irradiated with 100 keV protons observed by Foran et al. [88].

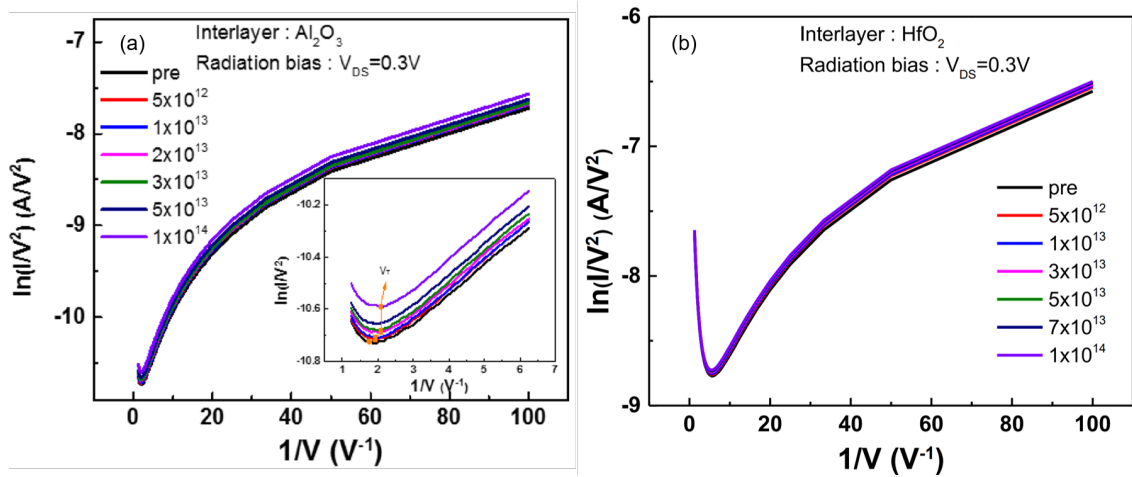


Figure 39. FN plots of the I - V data shown in Figure 38. The inset of (a) shows the evolution of the transition from direct tunneling to FN tunneling with increasing proton fluence.

The lack of X-ray radiation response in both heterostructures (Figure 37) suggests that ionizing-dose-induced depassivation of defect precursors plays little to no role in the radiation

response of the heterostructure device's behavior. In contrast, the noticeable response to proton irradiation in the Al_2O_3 interlayer heterostructure, but not the HfO_2 interlayer heterostructure, suggests that physical displacement damage (such as vacancy formation) in the Al_2O_3 may lead to trap-assisted tunneling. The displacement of light atoms (i.e. oxygen) may create defect states with energy levels aligning close to the conduction band of the MoS_2 .

To understand the nature of the proton-induced defects, DFT calculations were performed using the VASP code [14, 15]. The exchange-correlation functional was calculated using the Perdew, Burke, and Ernzerhof generalized gradient approximation [16] with a van der Waals interaction correction [17] and pseudopotentials [18]. A 550 eV plane-wave-cutoff energy was employed and a $2 \times 2 \times 1$ k-point grid was used for Brillouin-zone integrations. Atomic positions were relaxed until all forces were less than 0.01 eV/Å.

Because the primary layer-dependent differences in the electronic structure of MoS_2 occur between one and two layers, the MoS_2 was represented as a bilayer for calculations. HfO_2 was modeled using the monoclinic phase, and the θ - Al_2O_3 phase was chosen due to its lower density and oxygen-bond coordination allows for a better comparison with amorphous gate oxides [89, 90]. The oxides were 1 nm thick oriented along the [100] direction, and the lateral dimensions were chosen to minimize interfacial strain with the MoS_2 . Both heterostructure models exhibit the expected type-I band alignment.

Oxygen vacancies in Al_2O_3 introduce two unique defect levels: a fully occupied level near the Al_2O_3 valence band and an empty level near the Al_2O_3 conduction band. These states are shown in Figure 40 (a) with respect to the MoS_2 and Al_2O_3 band structures. Neither of these states are near the MoS_2 conduction band, and therefore should not contribute to trap assisted tunneling.

However, partial passivation of the oxygen vacancy by hydrogen causes significant shifts in the defect energy levels. These shifts can be seen in Figure 40 (a) as the $V_o + H$ states, which correspond to an unoccupied interfacial (I) and near interfacial (NI) which yield unoccupied states 0.24 eV above and 0.2 eV below the MoS_2 conduction band, respectively. Additionally, passivated oxygen vacancies in the bulk of the oxide, corresponding to the states labeled as B in Figure 40, yield an occupied state 0.05 eV below the MoS_2 conduction band. Sources of hydrogen to passivate these oxygen defects by diffusing through the interface include lower energy protons from irradiation and hydrogen captured during ALD. Aluminas have previously been shown to easily absorb hydrogen [91, 92], and therefore partially passivated oxygen vacancies likely affect the increase in tunnel current after exposed to proton irradiation.

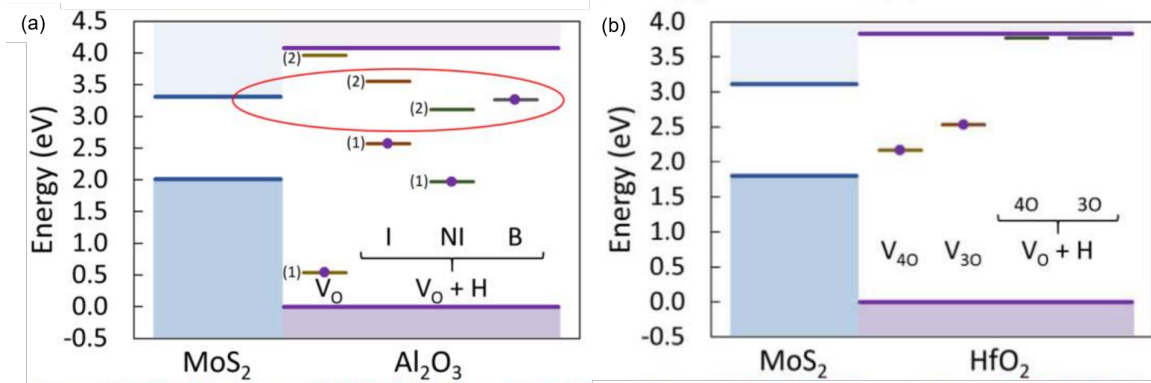


Figure 40. Modeled band alignment and defect energies for relevant defects at the $\text{MoS}_2/\text{Al}_2\text{O}_3$ (a) and $\text{MoS}_2/\text{HfO}_2$ (b) interfaces. The red oval in (a) highlights the defect levels most likely to contribute to trap assisted tunneling.

In the case of HfO_2 , oxygen vacancies introduce a hole trap 0.58 or 0.94 eV below the MoS_2 conduction band for 3-fold and 4-fold coordinated vacancies, respectively. These defect levels can be seen in Figure 40 (b). When passivated, these defect energies move close to the HfO_2

conduction band. In both the passivated and unpassivated vacancy cases, no defect states align closely with the MoS₂ conduction band, and therefore these defect states likely do not contribute to trap assisted tunneling in the tunnel junction heterostructures, which is consistent with the lack of irradiation response seen in Figure 38 (b).

Conclusions

Purely vertical MoS₂ heterostructures were fabricated to further explore the 2D/insulator interface. The MoS₂ heterostructures demonstrated resilience to X-ray irradiation, where little to no response was observed for doses up to 1 Mrad(SiO₂). When exposed to proton irradiation, Al₂O₃ interlayer devices exhibited a radiation response, where the FN tunnel current voltage threshold decreased with increasing proton fluence. Conversely, the HfO₂ interlayer structures did not exhibit any response to proton irradiation. DFT calculations reveal that passivated oxygen vacancies in Al₂O₃ lead to defect states closely aligned with the MoS₂ conduction band, which likely contribute to trap assisted tunneling. No such defect states occur in HfO₂, where both passivated and unpassivated oxygen vacancies yield defect energies strongly misaligned with the MoS₂ conduction band, consistent with the lack of observed device response to proton irradiation for the HfO₂ interlayer structures.

In summary, this work explored the effect of X-ray and proton irradiation on 2D heterostructure devices. These results indicate the importance of the interface between the 2D material and surrounding dielectric. Various defect and impurity complexes can significantly influence device performance, and therefore understanding how surrounding layers impact 2D heterostructure device performance and reliability is of the utmost importance. Understanding the

influence of these defects allows for engineering device architectures by choosing material systems that are resilient to defect effects.

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