Defect passivation of transition metal dichalcogenides via a charge transfer van der Waals interface

Jun Hong Park,1 Atresh Sanne,4 Yuzheng Guo,5 Matin Amani,6 Kehao Zhang,7 Hema C. P. Movva,4 Joshua A. Robinson,7 Ali Javey,6 John Robertson,8 Sanjay K. Banerjee,4 Andrew C. Kummel3,9*

Integration of transition metal dichalcogenides (TMDs) into next-generation semiconductor platforms has been limited due to a lack of effective passivation techniques for defects in TMDs. The formation of an organic-inorganic van der Waals interface between a monolayer (ML) of titanil phthalocyanine (TiOPc) and a ML of MoS2 is investigated as a defect passivation method. A strong negative charge transfer from MoS2 to TiOPc molecules is observed in scanning tunneling microscopy. As a result of the formation of a van der Waals interface, the gating on/off ratio in back-gated MoS2 transistors increases by more than two orders of magnitude, whereas the degradation in the photo-luminescence signal is suppressed. Density functional theory modeling reveals a van der Waals interaction that allows sufficient charge transfer to remove defect states in MoS2. The present organic-TMD interface is a model system to control the surface/interface states in TMDs by using charge transfer to a van der Waals bonded complex.

RESULTS

Surface treatments using substitution of extrinsic atoms or adsorption of molecules have been used to enhance photoluminescence (PL) (18–21), whereas the deposition of thick organic films to form p–n junctions has been used for potential photodetector applications (22). However, most of these treatments only improve the PL performance without enhancements of electronic performance, and the deposition of thick organic layers degrades electrical performance (20, 22).

Here, the deactivation of charged defect states is induced by the formation of an organic-inorganic van der Waals interface between single-layer titanil phthalocyanine (TiOPc) and single-layer MoS2. Metal phthalocyanines (MPc) are known to form uniform structured interfaces with various metal and semiconductor surfaces because the planar structure of π-conjugated rings induces a flat-lying MPc/substrate configuration (23–25). Moreover, most MPc have high thermal stability (26), and the flat-lying MPc/substrate structure ensures that the first layer of MPc is more tightly bound than all other layers, enabling a simple postdeposition anneal to form a uniform ML of MPc on TMDs. For passivation of TMDs, a single ML is used to simplify the bonding model. Among the various MPc molecules, TiOPc is chosen in this report to form a defect passivation layer, because it has an intrinsic net dipole at the central O-Ti group (27); consequently, a strong non-bonding interaction can be expected with MoS2, without the direct disruption of phase and band structures in MoS2. Strong charge transfer from MoS2 to TiOPc is observed with scanning tunneling microscopy (STM) and spectroscopy (STS). Density functional theory (DFT) modeling is consistent with a van der Waals interaction that allows sufficient charge transfer to remove midgap states in MoS2. As a result of the electric defect passivation at the TiOPc/MoS2 interface, the I_on/I_off in the back-gated transistors is increased by more than two orders of magnitude with the improvements of a subthreshold slope (SS), whereas the degradation of PL is fully suppressed.

INTRODUCTION

Because silicon complementary metal-oxide semiconductor (CMOS) technology has scaled down to a few nanometers, the performance of CMOS transistors has faced fundamental limitations, such as short-channel effects (1, 2). Layered transition metal dichalcogenides (TMDs) have been considered as next-generation semiconductor platforms (3–5) because their atomically thin body allows enhanced electrostatic gate control and atomically scaled precision thickness control of the channel (6, 7) while suppressing the formation of undesired dangling bonds on the channel (8, 9). In addition, several TMDs exhibit a direct band gap in a monolayer (ML), thereby broadening their applications to potential candidates for optoelectronic devices (10, 11).

One major obstacle to using TMDs for semiconductor or optoelectronic platforms is the existence of intrinsic defects (12–16). Because of volatile chalcogens in the compounds, TMDs typically have a deficiency of chalcogen atoms at their surfaces, resulting in trapping states or undesirable doping (12). Moreover, surface adsorbates introduced from fabrication processing or ambient air can perturb the electronic or optical properties of TMDs (17). The existence of these surface defects mostly results in the degradation of the I_on/I_off ratio in field-effect transistors (FETs) or poor luminescence quantum yields (13–15). Therefore, effective surface passivation of TMDs is pivotal to obtaining high-performance devices.

To passivate defect states in TMDs, the passivation method should deactivate only the defect states without a permanent change in the intrinsic crystal and electronic structure of TMDs. Moreover, the adsorbed molecules should be chemically and thermally stable on TMDs; consequently, they should not decompose or desorb during the fabrication processes nor during operation under ambient conditions.

Surface treatments using substitution of extrinsic atoms or adsorption of molecules have been used to enhance photoluminescence (PL) (18–21), whereas the deposition of thick organic films to form p–n junctions has been used for potential photodetector applications (22). However, most of these treatments only improve the PL performance without enhancements of electronic performance, and the deposition of thick organic layers degrades electrical performance (20, 22).

Here, the deactivation of charged defect states is induced by the formation of an organic-inorganic van der Waals interface between single-layer titanil phthalocyanine (TiOPc) and single-layer MoS2. Metal phthalocyanines (MPc) are known to form uniform structured interfaces with various metal and semiconductor surfaces because the planar structure of π-conjugated rings induces a flat-lying MPc/substrate configuration (23–25). Moreover, most MPc have high thermal stability (26), and the flat-lying MPc/substrate structure ensures that the first layer of MPc is more tightly bound than all other layers, enabling a simple postdeposition anneal to form a uniform ML of MPc on TMDs. For passivation of TMDs, a single ML is used to simplify the bonding model. Among the various MPc molecules, TiOPc is chosen in this report to form a defect passivation layer, because it has an intrinsic net dipole at the central O-Ti group (27); consequently, a strong non-bonding interaction can be expected with MoS2, without the direct disruption of phase and band structures in MoS2. Strong charge transfer from MoS2 to TiOPc is observed with scanning tunneling microscopy (STM) and spectroscopy (STS). Density functional theory (DFT) modeling is consistent with a van der Waals interaction that allows sufficient charge transfer to remove midgap states in MoS2. As a result of the electric defect passivation at the TiOPc/MoS2 interface, the I_on/I_off in the back-gated transistors is increased by more than two orders of magnitude with the improvements of a subthreshold slope (SS), whereas the degradation of PL is fully suppressed.
of a ML MoS₂ flake; most of these defects are 1.5 Å deep and 2 nm in diameter, as shown in the left panel of Fig. 1B. On the basis of the present STM study and the previous published results (28, 29), these defects could be modeled as a few missing S atoms or both missing S and Mo atoms, as shown in the right panel of Fig. 1B. One of the defects is imaged via both empty-state (Fig. 1C) and filled-state modes (Fig. 1D) in an expanded STM image. Although the defects are shown as local depressions in both filled and empty states, the hexagonal atomic structure and the moiré pattern of the defects appear in only filled-state images.

A large electron population can be observed near defects of MoS₂, indicating that the vacancies in MoS₂ result in excess charge density (16), consistent with broken covalent bonds in the MoS₂ planes. As shown in the STS of Fig. 1E, two different local densities of states (LDOSs) are observed on MoS₂; a black STS, recorded far away from a defect in ML, has an apparent band gap of ~2.34 eV with a Fermi level (0 V) shifted to a conduction band (CB). This Fermi level is closer to the CB than to the valence band (VB) by about 0.3 V. Conversely, in the red STS, recorded close to a defect, large states are observed in the band gap, consistent with near metallic LDOS. The increase in band edge states results in an additional shift of the Fermi level toward the CB.

The band edge states are investigated by spatially resolved STS, as shown in Fig. 1F; multiple STSs were obtained adjacent to and far away from the defects. Large band edge states at the CB (shallow level) are observed when the tip is near a defect in MoS₂ (30). However, as the STM tip is moved away from the defects, the band edge states decrease significantly.

This negatively charged defect can be electrically deactivated by the adsorption of TiOPc molecules onto the MoS₂ ML. A few TiOPc molecules are deposited on MoS₂ MLs using molecular beam epitaxy at 300 K for 10 s, as shown in Fig. 2A. For sub-ML, the coverage of TiOPc molecules can be controlled by the deposition duration, as displayed in fig. S5. Each TiOPc molecule is observed as circular with a height of 0.3 nm, as shown in Fig. 2B, even though the TiOPc molecular structure is nearly square, as shown in the inset. It is hypothesized that single TiOPc molecules rotate on MoS₂ surfaces (31) because of the absence of locking, which is present at higher coverage.

To elucidate the electronic effects of single TiOPc molecule adsorption on MoS₂ MLs, spatially resolved STS is used, following a dashed arrow in Fig. 2C. In Fig. 2D, when the STM tip is positioned far away from the TiOPc molecules, the Fermi level is near the CB. However, as the STM tip approaches a TiOPc molecule, the Fermi level moves away from the CB to the middle of the band gap. Finally, positioning the STM tip near the TiOPc molecule results in the Fermi level moving close to the VB. From the present STS, it can be hypothesized that the excess negative charge in MoS₂ is transferred to TiOPc molecules. It is noted that although the deactivation of defect states via the adsorption of TiOPc molecules on MoS₂ relies on a charge transfer van der Waals interaction, as shown in fig. S7, other driving forces also might be used to passivate defect states, such as chemisorption on MoS₂. However, strong bonding forces can induce unintentional changes in the crystal or electric structure (32).

The TiOPc ML on the MoS₂ ML is investigated, as shown in Fig. 2E. With increasing deposition duration of TiOPc without postdeposition...
annealing, a hexagonal packed TiOPc ML is obtained with about 1.7-nm lateral spacing, and the center of each TiOPc molecule appears as a bright protrusion, consistent with the upward pointing of O–Ti to the vacuum (33). In the STS of Fig. 2E, a 1.7-eV band gap is observed with the Fermi level positioned near the lowest unoccupied molecular orbital. Once a TiOPc ML is formed on MoS2, it is thermally stable on MoS2, consistent with the tight binding between TiOPc and MoS2, as shown in fig. S10. Note that because TiOPc molecules have only van der Waals interactions with the MoS2 surface, it is hypothesized that the deposition of TiOPc does not induce the physical reconstructions of defects in the MoS2.

DFT calculations are used to elucidate the change of the electronic structure in MoS2 upon adsorption of TiOPc molecules. The projected density of states (PDOS) of a defect-free MoS2 ML with two additional electrons is shown by a black curve in Fig. 3A; there are no observable states in the band gap. The two electrons were added to make the MoS2 n-type consistent with the experimental data. S vacancies induce a large band gap state near the CB (orange dashed circle), as shown by the red curve, and reduce the band gap of 2e MoS2. This defect state near the CB can also be observed in defective MoS2 without the two electrons (neutral state), shown by an orange dashed circle in the blue curve. In both the 2e MoS2 and the neutral MoS2 cases, the defect states can be observed near the CB edges, consistent with the existence of defect states at shallow levels (30). These band gap states near the CB can result in unintentional doping or trapping states in transistors (12, 14–16). The DFT model of TiOPc passivation consisting of two TiOPc molecules on top of the MoS2 with a single S vacancy is shown in Fig. 3B. As shown in Fig. 3C, the band edge states are suppressed, and the band gap is restored to the original size in the PDOS of MoS2, consistent with electric deactivation of defect states. It is noted that a tiny state is observed at −0.8 eV in PDOS of MoS2. This state corresponds to the highest occupied molecular orbital of TiOPc (red curve) in TiOPc/MoS2, and it is included in the PDOS of MoS2 during the projections of orbitals.

To understand the source of passivation, the charge was calculated as shown in the Supplementary Materials. For the TiOPc passivated S(Vac)/MoS2 system with a net −2 charge, each TiOPc adsors a charge of 0.8 electrons, as shown in table S2. Even for an uncharged TiOPc passivated MoS2 system, each TiOPc adsors a charge of 0.5 electrons. This is consistent with previous studies showing aromatic molecules that lower the work function in metal surfaces via charge transfer (34).

The electrical characteristics of a four-point back-gated single-layer MoS2 FET (channel length of 10 μm and width of 3 μm) with/without a TiOPc passivation layer are investigated at a drain bias of 1 V, as shown in Fig. 4A. The black transfer curve is the sweep of bare MoS2 showing a threshold voltage, $V_{TH}$, of about −14 V with an $I_{ON}/I_{OFF}$ ratio of $10^4$. This depletion mode $V_{TH}$ is undesirably shifted to negative voltages, which is indicative of S vacancies in the channel and extrinsic charge dopants from the substrate (35). As shown in the red curve, the annealing of the same MoS2 FET in a UHV further degrades the $I_{ON}/I_{OFF}$ ratio with a negligible shift of the $V_{TH}$. Conversely, after the deposition of a TiOPc ML on the same MoS2 FET, the $I_{ON}/I_{OFF}$ improves to greater than $10^7$, because of a 100× reduction of the OFF-state leakage and a return of an ON-state drive current to the preannealed levels. In addition, the $V_{TH}$ positively shifts to 10 V because the TiOPc compensates for the excess charge. The SS below

![Fig. 2](http://advances.sciencemag.org/)

**Fig. 2. Effects of the formation of the interface at TiOPc/MoS2.** (A) Few TiOPc molecules deposited on a MoS2 ML at 300 K ($V_s = 2$ V, $I_t = 30$ pA). Inset shows the molecular structure of TiOPc. (B) Cross-sectional line trace of an adsorbed TiOPc molecule. (C) Single TiOPc adsorption with a black background. (D) Subset of $dI/dV$/$I/V$ spectra taken along the dashed arrow in (C). (E) Formation of a full-coverage ML TiOPc on a ML MoS2 and corresponding Fourier transform ($V_s = 2$ V, $I_t = 50$ pA). (F) STS of ML TiOPc on a ML MoS2.
the $V_{TH}$ also are improved from 6.7 to 1.6 V/dec by the deposition of a TiOPc ML, suggesting the deactivation of some of the channel defects.

The deposition of TiOPc ML does not induce degradation of the PL of a ML MoS$_2$ (Fig. 4B). To track the change in PL of MoS$_2$ upon TiOPc deposition, we performed measurements on the same flake after exfoliation, annealing of MoS$_2$ at 597 K in a UHV, and TiOPc deposition. Before annealing, the MoS$_2$ ML shows low luminescence with a broad spectrum, which can be attributed to emission from both free excitons and charged trions, which is typically observed in exfoliated MoS$_2$. After annealing, a 2× increase is observed in PL. Moreover, the overall full width at half maximum (FWHM) decreases from 95 to 52 meV, and the emission from the charged trion is quenched. An additional increase of PL intensity is observed after the deposition of a ML TiOPc on the annealed ML MoS$_2$ with no change in the FWHM. In addition, a 20-meV red shift is observed in the emission compared to annealed MoS$_2$, consistent with a 10-meV blue shift from bare MoS$_2$ (36). This modest improvement in TiOPc/MoS$_2$ could be interpreted as an increase in the quantum yield of excitons by the transfer of excess charge to TiOPc (37).

**DISCUSSION**

The electrical deactivation of defect states at the interface of TiOPc/MoS$_2$ has been elucidated using STM and STS. The depletion of sulfur results in an intrinsic n-shifted electronic structure in bare MoS$_2$, whereas the formation of a TiOPc/MoS$_2$ interface induces a negative charge transfer from MoS$_2$ to TiOPc. It is noted that although there is no clear evidence that defect sites can provide preferable adsorption sites for TiOPc molecules during observation in STM, it can be hypothesized...
that the total amount of charge transfer from a ML MoS₂ to adsorbed TiOPc molecules can be tuned by the coverage of TiOPc molecules on MoS₂. Moreover, the van der Waals interaction at the interface of TiOPc and MoS₂, such as the direction of charge transfer or the amount of charge transfer, might be tuned by chemical functionalization of the MPCs, such as adding additional groups to the benzene rings or modifications of central atoms. For example, bare CuPc molecules are p-type complexes under ambient conditions, whereas F₃₃CuPc molecules are n-type complexes under ambient conditions (38, 39); consequently, the charge transfer with TMDs might be modified by the ligands on the MPCs. DFT reveals that formation of a van der Waals interface induces suppression of defect states in MoS₂. As a result, the I_on/I_off ratio and the Sₜ in back-gated FETs are greatly improved by the selective deactivation of defect states via the deposition of ML TiOPc, without changes in the band structure of MoS₂ nor degradation of the PL intensity, as shown in STM/STS, DFT, and PL. Conversely, the previous results for TMDs passivated chemically via an introduction of extrinsic atoms involved a permanent transition in crystal structure and therefore induced a change in the band gap of TMDs (40, 41). Adsorption of other organic molecules, such as alkanethiol or thick organic layers, also induced the degradations of the I_on/I_off ratio in MoS₂ FETs (20, 22). It is noted that in the present STM/STS and the DFT data, the defect states at shallow energy levels (near a CB edge) can be observed with S vacancies, whereas defects at deep energy levels (in the middle of a band gap) cannot be observed in STM/STS. Because the present TiOPc/MoS₂ charge transfer van der Waals interface relies on the nonbonding interaction, it may have limitations in passivating deep-level defect states. For deep-level defects, a strong interaction, such as chemical reaction, may be required. Therefore, the present result suggests that the defect states in TMDs can be controlled and passivated via using van der Waals interaction with organic ML.

MATERIALS AND METHODS

MoS₂ ML was prepared via two different methods, CVD growth and mechanical exfoliation from bulk. The details are included in the Supplementary Materials.

The TiOPc powder (95% purity) purchased from Sigma-Aldrich was purified by multiple sublimations with a differentially pumped effusion cell (Eberl MBE-Komponenten) attached to a UHV STM chamber. Afterward, the effusion cell was heated to 633 K with a rate of 1 K/s, while the MoS₂/HOPG samples were placed in a UHV chamber. During the deposition of TiOPc, the sample temperature was held at 300 K, and the coverage of TiOPc on MoS₂ was controlled by the deposition duration, as shown in the below separated part.

STM and STS (Omicron VT STM) were performed in a UHV chamber (2 × 10⁻¹¹ torr) using electrochemically etched tungsten tips, while the samples were cooled at 100 K using liquid nitrogen. Before performing STM and STS on MoS₂/HOPG or TiOPc/MoS₂/HOPG, the STM tips were calibrated on an Si (100) surface and bare HOPG surfaces.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/10/e1701661/DC1

REFERENCES AND NOTES


Acknowledgments: Funding: This work is supported by NSF grant DMR 1207213 and by LEAST (Low Energy Systems Technology)–STARnet, a Semiconductor Research Corporation (SRC) program, supported by the Microelectronics Advanced Research Corporation (MARCO), the Defense Advanced Research Projects Agency (DARPA), and by SRC NRI (Nanoelectronics Research Initiative) SWAN (South West Academy of Nanoelectronics). Y.G. would like to acknowledge the support from HPC Wales under project HPC2085 for computational recourse. Author contributions: J.H.P. and A.C.K. conceived and designed this experiment. J.H.P. performed the inorganic heteroepitaxial growth of MX2 on Ag(111), New J. Phys. 18, 113022–1–113022-20 (2016).
Defect passivation of transition metal dichalcogenides via a charge transfer van der Waals interface


Sci Adv 3 (10), e1701661.
DOI: 10.1126/sciadv.1701661