Selective Chemical Response of Transition Metal Dichalcogenides and Metal Dichalcogenides in Ambient Conditions

Jun Hong Park,^{†,‡,§} Suresh Vishwanath,^{\perp} Steven Wolf,[§] Kehao Zhang,^{\diamond} Iljo Kwak,[§] Mary Edmonds,[§] Michael Breeden,[§] Xinyu Liu,^{Δ} Margaret Dobrowolska,^{Δ} Jacek Furdyna,^{Δ} Joshua A. Robinson,^{\diamond} Huili Grace Xing,^{$\perp,\#$} and Andrew C. Kummel^{*,§,||}

[†]Center for Quantum Nanoscience, Institute for Basic Science (IBS), Seoul 03760, Republic of Korea

[‡]Department of Physics, Ewha Womans University, Seoul 03760, Republic of Korea

[§]Materials Science & Engineering Program and ^{II}Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093, United States

¹School of Electrical and Computer Engineering and [#]Department of Materials and Science Engineering, Cornell University, Ithaca, New York 14850, United States

⁽Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, United States

^APhysics Department, University of Notre Dame, Notre Dame, Indiana 46556, United States

Supporting Information



ABSTRACT: To fabricate practical devices based on semiconducting two-dimensional (2D) materials, the source, channel, and drain materials are exposed to ambient air. However, the response of layered 2D materials to air has not been fully elucidated at the molecular level. In the present report, the effects of air exposure on transition metal dichalcogenides (TMD) and metal dichalcogenides (MD) are studied using ultrahigh-vacuum scanning tunneling microscopy (STM). The effects of a 1-day ambient air exposure on MBE-grown WSe₂, chemical vapor deposition (CVD)-grown MoS₂, and MBE SnSe₂ are compared. Both MBE-grown WSe₂ and CVD-grown MoS₂ display a selective air exposure response at the step edges, consistent with oxidation on WSe₂ and adsorption of hydrocarbon on MoS₂, while the terraces and domain/grain boundaries of both TMDs are nearly inert to ambient air. Conversely, MBE-grown SnSe₂, an MD, is not stable in ambient air. After exposure in ambient air for 1 day, the entire surface of SnSe₂ is decomposed to SnO_x and SeO_x, as seen with X-ray photoelectron spectroscopy. Since the oxidation enthalpy of all three materials is similar, the data is consistent with greater oxidation of SnSe₂ being driven by the weak bonding of SnSe₂.

KEYWORDS: WSe₂, MoS₂, SnSe₂, STM, STS, air exposure

INTRODUCTION

A monolayer (ML) of graphene has been demonstrated as a two-dimensional material with ultrafast mobility, ^{1,2} unique optical properties, ^{3–5} and high mechanical in-plane strength.^{6,7} However, the absence of a band gap in single-layer graphene has been a major challenge for integration into digital logic circuits. Alternatively, layered compounds, such as transition metal dichalcogenides (TMDs) of the form MX₂ (M: metal

atom, X: chalcogen atoms), have been explored for electronic and optoelectronic applications^{8–11} because of their finite band gaps.^{12–14} In addition, their band gaps and optical properties can be tuned by combining various chemical compositions in

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Figure 1. STM of clean surfaces of TMDs. (a) Schematic diagram of WSe₂. (b) Large area STM image of WSe₂/HOPG in the empty state ($V_S = 2$ V, $I_T = 20$ pA). (c) Filled states STM images showing moiré patterns of WSe₂ ML on HOPG ($V_S = -1.2$ V, $I_T = 80$ pA). (d) Atomically resolved filled state STM image of WSe₂ ML ($V_S = -1$ V, $I_T = 160$ pA). (e) STS of clean WSe₂ ML on HOPG. (f) Schematic diagram of MoS₂. (g) Large area STM image of MoS₂/HOPG in the empty state ($V_S = 2$ V, $I_T = 40$ pA). (h) Filled states STM images showing moiré patterns of MoS₂ ML on HOPG. (f) Schematic diagram of MoS₂. (g) Large area STM image of MoS₂/HOPG in the empty state ($V_S = 2$ V, $I_T = 40$ pA). (h) Filled states STM images showing moiré patterns of MoS₂ ML on HOPG ($V_S = -1.5$ V, $I_T = 100$ pA). (i) Atomic resolved filled state STM image of MoS₂ ML ($V_S = -1$ V, $I_T = 240$ pA). (j) STS of clean MoS₂ ML on HOPG.

 MX_2 or by controlling the number of layers; therefore, atomically thin transistors and diodes can be fabricated. $^{15-18}$

For practical device applications, after the growth of highquality TMDs, they must be transferred to ambient conditions for device fabrication. As a result, the effects of air exposure must be elucidated. Previously, multiple surface analyses have been performed on TMDs grown via molecular beam epitaxy¹⁹⁻²⁶ or chemical vapor deposition (CVD).²⁷⁻³⁰ Simultaneously, the various surface states in clean TMDs, such as domain boundaries, single or multiple missing vacancies, have been carefully probed to predict their physical or electric impacts on TMDs.³¹⁻³⁷ However, there are only a few reports of the effect of air exposure on the electric and optical performance or photoluminescence of TMD devices.^{38,39} Therefore, molecular-scale observations of TMDs exposed to ambient conditions are required to understand the mechanism of electrical and optical perturbations induced by air exposure.⁴⁰

In the present report, air stabilities of MoS₂ and WSe₂ are investigated since MoS₂ and WSe₂ have been most intensively studied for logic⁸⁻¹¹ and optoelectrical applications.^{16,41-43} Previously, after exposure of MBE WSe₂ in ambient air for 1-9 weeks, the selective oxidation of step edges was reported using ultrahigh-vacuum (UHV) scanning tunneling microscopy (STM) and spectroscopy (STS).⁴⁰ In the present report, these techniques are extended to chemical vapor deposition (CVD)-grown MoS₂; these are the most commonly available growth techniques for each material. Although CVD-grown MoS₂ has stronger interactions with hydrocarbons than MBEgrown WSe₂, both TMDs show similar selective response at the step edges to air exposure. In addition, the chemical responses of these TMDs to ambient conditions are compared to airexposed MBE-grown SnSe₂, since a vertical tunnel junction of WSe₂ and SnSe₂ has been expected to show high electric performance with a suitable abrupt band offset.^{44,45} These comprehensive surface studies across the TMDs and MDs can provide fundamental explanations for the effect of air exposure.

RESULTS AND DISCUSSION

Observation of Terraces of TMDs. Prior to air exposure, MBE-grown WSe₂ samples (Figure 1a) are investigated using UHV STM. It is noted that WSe₂ samples were capped with a Se adlayer in the MBE chamber to prevent unintentional oxidation during the sample transfer to a STM chamber. The Se capping layer is removed by annealing at 623 K in the STM chamber. As shown in Figure 1b, sawtooth-shaped islands of monolayer (ML) WSe2 are observed on the highly oriented pyrolytic graphite (HOPG) surface. Bilayers (BL) are also deposited on the top of ML WSe2. A hexagonal moiré pattern with about 1.1 nm spacing in the terrace can be observed in the zoomed in STM image of Figure 1c, resulting from the potential overlapping between ML WSe2 and the underlying HOPG. As shown in the atom-resolved STM image of Figure 1d, a honeycomb lattice structure of Se atoms in ML WSe₂ is observed without any noticeable point defects or dislocations.⁴⁶ The electronic band gap of ML WSe₂ is about 2.07 eV in the STS of Figure 1c, and this value is consistent with previously reported electronic band gaps of ML WSe2.^{19,46,47} It is noted that to estimate the electronic band gap in STS, STS modeling was carried out as shown by the dotted line, described in previous studies.^{48–50}

In a similar manner, the surface of CVD-grown MoS₂ (Figure 1f) on HOPG is analyzed with STM before air exposure. It is noted that a capping layer was not employed in CVD-grown MoS₂; instead, the MoS₂/HOPG sample was annealed at 673 K for 3 h in the UHV chamber to remove any ambient adsorbates. As shown in Figure 1g, triangular MoS₂ islands are detected in the STM image of about 200 nm lateral size. It is noted that adsorbates or CVD residues are observed at a few step edges of clean MoS₂ with a defective local density of states, as shown in Figure S1. In Figure 1h, the hexagonal moiré pattern of about 3.8 nm spacing is observed in ML MoS₂, which is larger than the moiré pattern of ML WSe2. In an atom-resolved STM image of Figure 1i, a hexagonal array of S atoms is observed. As shown in Figure 1j, the electronic band gap of ML MoS₂ is about 2.26 eV, consistent with previously reported STS results.^{31,51} Although both MoS₂ and WSe₂ have similar



Figure 2. STM/STS of air-exposed surfaces of TMDs on HOPG. (a) Air-exposed terrace of WSe₂ ML ($V_S = 2$ V, $I_T = 20$ pA). (b) STS of air-exposed terrace in WSe₂ ML. (c) Air-exposed step edge of WSe₂ ML after annealing at 523 K for 1 h ($V_S = 2$ V, $I_T = 40$ pA). (d) STS of air-exposed step edges in WSe₂ ML with two different locations. (e) Schematic diagram of chemical response of WSe₂ to ambient air. (f) Air-exposed terrace of MoS₂ ML ($V_S = 2$ V, $I_T = 20$ pA). (g) STS of air-exposed terrace in MoS₂ ML. (h) Air-exposed step edge of MoS₂ ML after annealing at 723 K for 1 h ($V_S = 2$ V, $I_T = 20$ pA). (j) STS of air-exposed terrace in MoS₂ ML. (h) Air-exposed step edge of MoS₂ ML after annealing at 723 K for 1 h ($V_S = 2$ V, $I_T = 20$ pA). (i) STS of air-exposed step edges in MoS₂ ML with two different locations. (j) Schematic of chemical response of MoS₂ to ambient air.

hexagonal atomic structures for the topmost chalcogen atoms, ML MoS₂ has a larger electronic band gap (about 0.2 eV) than ML WSe₂. This observation of a larger electronic band gap in ML MoS₂ than in ML WSe₂ is consistent with a larger optical band gap of ML MoS₂ versus ML WSe₂.^{13,52}

After STM imaging of the clean WSe₂ and MoS₂ surfaces, the samples are exposed to ambient air for 1 day and then transferred back to the STM chamber. As shown in Figure 2a, a very small coverage of air-induced adsorbates can be observed on the terraces of ML WSe₂ consistent with the terrace being nearly inert without noticeable oxidation, aligning with previous STM results.⁴⁰ It is noted that the adsorbates are probably a mixture of hydrocarbons, H₂O, and O₂ introduced from ambient air. Due to the inertness of the terrace of WSe₂, ML WSe₂ still maintains about a 1.98 eV band gap, as shown in Figure 2b.

Observation of Step Edges of TMDs after Air **Exposure.** In contrast to the terraces of WSe₂, the step edges of WSe2 ML display changes in the morphology and electronic band gap after ambient exposure. As shown in Figure 2a, after air exposure, the entire step edge of WSe_2 is decorated by bright protrusions, consistent with selective oxidation. To study the air-exposed step edges without air-induced weakly bound adsorbates, the sample was annealed at 523 K for 1 h, as shown in Figure 2c. Two different morphology changes, a short feature³⁰ and a tall feature (blue), are revealed at the airexposed step edges. To track the electronic transition, STS was carried out on two areas of the air-exposed surface: the short step edge and the tall step edge, as shown in Figure 2d. The clean WSe2 step edge has an about 1.1 eV band gap with a Fermi level pinned near the valence band (VB).⁴⁰ It is noted that compared to the position of the Fermi level at the terrace, the position of the Fermi level at step edges is changed. Conversely, after air exposure, the short step edge shows a

slightly larger band gap than the clean step edge, as shown by a red curve, with the Fermi level position near VB. It can be concluded that the step edge reacts with ambient molecules or forms a partially oxidized edge, consistent with XPS of air-exposed WSe₂ in Figure S6. Conversely, the tall step edge (blue dot) has a wider band gap than the clean surface and short step edge (about 2.4–2.5 eV), consistent with the formation of WO_x with a substoichiometric ratio, as shown in Figure 2e.⁴⁰ It is noted that adsorbates for air exposure exist along the step edges, and they can be attached to STM tips during STS measurements; therefore, the stability of the STM tip has been confirmed by performing STS on HOPG surfaces or ML TMDs terraces, immediately after performing STS at the step edges.

If the step edges of WSe_2 are further exposed to additional ambient air, full oxidation of step edges can be observed, shown in Figure 3 of ref 40. However, the oxidation of step edges in WSe_2 appears to be a self-terminating process; therefore, the oxidation in ambient air does not propagate into the internal chalcogenide layers. Consequently, even after exposure of WSe_2 in air for 9 weeks, the oxidation with air exposure is observed only at step edges, while it is not detected on the internal terraces.

After air exposure of CVD MoS_2 for equivalent duration to MBE WSe₂, extensive adsorption of air-induced adsorbates can be observed in STM. In Figure 2f, nearly all step edges of MoS_2 are decorated by air-induced adsorbates, which have a narrow band gap, as shown in Figure S2. It is noted that the adsorbates at the step edges are mostly ambient carbon composites mixed with H_2O or O_2 , as shown in XPS of Figure S7; therefore, they may not act as traps or lower the mobility unless they have strong dipoles. However, since they have narrower band gaps than internal terraces, they may act the leakage sources in multigrain vertical junctions. Conversely, only a few adsorbates



Figure 3. STM bias dependence of domain boundaries in WSe₂ and grain boundaries in MoS₂ before air exposure. (a) STM of a domain boundary of clean WSe₂ ML with different sample biases ($I_T = 60$ pA). (b) STS of a clean domain boundary in clean WSe₂ ML. (c) STM of a grain boundary of clean MoS₂ ML with different sample biases in STM ($I_T = 40$ pA). (d) STS of a clean grain boundary in clean MoS₂ ML.

are observed on the terrace of MoS_2 and the terrace of ML MoS_2 , which maintains an approximate 2.15 eV band gap; this is nearly the same band gap of clean ML MoS_2 , as shown in Figure 2g.

The hydrocarbon adsorbed at the step edges of MoS₂ has strong binding to MoS₂ with a high thermal stability. Even after annealing at 723 K for 1 h, the large coverage of air-induced adsorbates still can be observed at the step edges of MoS_2 , as shown in Figure 2h. Because of the existence of tightly bound hydrocarbon, two different local density of states (LDOS) can be observed in STM (Figure 2i). Before air exposure, the clean step edge of ML MoS₂ has an about 1.4 eV band gap with the Fermi level pinned near VB, similar to the step edge of ML WSe2. It is noted that this STS is performed on the clean (adsorbates or CVD residue free) step edges of MoS_2 . After air exposure, the tall step edges (blue dot) with hydrocarbon have very large band edge states at both the valence and the conduction bands, as shown by the blue curve. Conversely, the short step edge (red dot) has a LDOS with less band edge states than the tall step edge; consequently, the short step edge has a larger band gap. Since the hydrocarbon has a narrow band gap, as shown in Figure S2, it can be concluded that the tall step edge contains a large amount of hydrocarbon consistent with the LDOS having a narrow band gap. Conversely, the short step edge contains less hydrocarbon than the tall step edge, yielding larger band gaps than the tall step edges. Therefore, the data is consistent with air exposure inducing the adsorption of hydrocarbon at the step edges with strong binding. It is noted that since the hydrocarbon adsorbs at both the tall and the short step edges, it is hard to determine whether the step edges of MoS₂ are oxidized in ambient air.

On the basis of the STM results, it can be concluded that the MoS_2 step edges have stronger interactions with hydrocarbon than the WSe_2 step edges. The observed adsorption of conductive hydrocarbons or the selective oxidation may act as a leakage source or as an insulating barrier for charge carriers, respectively.^{53,54} Consequently, cleaning or functionalization of TMDs may be required prior to the fabrication process.

Observation of Domain/Grain Boundaries of TMDs before and after Ambient Exposure. The domain/grain boundaries are probed with STM/STS before and after equivalent air exposure. In Figure 3a, a large flake of clean ML WSe₂ is observed in STM with variable sample biases. At ± 2 V, both filled and empty state modes show planar and smooth terraces and step edges, without any noticeable features on the terrace. However, as the sample bias decreases to ± 1 V, the brightness of domain boundaries and the step edges are enhanced across the entire terrace. The brightness of these defect states (domain boundaries and step edges) is more enhanced in the empty state images than in the filled state images. These domain boundaries have a band gap of about 1.11 eV, as shown in Figure 3b, which is similar to the band gap of the step edges (black curve of Figure 2d). However, if the domain boundaries are induced mainly by broken bonds in the crystal structure similar to the step edges, the domain boundaries should also be observed in STM images at a bias of ± 2 V. In addition, the observed bias dependence of domain boundaries in WSe2 is similar to previous STM studies of the domain boundaries in silicene, which involve atomic strain with lattice mismatches between two domains.⁵⁵ Therefore, it can be hypothesized that the present MBE-grown WSe₂ also has the atomic strain along the domain boundaries. It is noted that the



Figure 4. STM bias dependence of the domain boundary in WSe₂ and grain boundary in MoS₂ after air exposure. (a) STM of a domain boundary of air-exposed WSe₂ ML with different sample biases ($I_T = 40$ pA). (b) STS of a clean domain boundary in air-exposed WSe₂ ML. (c) STM of a grain boundary of air-exposed MoS₂ ML with different sample biases in STM ($I_T = 40$ pA). (d) STS of air-exposed grain boundary in MoS₂ ML.

existence of strain at domain boundaries also has been confirmed in WS₂, as shown by previous results.⁵⁶

The grain boundaries of monolayer MoS₂ are investigated with STM. As shown in Figure 3c, during CVD growth, two grains are merged together on the HOPG surface, creating grain boundaries that display a bright center surrounded by a trench. In addition, the brightness of the grain boundaries in MoS_2 is weakened in empty state imaging (+2 V), while it is enhanced in the filled states (-2 V). As the sample bias is decreased to ± 1 V, the brightness of the MoS₂ grain boundaries is additionally enhanced in both filled and empty state imaging. The band gap of the grain boundaries in MoS_2 is about 0.82 eV with a Fermi level close to the VB, as shown in the STS in Figure 3d; this is distinct from the STS of the bare step edges (black curve of Figure 2i and STS of Figure S1(b)). The observed grain boundaries in MoS₂ also have been observed in previous STM/STS studies on CVD-grown MoS₂.^{35,36} Although there is no atomically visualized proof in the present report, it is possible that composites of Mo and S (from CVD) and C (from ambient) may be formed along the area where two grains merge, resulting in about 2 nm wide grain boundaries which are chemically passive.³⁵ Therefore, grain boundaries already can be passivated by Mo, S, and carbon composites.

It is noted that the observed abrupt changes of TMD domain/grain boundary band gaps are also consistent with the previously reported STM/STS studies.^{35,36} Since these abrupt changes of the band gap on both WSe₂ and MoS₂ domain/grain boundaries involve defects states, it is possible that these can act as the origin of trapping states or potential walls for transport carriers, similar to previously published cases of the charge transport in the thin film transistors.^{57–60} It is noted that although the previously published STS result of the grain boundary in ML MoS₂ also had a similar band gap about 1.55

eV, the brightness of the grain boundary (in previous report) was enhanced at 1.3 V, while it diminished at -0.5 V, opposite to the present STM result.³⁵ It is possible that the bonding configurations or chemical composition of the grain boundaries in the previous report are different from the present grain boundaries in MoS₂, resulting in the different behavior of bias dependence in STM imaging.

As shown by STM, the domain boundaries of WSe2 are nearly inert in ambient air without chemical or electronic modifications, in contrast to the step edges of WSe₂. As shown in Figure 4c, after exposure to ambient air for 1 day, the domain boundaries in the WSe2 terrace maintain a nearly identical bias dependence to the clean domain boundaries. Conversely, the oxidized step edges are modified to bright protrusions, causing the step edges to no longer show the bias dependence. In addition, STS reveals that domain boundaries maintain a narrow band gap, 1.10 eV, nearly identical to the clean domain boundaries. It can be hypothesized that although there are structural or electronic perturbations in the domain boundaries of WSe₂, the Se and W atoms in crystals of WSe₂ maintain their bonding; consequently, the formation of the oxidation states at domain boundaries can be suppressed in ambient air, consistent with preventing oxidation of domain boundaries. It is noted that although STM and STS reveal that step edges and domain boundaries of clean WSe₂ have nearly identical bias dependence and band gap, their reactivities to ambient air are totally different.

The grain boundaries of MoS_2 also are nearly inert in ambient air, as shown in the STM and STS results. After air exposure for 1 day, asymmetric bias dependence can be observed in STM, which shows enhanced brightness in the filled state as opposed to the empty state. Similar to the clean grain boundaries of MoS_2 , the brightness of the air-exposed



Figure 5. Clean surfaces of $SnSe_2$. (a) Large area STM image of clean $SnSe_2$ on HOPG ($V_S = 2 V$, $I_T = 20 pA$). (Bottom) Cross-sectional atomic structure of $SnSe_2$. (b) Line trace following the white dashed line in a. (c) Atomically resolved STM image of clean ML $SnSe_2$ ($V_S = 1.2 V$, $I_T = 140 pA$). (d) STS of clean ML and BL $SnSe_2$ showing 1.51 and 1.19 eV band gaps, respectively.



Figure 6. Air exposure-induced decomposition of SnSe2. (a) Air-exposed SnSe2 layer on HOPG for 1 day. (b) STS of air-exposed SnSe2 surface.

grain boundaries in MoS_2 are enhanced at both filled and empty state biases (± 1 V). STS shows a band gap, about 0.85 eV at air-exposed grain boundaries, identical to the grain boundaries of clean MoS_2 . Therefore, it can be concluded that the grain boundaries of MoS_2 can maintain their atomic and electronic structure in ambient air. It can be hypothesized that the even though broken bonds exist in the grain boundaries of MoS_2 , these broken bonds would be terminated with the adsorption of additional S, Mo, or CVD residue during growth; consequently, possible dangling bonds are already passivated prior to air exposure.

It is noted that although both domain/grain boundaries of WSe_2 and MoS_2 in the present report are nearly inert after exposure in air for 1 day, it is possible that these domain/grain boundaries can be oxidized by the longer exposures in air. In

addition, if there is a large density of defects at the domain/ grain boundaries, they also may be more reactive to ambient air even on short time scales. It is noted that additional STS of step edges and domain/grain boundaries are shown in Figure S9.

Decomposition of SnSe₂ Layers in Ambient Air. $SnSe_2$ grown on HOPG via MBE is investigated with STM and STS as an example of air-exposed metal dichalcogenides (MDs) with weak internal bonding. After decapping of the Se adlayer in the UHV chamber at 523 K for 15 min, an atomically flat $SnSe_2$ layer can be observed on HOPG as shown in the STM image of Figure 5a with ML, bilayer (BL), and trilayer growth.³⁰ In Figure 5b, a line trace following the white dashed line in Figure 5a shows ~0.7 nm height for each layer, consistent with three atomic layers (Se–Sn–Se) as shown in the bottom of Figure 5a. In an atomically resolved STM image of Figure 5c, a nearly

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hexagonal structure is observed with about 0.34 nm spacing. In the STS shown in Figure 5d, the band gap of ML $SnSe_2$ is about 1.51 eV, while BL $SnSe_2$ shows a band gap of about 1.19 eV. It is noted that both ML and BL have the Fermi level pinned near the CB.^{61–64}

After exposure in ambient air for 1 day, STM imaging shows that the entire $SnSe_2$ layer is decomposed. As shown in the STM image in Figure 6a, the two-dimensionally layered $SnSe_2$ disappears with air exposure and only particles are observed across the surface, consistent with the decomposition of $SnSe_2$. It is noted that in the STM image of Figure 6a, after air exposure of $SnSe_2$, the entire surface roughness is increased significantly. Consequently, the STM tip is unstable and creeping on air-exposed $SnSe_2$ during STM imaging. As a result, very strong noise can be observed along the STM scan direction. As a result of this decomposition, large state appears in the STS band gap as shown in Figure 6b: the band edge states extend to the Fermi level (0 V), consistent with a near zero band gap.

The decomposition and oxidation of $SnSe_2$ in ambient air was confirmed in X-ray photoelectron spectroscopy (XPS). As shown in Figure 7a and 7b, before exposure in ambient air, XPS



Figure 7. Chemical analysis of SnSe₂ layer on HOPG, before and after air exposure, using XPS. (a) XPS spectra of Sn 3d before and after air exposure. (b) XPS spectra of Se 3d before and after air exposure. (c) XPS spectra of O 1s before and after air exposure. (d) Proposed model of decomposition of SnSe₂ based on XPS.

revealed two Sn peaks at 494.5 and 486 eV, corresponding to Sn 3d 3/2 and Sn 3d 5/3, respectively, while a single Se 3d peak arose at 57.7 eV.⁶⁵ The element ratio of Se/Sn in clean SnSe₂ is about 1.71; this observation of substoichiometric ratio in clean SnSe₂ is consistent with the partial formation of SnSe or existence of excess Sn, as shown in Figure S10. It is noted that the STS was performed on the most ordered regions of the sample, which may have excluded the substoichiometric region. However, after exposure of SnSe₂ to ambient air, both Sn 3d peaks shift to 0.8 eV higher binding energy, consistent with a chemical transition of Sn to oxidized states.⁶⁶ In addition, the

Se 3d peak is separated into two peaks; a larger peak is observed at 59.1 eV corresponding to $\text{SeO}_{xy}^{61,67,68}$ while a smaller peak is observed at 55 eV, consistent with SnSe_2 or SnSe. The existence of SeO_x can be confirmed by a significant increase of signal in O 1s, as shown in Figure 7c. This data is consistent with air exposure of SnSe_2 resulting in decomposition and oxidation to SnO_x and SeO_{xy} as shown in Figure 7d. As a result of decomposition, the Se/Sn ratio decreases to 0.68, consistent with partial desorption of SeO_{xy} .

Oxidation can be kinetically or thermodynamically controlled; a calculation of accurate kinetics barrier requires complex DFT calculations and detailed knowledge of the initial. transition, and final states. Therefore, without such detailed knowledge one can only estimate the propensity to oxidation from the bond strengths of the initial state since their bonds will be broken in oxidation and from the overall exothermicities of oxidation. The heats of oxidation of all three 2D materials are in a range from -626 to -672 kJ/mol; therefore it is hypothesized that the relative reactivity for oxidation is dominated by kinetics rather than thermodynamics. Comparing the thermodynamic heats of formation, WSe₂ and MoS₂ have formation energies of -185.3 and a -271.8 kJ/mol, respectively, while SnSe₂ has a -126.9 kJ/mol enthalpy of formation.⁶⁹⁻⁷¹ Therefore, if the three materials have similar transition states, it is likely that SnSe₂ will have a lower activation barrier to oxidation. Experimentally, the results suggest that the fabrication of transistors with SnSe₂ would require an additional protection layer to prevent oxidation of SnSe₂ layers.

CONCLUSIONS

The impacts of air exposure on various TMDs (WSe₂ and MoS₂) and MDs (SnSe₂) are investigated via STM, STS, and XPS. WSe₂ and MoS₂ show a selective reactivity at step edges to ambient air with partial oxidation (WSe₂) and adsorption of hydrocarbons (MoS_2) , while the terraces on both TMDs are nearly inert. MoS₂ has a stronger interaction with hydrocarbons, which prevented hydrocarbon desorption even with annealing at 723 K. In the case of domain boundaries/grain boundaries in WSe₂ and MoS₂ TMDs, they maintain their unique bias dependence in STM and narrow band gaps in STS after air exposure. The selective oxidation and adsorption of hydrocarbon may not induce degradation in intrinsic transistor channels consisting of single-grain multidomain TMDs; however, it could be problematic in ohmic contact formation (e.g., extra barrier induced by oxidation/adsorption) or undesired leakage (e.g., via edge states) in vertical transistors. In contrast to the selective step reactivity of WSe₂ and MoS₂ in air, SnSe₂ is extremely unstable in ambient air, as confirmed in STM and XPS. After exposure in ambient air for an equivalent duration, all SnSe₂ layers were decomposed and oxidized to SnO_x and SeO_x . On the basis of observed STM and XPS, the summary of air stability of WSe₂, MoS₂, and SnSe₂ is shown in Table 1. These comprehensive surface studies across the TMDs and MDs can provide fundamental explanations for the effect of air exposure on TMDs as a difference of activation barriers for chemical reaction as opposed to exothermicity of oxidation.

METHODS

The deposition of WSe_2 was performed via molecular beam epitaxy¹⁹ in an ultrahigh-vacuum (UHV) chamber. HOPG substrates were heated to 1073 K over 15 min and then held at 1073 K for 15 min to remove potential contaminants. Afterward, HOPG samples were

Table 1. Summary of Air Stability of WSe₂, MoS₂, and SnSe₂

	WSe ₂	MoS_2	SnSe ₂
terrace, after air exposure for 1 day	nearly inert	nearly inert	decomposition to SnO_x and SeO_x
	(band gap change: 2.07 eV \rightarrow 1.98 eV)	(band gap change: 2.26 eV \rightarrow 2.15 eV)	
step edge, after air exposure for 1 day	oxidation	adsorption of carbon composite	
domain/grain boundary, after air exposure for 1 day	nearly inert	nearly inert	
	(band gap change: 1.11 eV \rightarrow 1.10 eV)	(band gap change: 0.82 eV \rightarrow 0.98 eV)	

cooled to 670 K to grow WSe₂. During growth of WSe₂, elemental W from an e-beam source and elemental Se from a Knudsen cell were dosed simultaneously on a HOPG sample held at 670 K. After growth of WSe₂ on HOPG, the Se flux was maintained at a beam equivalent pressure of 1.1×10^{-7} Torr and the sample was annealed under a Se flux first at 773 K for 3 min and subsequently at 873 K for 7 min. Afterward, the sample was cooled to 263 K under a Se flux to cap WSe₂, thereby preventing unintentional oxidation of samples during transport to a separate UHV system for STM and STS.

The deposition of $SnSe_2$ was performed in the same MBE chamber. However, deposition of $SnSe_2$ at high temperature can induce decomposition; therefore, low-temperature (473 K) MBE was employed. During growth, Sn and Se sources were dosed on HOPG samples; then similar Se capping layers were employed on $SnSe_2$ to protect the surface from ambient air during transfer to the STM chamber.

After transport of Se-capped WSe₂ and SnSe₂ via a home-built vacuum case, the samples were introduced in a UHV chamber (Omicron. Inc.: base pressure 1×10^{-10} Torr) through a load lock (base pressure 5×10^{-8} Torr) to perform STM/STS analysis. Prior to STM/STS analysis, for WSe₂/HOPG, the Se capping layers were removed by annealing at 723 K for 3 h. Conversely, for SnSe₂/HOPG, the Se capping layers were removed by annealing at 523 K for 15 min. All STM/STS was performed using electrochemically etched W tips at 100 K.

To compare MBE-grown WSe₂, the deposition of MoS_2 was performed on HOPG using chemical vapor deposition (CVD). It is noted that the growth of MoS_2 via MBE has not been developed yet. MoO_3 powder (Sigma-Aldrich) was placed at the center of furnace and then vaporized by annealing at 1023 K, with the HOPG samples placed above the MoO_3 powder. Simultaneously, S powder (Sigma-Aldrich) was located upstream in the furnace and then vaporized by annealing at 453 K. A 100 sccm of Ar gas transferred the S vapor to HOPG to deposit MoS_2 . After transfer to the STM, the $MoS_2/HOPG$ samples were annealed at 623 K for 3 h to remove any ambient molecules, which were potentially introduced during shipping. All STM/STS was performed using electrochemically etched W tips at 100 K, similar to WSe₂ and SnSe₂ cases.

After STM imaging of the clean surface of WSe_2 , MoS_2 , and $SnSe_2$, all samples were transferred from the UHV chamber into ambient air. After 1 day, the air-exposed samples were transferred into the UHV chamber and STM/STS were performed using the same methods as employed for the clean samples.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b08244.

Additional experimental STM, STS, and XPS data (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: akummel@ucsd.edu.

ORCID [©]

Jun Hong Park: 0000-0001-5138-1622 Joshua A. Robinson: 0000-0001-5427-5788 Andrew C. Kummel: 0000-0001-8301-9855

Author Contributions

This manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. J.H.P. and A.C.K. conceived and designed this experiment. S.V. performed the MBE growth of WSe₂ and SnSe₂, under the supervision of X. L., J. F., and H.G.X. K.Z. provided CVD-grown MoS₂ sample under the supervision of J. R. J.H.P. performed the STM experiments. J.H.P. and A.C.K. analyzed the STM/STS data. S.W., I.K., and M.E. performed XPS.

Notes

The authors declare no competing financial interest.

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