

One Dimensional Metallic Edges in Atomically Thin WSe₂ Induced by Air Exposure

Rafik Addou¹, Christopher M. Smyth¹, Ji-Young Noh¹, Yu-Chuan Lin², Yi Pan³, Sarah M. Eichfeld², Stefan Fölsch³, Randall M. Feenstra⁴, Joshua A. Robinson², Kyeongjae Cho¹, and Robert M. Wallace¹

¹ Department of Materials Science and Engineering, University of Texas, Dallas, Richardson, TX 75080, USA

² Department of Materials Science and Engineering and Center for 2-Dimensional and Layered Materials, The Pennsylvania State University, University Park, PA 16802, USA

³ Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany

⁴ Department of Physics, Carnegie Mellon University, Pittsburgh, PA 15213, USA

ABSTRACT

Transition metal dichalcogenides are a unique class of layered two-dimensional (2D) crystals with extensive promising applications. Tuning the electronic properties of low-dimensional materials is vital for engineering new functionalities. Surface oxidation is of particular interest because it is a relatively simple method of functionalization. By means of scanning probe microscopy and X-ray photoelectron spectroscopy, we report the observation of metallic edges in atomically thin WSe₂ monolayers grown by chemical vapor deposition on epitaxial graphene. Scanning tunneling microscopy shows structural details of WSe₂ edges and scanning tunneling spectroscopy reveals the metallic nature of the oxidized edges. Photoemission demonstrates that the formation of metallic sub-stoichiometric tungsten oxide (WO_{2.7}) is responsible for the high conductivity measured along the edges. *Ab initio* calculations validate the susceptibility of WSe₂ nanoribbon edges to oxidation. The zigzag terminated edge exhibits metallic behavior prior the air-exposure and remains metallic after oxidation. Comprehending and exploiting this property opens a new opportunity for application in advanced electronic devices.

KEYWORDS. tungsten diselenide WSe₂, air oxidation, metallic edge, scanning probe microscopy, X-ray photoelectron spectroscopy, ab initio calculations

1. Introduction

During the fabrication of nanoelectronic and optoelectronic devices, exposure to air and solvents is unavoidable. Therefore, it is crucial to understand the effect of the ambient air exposure on both the topography and the electronic properties. Air-exposed WSe₂ thin films grown by molecular beam epitaxy (MBE) exhibiting a large band gap of 3.15 eV at step edges induced by air adsorbates, while terraces remained unaltered have been recently reported according to scanning tunneling spectroscopy [1]. Atomically thin WSe₂ has also been studied following thermal oxidation using ozone (O₃) at temperatures below 100 °C [2-3]. The tungsten oxide film grew uniformly and in an atomically flat manner with a self-limiting layer-by-layer oxidation from mono- to tri-layers. Both Raman spectroscopy and photoluminescence showed that the oxide layer is decoupled from the underlying WSe₂ layer. The sub-stoichiometric WO_x (2 < x < 3) interfacing with WSe₂ (WO_x/WSe₂) resulted in p-type doping caused by surface charge transfer and exhibited a low hole Schottky barrier. Additionally, Raman spectroscopy and near-field microwave impedance microscopy has been employed to study WSe₂ flakes following annealing to 400 °C under ambient pressure. Oxidation occurred at the flake edge and propagated toward

the center. In addition, terraces with defective areas are also susceptible to oxidation. The oxidized area exhibited much higher local conductivity than WSe₂ and WO₃ [4]. Such low temperature O₃ exposure generated by ultraviolet light has also been demonstrated to functionalize the exfoliated WSe₂ surface for subsequent atomic layer deposition of dielectrics [5].

In transition metal dichalcogenide (TMD) layers, the step edge represents an energetically favorable reaction site with the presence of dangling bonds and broken symmetry of the crystallographic arrangement, which introduces additional states to the intrinsic band structure [6]. First-principles calculations, STM, and STS have been used to study the properties of MoS₂ nanoclusters and edges [7-9]. The nanoscale conductance distribution of the edge states and its contribution to the charge transport were explored experimentally using microwave impedance microscopy (MIM). Moreover, the (MIM) electrical data clearly demonstrate the contribution of edge states to the channel conductance [10].

The exploration of transition metal oxide (TMO) dopants and contacts on TMDs have attracted tremendous considerations for device applications such as field effect transistors (FETs). Both theoretical and experimental work have shown a low hole Schottky barrier in a device employing MoO_x or WO_x as top contacts on MoS₂ and WSe₂ [11-13]. The interface chemistry and band alignment of MoO_x/WSe₂ and MoO_x/MoS₂ heterostructures determined by X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) highlight the promising application of MoO_x as a hole injection layer for p-FETs based on TMDs [11,13]. Oxygen vacancies in sub-stoichiometric TMO generate a metallic-like behavior due to the formation of defect states near the band gap edge. In a WO₃ crystal, the formation of an oxygen vacancy causes a local rearrangement of atoms in a W-O octahedron causing some tungsten atoms to have fewer oxygen atoms as the first neighbors. The new rearrangement results in the removal of four bands from the valence bands below the energy gap and, thus, the Fermi level shifts towards the vacuum level [14-15]. The high electronegativity of TMOs has been explored as a hole injection barrier with better performance than the prototypical high work function metals such as Pd and Au.

In this work, we investigate the step edge properties of WSe₂ monolayers grown by metal-organic chemical vapor deposition (MOCVD) on epitaxial graphene. Microscopy and spectroscopy measurements show that the WSe₂ edges exhibit weakly metallic behavior and the terraces remain intact. The metallic-like behavior is in contrast to a recently reported large band gap measured on MBE-grown WSe₂ edges [1]; we demonstrate that this apparent discrepancy arises in part from the manner in which the data plotted and viewed, which can lead to an emphasis either midgap states (for the metallic-like behavior) or band-edge states (for the larger gap). Our conclusion of predominant metallic-like behavior is consistent with XPS, which reveals the presence of only WO_x (SeO_x is below the XPS detection limit) on the surface, with x ranging from 2.6 to 2.7. Previous reports indicated the metallic nature of WO_x, with $x < 2.9$ [14-15]. First principles calculations based on DFT revealed a metallic behavior of oxidized zig-zag WSe₂ edges.

2. Methods

2.1 Sample Growth

Epitaxial graphene (EG) was produced via silicon sublimation of the Si face of 6H-SiC (0001) (purchased from *II-VI Inc.*) at 1600 °C in a 200 Torr environment filled with pure Ar inside a heating crucible made of pure graphite [16]. The SiC substrates were pre-etched at 700 Torr with

flowing 10 % H₂/Ar mixtures (total 500 sccm) to remove subsurface damage due to substrate-polishing. The WSe₂ was grown on epitaxial graphene via a metal-organic chemical vapor deposition (MOCVD) process [17]. The precursors chosen for WSe₂ synthesis are W(CO)₆ and (CH₃)₂Se, which provide W and Se, respectively. In order to eliminate carbon contaminations in the materials, a 100% H₂ environment was utilized. The WSe₂-EG had been placed in a box filled with N₂ prior to the subsequent characterization. The sample was exposed to air during the AFM imaging, ex-situ transfer, and shipping to UTD for STM and XPS characterization.

2.2. Surface characterization

Ex-situ characterization of the aged WSe₂/EG/SiC(0001) was performed using an ultra-high vacuum (UHV) system with base pressure $\sim 1 \times 10^{-10}$ mbar described in detail elsewhere [18]. Room temperature scanning tunneling microscopy (STM) images were obtained using a variable temperature STM, with an etched tungsten tip [19]. Room temperature scanning tunneling spectroscopy (STS) data were collected in a single point and averaged from at least 15 sweeps to obtain a single curve. Then, a direct differentiating of the I-V curves was plotted in linear and log scale. The UHV system is also equipped with a monochromatic Al K α source ($E = 1486.7$ eV) and an Omicron Argus detector operating with pass energy of 15 eV. The spot size used during the acquisition is 630 μm . The analyzer spectrometer energy scale was calibrated using sputter cleaned Au and Cu polycrystalline foils as indicated in the ASTM E2108 procedure [20]. The aged sample was transferred to UHV through load lock and characterized without any annealing. The reference sample is a freshly exfoliated bulk sample purchased from *HQ Graphene* [21]. The atomic force microscopy (AFM) images were obtained in ambient conditions using *Brucker* microscope. A *Createc* low-temperature STM operated at 5 K was used for additional STM and STS measurements, with dI/dV spectra acquired using a lock-in amplifier operated at frequency of 675 Hz and with modulation voltage of 50 mV. In those measurements, we use an STS measurement method that yields relatively high dynamic range [22], in which the tip-sample separation is varied as a function of applied sample bias voltage V . A ramp is applied to the tip-sample separation according to $\Delta s(V) = a (|V| - |V_0|)$, where the constant a is typically taken to be 1-2 Å/V for our measurements and V_0 refers to the sample bias for the constant-current operation of the STM immediately preceding the acquisition of the spectrum. The exponential increase in conductance arising from this variation in tip-sample separation is then normalized by multiplying the data by a factor of $\exp(2\kappa\Delta s(V))$, where κ is an experimentally determined decay constant. Values of κ , measured in each experiment, were typically found to be about 10 nm⁻¹. This normalization does not affect any detailed structure in the spectra, but it improves the dynamic range by 1-2 orders of magnitude, thus yielding enhanced detection sensitivity for band-edge features and/or in-gap states. A noise level for the conductance is measured with the tip withdrawn from the surface; subsequent normalization with the same method then yields a voltage-dependent noise level for each spectrum.

2.3. Computational details

Theoretical calculations based on density functional theory (DFT) [23-24] are performed as implemented in the Vienna Ab initio Simulation Package (VASP) [25-26]. The projector augmented wave (PAW) pseudopotentials [27-28] and the Perdew-Burke-Ernzerhof (PBE) [29] functional for the exchange-correlation energy of electrons are employed. A kinetic energy cutoff of 400 eV for the plane-wave basis set expansion is used. The atomic structures are relaxed until energy, and the energy convergence and Hellmann-Feynman force convergence criteria are less than 10⁻⁴ eV and 0.01 eV/Å, respectively. The optimized in-plane lattice constant

of WSe₂ is calculated to be 3.314 Å, and the distance between top and bottom Se atoms in a Se-W-Se is 3.352 Å. The vacuum thickness of about 18 Å is used to avoid the interaction between periodic layer images. The nanoribbon widths are chosen to be 20.4 Å for ZWSe₂ and 21.7 Å for A-WSe₂, respectively, which are large enough to maintain the bulk electronic structure at inner Mo atom. A Γ -centered 1×15×1 for zigzag edge and 1×9×1 k-point mesh for armchair edge are employed. The band gap is calculated to be 1.55 eV in our PBE calculation. The WSe₂ nanoribbons have two edge termination of zigzag (Z-WSe₂) and armchair (A-WSe₂), and the formation energies of the WSe₂ nanoribbon is calculated as follow:

$$E_{edge}^{form} = \frac{1}{2L} [E_{edge} - N_W E_{WSe_2} + (N_{Se} - 2N_W) \mu_{Se}]$$

E_{edge} is the total energy of WSe₂ including edge, E_{WSe_2} is the total energy of the pristine single-layer WSe₂ per a formula unit, L is the length of the edge, and N_W and N_{Se} are the number of the W and Se atoms in the WSe₂ nanoribbon system. We found excessive Se in Se-terminated edge configuration while a Se deficiency in W-terminated edge configuration. The chemical potential of Se represented as μ_{Se} is dependent on the experimental condition, and we choose the Se orthorhombic crystal as the Se reservoir corresponding to the Se-rich limit condition. The heat of formation of a single-layer WSe₂ ($H_{WSe_2} = \mu_{Se, max} - \mu_{Se, min}$) is 0.84 eV satisfying the thermal equilibrium relation of $\mu_W + 2\mu_{Se} = E_{WSe_2}$.

3. Results and discussion

3.1. Surface imaging and electronic structure of WSe₂ edge and grain boundary

The surface topography of the pristine epitaxial graphene prior the growth of WSe₂ exhibits a clean and uniform surface over an area of 1 μm $\times$ 1 μm (Figure S1a, Supporting Information). The high resolution STM image and corresponding STS confirms the expected honeycomb structure and the metallic character of the underlying Epi-Gr (Figure S1b-c, Supporting Information). The as-grown atomically thin WSe₂ presents high quality monolayers with WO_x and SeO_x compounds below the XPS detection limit as reported in our previous work [16,30-31]. Some areas show that the growth also follows a 3D fashion (Figure S2). The AFM images in Figure 1a-b show a comparison of the topography of a WSe₂ thin film freshly grown (Figure 1a) and after air exposure (Figure 1b). Step edge decoration is observed following air exposure on both monolayer (ML) and bilayer (BL) WSe₂. The surface of fresh (slight oxidation) and aged (strong oxidation) samples also show the presence of particles/clusters located at the 6H-SiC(0001) step edges. The presence of such particles on both samples implies they form from adsorbates or the precursor products [32].

To inspect the quality of graphene and WSe₂ after air-exposure, the atomic structure and band gap measurements were recorded on flat regions far from defects such as step edges or pinholes as highlighted in Figure 1c. The STM image displays the presence of BL-WSe₂ on top of the Epi-Gr/SiC substrate. The dark pits are developed on the SiC substrate during surface preparation and/or on the graphene layers during the growth process (Figure S1d) [33]. These structural defects in graphene can be translated to the WSe₂ overlayer resulting in local degradation of the vertical heterostructure (WSe₂/Epi-Gr) [16]. Figures 1d-f show the atomic resolution and conductance dI/dV spectra measured on Epi-Gr, ML-, and BL-WSe₂, respectively. The moiré pattern with periodicity of ~ 1.6 nm recorded on graphene surface (Figure 1d) is indicative of rotated lattices of the topmost two graphene layers with respect to each other by an angle of 8.7°, as previously reported for multilayer Epi-Gr grown on a 6H-SiC substrate [34]. On similar samples, cross-sectional transmission electron microscopy showed the growth of three graphene layers on the SiC substrate [16,30]. The lattice parameter of the graphene unit cell is

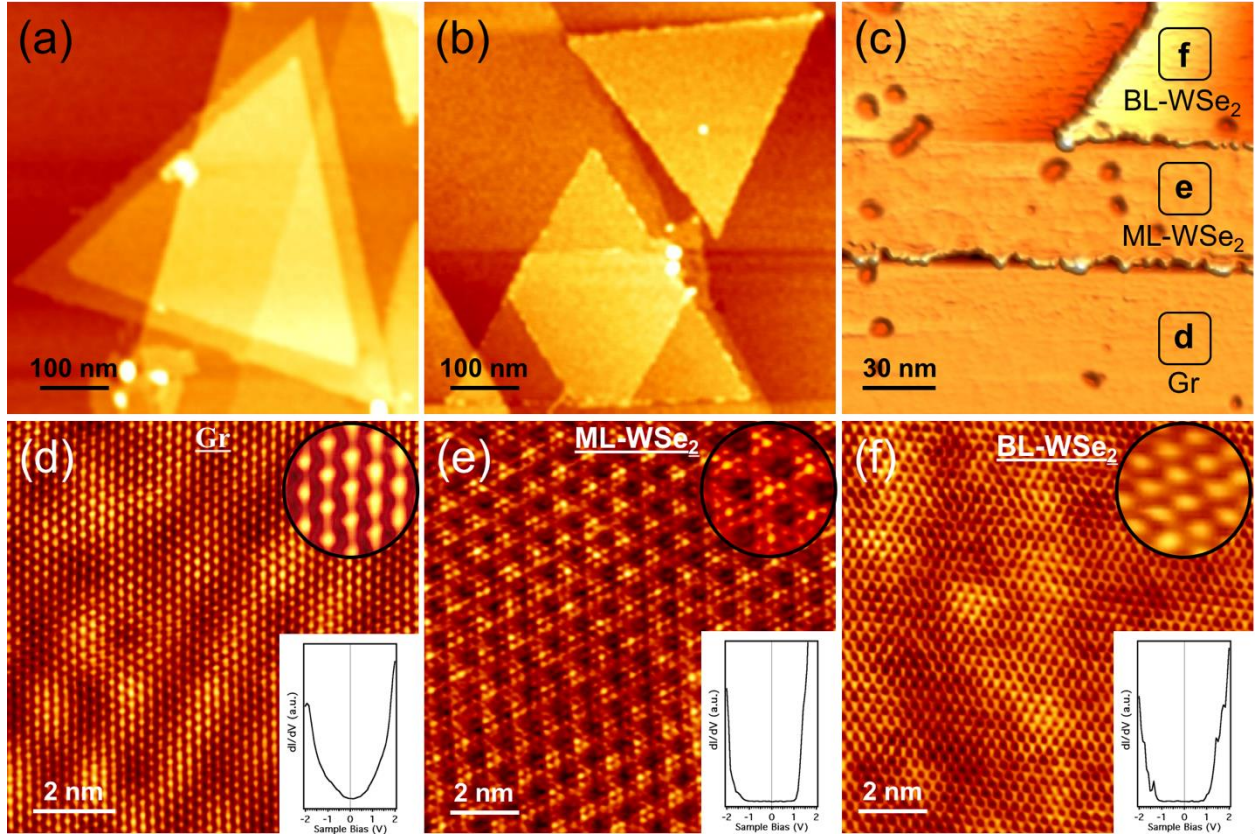


Figure 1. Surface imaging of atomically thin WSe₂. (a) AFM image of an as-grown WSe₂ thin film, and (b) after storage of 2 months in N₂ box. (c) STM image ($V_b = 0.5$ V, $I_t = 0.5$ nA) measured on an aged WSe₂ sample. (d, e, f) STM images showing the atomic resolution recorded on (d) a clean area of epitaxial graphene ($V_b = 0.25$ V, $I_t = 3.0$ nA), (e) monolayer WSe₂ ($V_b = 0.2$ V, $I_t = 1.7$ nA), and (f) bilayer WSe₂ ($V_b = 0.33$ V, $I_t = 1.5$ nA) as labeled in panel (c). Inset: high magnification and STS spectra recorded on each terrace (Gr, d), (ML, e), and (BL, f).

measured to be $\sim 0.26 \pm 0.02$ nm and the conductance dI/dV indicates the expected metallic conductivity (inset Figure 1d) [35]. Due to the lattice misfit between the WSe₂ monolayer and underlying graphene layer, a different moiré pattern is observed (Figure 1e) with a periodicity of 0.98 ± 0.05 nm. Also, the atomic structure of BL-WSe₂ was well resolved with a lattice constant measured at 0.33 ± 0.03 nm [16,47]. Based on the moiré pattern periodicity and the WSe₂ lattice constant, the rotation angle is found to be $\sim 0^\circ$, in agreement with previous reports [1,16,36]. The band gap measured from ML-WSe₂ is 2.26 ± 0.1 eV with the valence band maximum (VBM) located at -1.18 eV and conduction band minimum (CBM) at ~ 1.08 eV. Figure 1f shows the atomic structure of BL-WSe₂ with the expected lattice constant of 0.33 nm and a band gap of ~ 1.8 eV with the VBM (CBM) located at -1.1 eV (0.7 eV). The high resolution images do not reveal any formation of mirror-twin domain boundaries as observed on MoTe₂ and MoSe₂ surfaces induced by significant chalcogen deficiency [37-39].

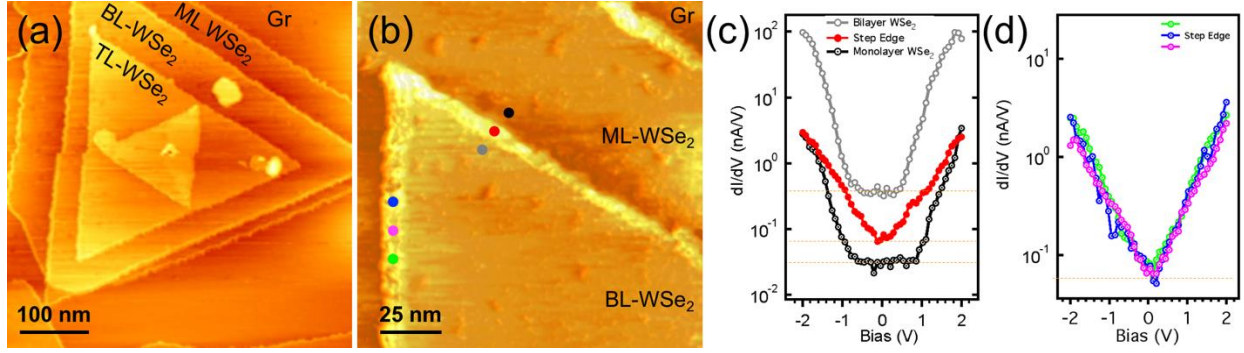


Figure 2. Topography and electronic characterization of aged WSe₂. (a) STM image ($V_b = 2$ V, $I_t = 0.5$ nA) of the oxidized WSe₂ surface showing a four-layer island with edge oxidation. (b) STM image ($V_b = 1.7$ V, $I_t = 0.5$ nA) recorded on the edge of monolayer and bilayer WSe₂. (c) dI/dV spectra in log scale measured on three different areas across the edge as indicated in (b). (d) Three dI/dV spectra obtained along the WSe₂ edge. The linear scale of (c) and (d) are presented in Figure S5. The orange dashed line present the noise level.

Figure 2 shows room temperature STM and STS measurements recorded from an aged WSe₂ sample. The large STM image in Figure 2a and the close-up view in Figure 2b show edge decoration along the triangular domains of both ML- and BL-WSe₂. The width of the decorated edge extends to 8 nm with noticeable bias dependence. To understand the bright contrast localized on the edge, the dI/dV spectra in Figure 2c are measured across and along the edge as highlighted in Figure 2b. The STS clearly shows weakly metallic behavior of the step edge, *i.e.* with conductance tails extending in from the band edges indicative of a V-shaped density-of-states throughout the band gap, similar to that previously observed *e.g.* on semimetallic multilayer graphene [40]. A well-defined band gap is observed on the ML- and BL-WSe₂ terraces, as expected. The bright contrast at the edges detected by STM imaging are caused by the metallic nature and possible variation in the height after the oxidation (Figure S3). It is worth noting that the STS data recorded on a disordered step edge exhibit a wide variety of states throughout the WSe₂ band gap, and thus it is not obvious how to determine the band gap accurately at the step edge. Our results recorded on different oxidized step edges all exhibit 'weakly metallic' or 'semi-metallic' behavior, *i.e.* with a "V-shaped" density of states extending down to essentially a zero density of states at the Fermi energy (Figure S4-S5). Any apparent gap in this density of states would have a magnitude of only a few tenths of an eV or less.

This metallic edge can be regarded as a one-dimensional conducting wire in contact with a 2D semiconductor (Figure 2b and S3b). The clean BL/ML-WSe₂ heterojunction has been studied previously using STS at 77 K. The measured conductance spectra revealed new edge states emerge in the vicinity of the band gap, reducing its magnitude to 0.8 eV [41]. The deviation in the band gap value between the center of the terrace and the WSe₂ edge will be clarified below by our DFT calculations. Metallic zigzag edges have been theoretically predicted and experimentally verified on single-layer MoS₂ nanoclusters by means of DFT calculations and STM [7-8], as well as in ML- and BL-WSe₂ [41].

Additional STM and STS data were acquired at a low temperature of 5 K to further investigate the edge states, as displayed in Figure 3. A surface region containing both ML and BL WSe₂, as well as trilayer (TL) WSe₂, is shown in Figure 3(a). Steps at the edges of the WSe₂ islands are seen, with the irregular features at the step edges that are characteristic of aged WSe₂. Locations of two STS spectra each from a step edge and from the BL-WSe₂ terrace are indicated in the image, and resulting averaged spectra are displayed in Figure 3(b) (numerous additional



Figure 3. Topography and electronic characterization of aged WSe₂, acquired at low temperature of 5 K. (a) STM image ($V_b = 2$ V, $I_t = 0.02$ nA) of the oxidized WSe₂ surface showing edges between ML and BL WSe₂ and between BL and TL WSe₂. (b) dI/dV spectra measured at the step edge and the BL WSe₂ locations indicated in (a).

spectra from both ML and BL-WSe₂ will be presented elsewhere). For the BL-WSe₂ spectrum, a clear band gap of width 1.95 ± 0.1 eV is observed. At the step edges, states extending into that gap are seen. A small residual gap still occurs at the step edge, with width ~ 0.3 eV. This small gap is typical of results acquired at other locations along the step edges, indicative of the weakly metallic nature of the edges. The larger range of these spectra compared to those of Figures 1 and 2 permit comparison to the prior results of Park et al.[1]. In particular, those workers concluded that a *larger* band gap was formed on the oxidized (aged) WSe₂ step edges [1], which is in apparent conflict with our conclusions of states extending into the band gap, producing a residual gap of only a few tenths of an eV. However, as seen in Figure 3(b), if we view the part of the spectrum that extends above the band edges, e.g. below about -1.0 or above 1.2 V, then indeed a larger gap does appear for the aged spectrum. It is only when the energy range within the band gap is focused upon that the small, residual gap arising from midgap states is seen. Such midgap states are, actually, also apparent in the spectra of Park et al. [1], as seen by the weak “tails” of states extending from the VBM and CBM into the band gap. We conclude that our data and that of Park et al. [1] is consistent, but that the manner of presenting the data differs (with a “normalized conductance” used in Ref. [1]), which tends to emphasize different parts of the spectra.

3.2. Surface chemistry of aged WSe₂ surface

Since STM and STS techniques cannot provide unambiguous elemental (chemical) analysis, the WSe₂ film was also studied by XPS. Figure 4a shows the W 4f and Se 3d core level spectra. Analysis of these spectra via peak fitting indicates the presence of W-O bonding in addition to W-Se bonding. The Se 3d_{5/2} core level indicates the presence of two components separated by ~ 0.35 eV detected at 54.35 eV and 54.70 eV (Figure 4a, black and gray peaks). Such splitting is not caused by the presence of metallic Se⁰ or SeO_x, where the corresponding Se 3d peaks are expected at a much higher binding energy around 55.5 and 59.3 eV, respectively [5,42]. Using the total integrated area, the Se:W ratio is estimated to be 2.25 ± 0.20 . It is known that an excess of Se is responsible for p-type doping often found in WSe₂ [43-44]. The W 4f_{7/2} core level in Figure 4a shows the same splitting with similar peak separation (black and gray spectra) of ~ 0.35 eV (Table 1). Metallic tungsten, which is expected to exhibit a W 4f_{7/2} core level with binding energy of ~ 31.2 eV, is below the detection limit of XPS [45-46]. The two

components observed in W 4f and Se 3d core level spectra are explained by work function variations due to the presence of both n- and p-type conductivities present across the WSe₂ film. It is also possible that the two components arise due to the formation of a dipole upon interfacing with WO_x. Similar observations were reported on MoS₂ and WSe₂ bulk crystals and thin films [47-50]. XPS measurements obtained from the reference sample, a freshly exfoliated bulk WSe₂ surface, show a single chemical state in each of the W 4f and Se 3d core level spectra. The valence band edge position (~ 1.24 eV) is consistent with n-type WSe₂. It is worth noting that the presence of tungsten oxyselenide WO_xSe_y would be detected near the same binding energy as n-WSe₂ (gray spectra) [45].

The W 4f_{7/2} (W 4f_{5/2}) core level associated with WO_x is detected at a higher binding energy of ~ 35.25 eV (37.40 eV) from the WSe₂ chemical states and are in excellent agreement with the reported W⁵⁺ chemical state in sub-stoichiometric WO_x [3]. The O 1s core level (Figure 4b) is dominated by chemical states associated with C-O (Figure S6) and O-H bonds (air adsorbates), [51] while the low binding energy shoulder detected at ~ 530.55 eV corresponds with the presence of WO_x [45,52]. The O:W ratio was found to be ~ 2.7 in excellent agreement with reported sub-stoichiometric metallic WO_{2.72} [53-55]. The Fermi level is located at ~ 0.6 eV above the VBM (Figure 4c) revealing that this sample is p-type. The p-type conductivity measured on this sample can be caused either by the excess of Se and/or by the surface electron transfer from WSe₂ to the sub-stoichiometric WO_x. The presence of impurities below the XPS detection limit could also be responsible for the p-type doping [48].

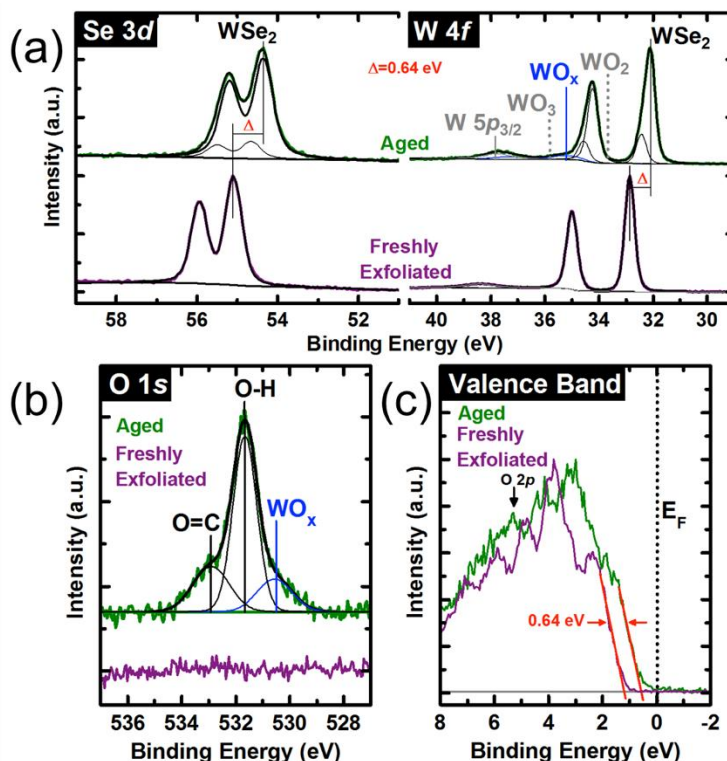


Figure 4. Photoemission investigation of aged WSe₂. (a) Se 3d, W 4f, and W 5p core level spectra. (b) O 1s core level spectrum. (c) Valence band edge spectrum. There is an uncertainty of ± 0.05 eV when determining the binding energy for all core levels.

Table 1. Binding energy of different compounds measured in an oxidized/aged WSe₂ film. Gray cells indicate that the chemical state is below the XPS detection limit (<0.1 at. %).

		Compound					
		p-WSe ₂	n-WSe ₂	WO _x	W ⁰ -metal	SeO _x	Elemental Se ⁰
Binding energy (eV)	W 4f _{7/2}	32.10	32.45	35.25	.	.	.
	W 4f _{5/2}	34.25	34.60	37.4	.	.	.
	Se 3d _{5/2}	54.35	54.70	.	.	.	.
	Se 3d _{3/2}	55.20	55.55	.	.	.	.
	O 1s	.	.	530.55	.	.	.

3.3. Calculations of oxidized WSe₂ nanoribbons

Both DFT calculations and STM have shown that the zigzag edges in MoS₂ nanoribbons exhibit distinct metallic states [7-8]. The armchair-edged nanoribbons of MoS₂ have been theoretically shown to exhibit a small gap (0.56 eV with the DFT-PBE approximation). However, armchair nanoribbons are usually not observed in experiments because zigzag MoS₂ ribbons have considerably lower formation energy [56]. So far, theoretical calculations indicate that zigzag edges in MoS₂ are metallic [57]. In the present work, *ab initio* calculations based on density functional theory (see computational methods) are performed on pristine and oxidized zigzag (Z) and armchair (A) edges in WSe₂ nanoribbons as displayed in Figure 5a. The Se-terminated edge in zigzag nanoribbons (ZWSe₂-Se) is the most stable edge configuration (0.2 eV at Se deficient limit condition). The formation energies of W-terminated armchair and zigzag edges (AWSe₂-W and ZWSe₂-W) are very high and present the most unfavorable configurations (Figure 5b). Thus, it is unlikely for the W-terminated edge to form. We will therefore consider only ZWSe₂-Se nanoribbons for edge oxidation calculations because the Se-terminated WSe₂ edge will be observed under equilibrium conditions assuming constant stability of this edge termination regardless of chemical environment. The armchair WSe₂ (AWSe₂, middle configuration in Figure 5a), AWSe₂-W, ZWSe₂-W, and AWSe₂-Se are discussed in the Supporting Information. The formation energy shown in Figure 5b is plotted as a function of Se chemical potential, and the formation energy of Se- and W-terminated edges change according to Se chemical potential. The increase in Se chemical potential indicates an increase in Se source in the environment, thus, as the Se chemical potential increases, the formation energy of a Se-terminated edge decreases (becomes more favorable), while the W-terminated edge becomes less stable. However, because the composition ratio of W and Se in AWSe₂ is 1:2, the formation energy of AWSe₂ without excess Se does not change according to the Se chemical potential.

In the total density of states (DOS) plots, ZWSe₂-W, AWSe₂-Se, and ZWSe₂-Se exhibit metallic behavior as shown in Figure 4a. The Fermi level exists at 0.3 eV, 0.2 eV, and 0.6 eV above the VBM in ZWSe₂-Se, AWSe₂-Se, and ZWSe₂-W, respectively. Due to the edge states, the DOS reveals an intrinsic p-type behavior. The energetically favored Se-terminated ZWSe₂ exhibits a greater degree of p-type doping compared to the W-terminated ZWSe₂. In contrast, edge states in AWSe₂-W and AWSe₂ which narrow the band gap are predicted. The induced edge states in AWSe₂-Se and AWSe₂-W exhibit reduced band gaps of 0.4 and 0.7 eV, respectively, from that of pristine WSe₂ (1.45 eV).

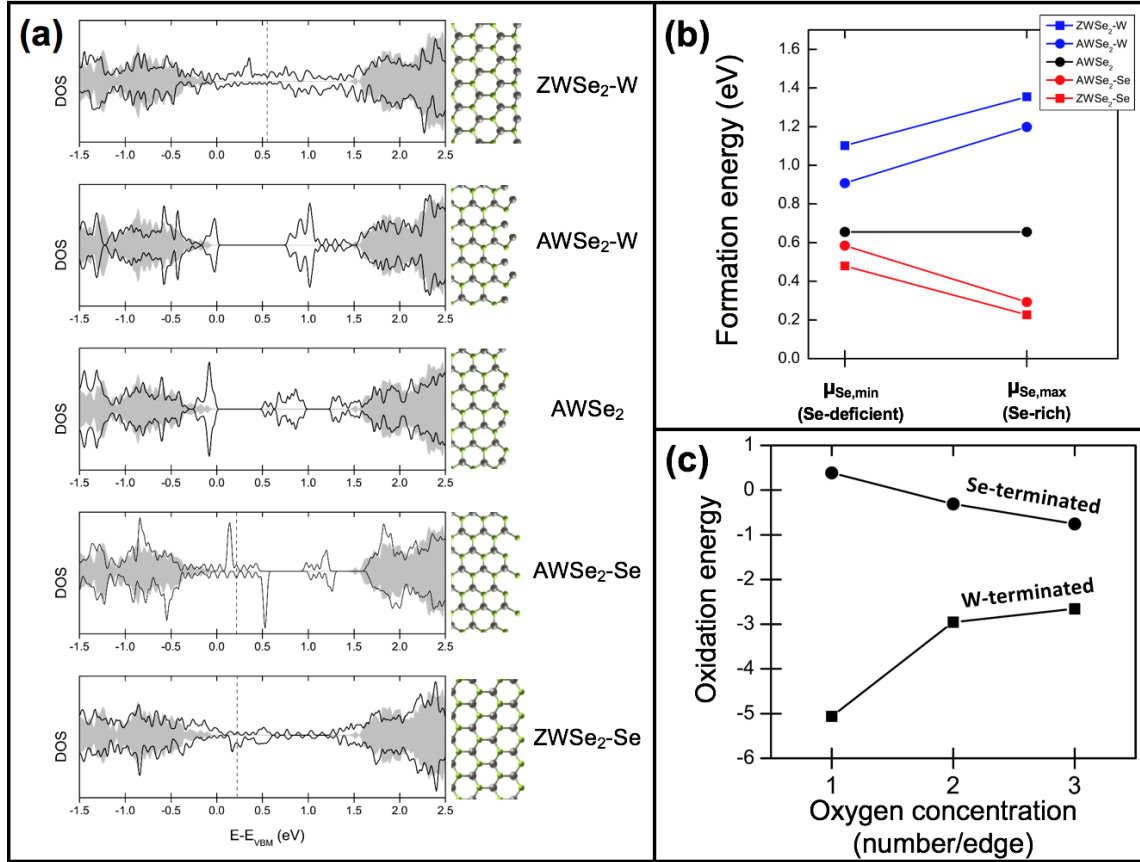


Figure 5. (a) Density of states of the WSe₂ nanoribbons with five different configurations: W-terminated ZWSe₂, W-terminated AWSe₂, neutral AWSe₂, Se-terminated AWSe₂, and Se-terminated ZWSe₂. The atomic configurations are inserted. DOS are aligned to the VBM of the pristine monolayer WSe₂ filled with gray color, the Fermi levels are indicated by vertical dashed lines. (b) Formation energy of the WSe₂ nanoribbons according to the chemical environment condition. The blue, black, and red lines represent the W-terminated edges, neutral edges, and Se-terminated edges, respectively. The zigzag phase is indicated by square points, and the armchair phase is indicated by circle points. (c) Oxidation energy of the ZWSe₂ nanoribbons. The Se-terminated and W-terminated edges are indicated as circle and square points, respectively. Gray (green) sphere presents W (Se) atoms.

Our calculations show that edge oxidation is thermodynamically favorable. W-terminated edges are less favored than Se-terminated edges, however, the oxidized formation energies are much lower at W-terminated edges than at Se-terminated edges regardless of the number of oxygen atoms (Figure 5c). Figure 6 displays the atomic arrangement and the density of states of oxidized ZWSe₂ with Se-terminated edge as the oxygen concentration increases. The WSe₂ edges initially have a Se-terminated edge before oxygen reaction (Figure 6a). With low oxygen concentration, O atoms bond to the ZWSe₂-Se edge to form Se-O bonds (Figure 6b). However, with increased oxygen concentration, the oxygen atoms participate in the dissociation of Se atoms from the edge, and additional oxygen atoms replace the dissociated Se site with W-O bond formation (Figure 6c). When oxygen atoms replace the edge Se atoms, the edge states retain their metallic character. However, the Fermi level position shifts closer to the VBM, indicating that p-type doping is enhanced by edge oxidation via Se dissociation in ZWSe₂-Se (Figure 6d). Under very high oxygen concentrations, sub-stoichiometric WO_x (x<3) is formed and very weakly bound to the edge. Even though WO₃ is semiconducting, WO_x formed at the edge of WSe₂ has

many dangling bonds introducing defect states within the band gap. Thus, ZWSe_2 remains metallic.

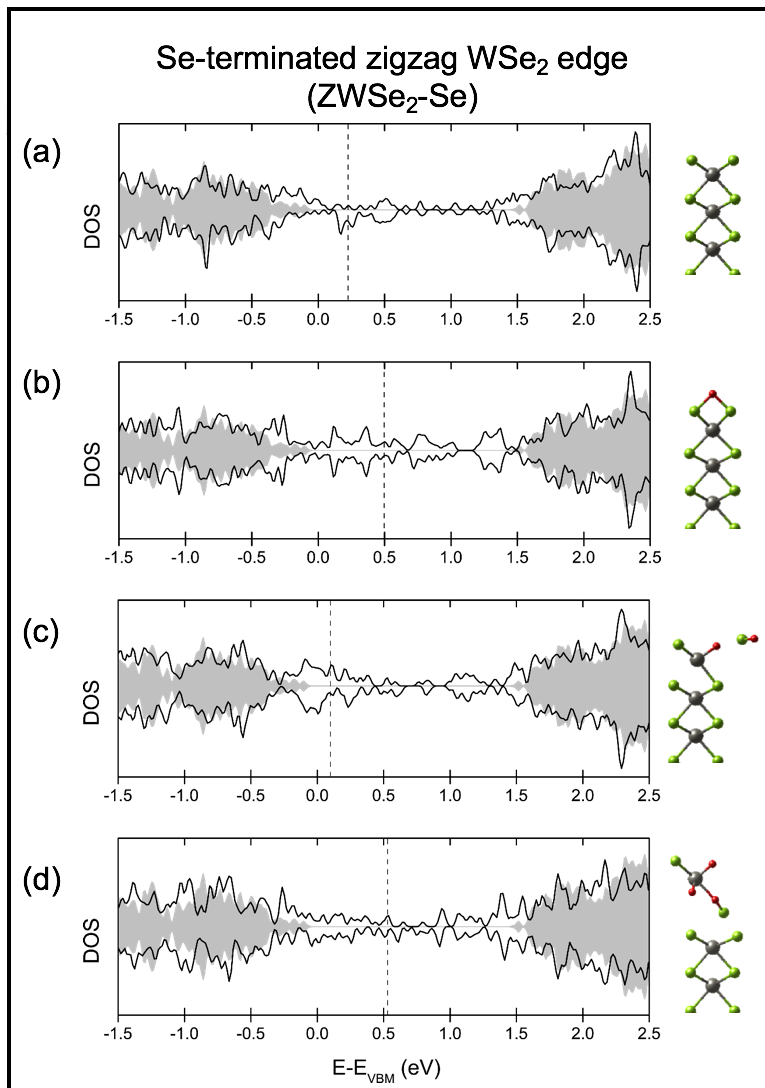


Figure 6. Density of states of the Se-terminated ZWSe_2 . (a) Pristine edge (without oxygen), and with increasing oxygen (red sphere) concentration: (b) 1 O atom, (c) 2 O atoms, and (d) 3 O atoms. The atomic arrangement is inserted in each configuration. DOS are aligned to the VBM of the pristine monolayer WSe_2 filled with gray color, the Fermi levels are indicated by vertical dashed lines.

W edge termination of ZWSe_2 is less favored than Se edge termination, however, and the oxidized formation energies are much lower for $\text{ZWSe}_2\text{-W}$ than $\text{ZWSe}_2\text{-Se}$ regardless of the number of oxygen atoms (Figure S7). The number of Se atom sites filled by oxygen atoms increases with increasing concentration of oxygen resulting in a Fermi level shift towards the VBM. After oxygen atoms have replaced all edge Se atom sites, the Fermi level resides at the VBM. Under high oxygen concentrations, Se edge termination can be restored by desorbing the substructure of WO_x ($x < 3$).

4. Summary

In summary, the surface properties of an air-oxidized WSe₂ thin film grown by chemical vapor deposition was characterized using AFM, STM, STS, and XPS, and supported by *ab initio* calculations. On the WSe₂ sample exposed to ambient air at room temperature, we observed that the oxidation initiates at the edges and the terraces remain inert and intact, exhibiting the H-WSe₂ structure with the expected band gap (2.2 eV for ML and 1.8 eV for BL-WSe₂). The STS reveals a metallic behavior at the edge caused by the formation of tungsten oxide (WO_{2.7}) as demonstrated by photoemission measurements. The *ab initio* calculations performed on both WSe₂ zigzag and armchair edge before and after oxidation support the metallic conductivity measured on the edges. Our findings demonstrate possible passivation of the edge states. The grown WSe₂ reveals p-type conductivity caused by excess of Se and/or charge transfer by contacting with the WO_{2.7}. Engineering the properties of 2D materials by means of air exposure or controlled treatment will lead to novel electrical properties, *e.g.* the oxide film may be used as an effective hole injection layer to the TMD channel and could be employed as a tunnel barrier between metal contacts and the TMD, which is expected to reduce the Schottky barrier height [11,59]. Most applications require the control of disorder and inhomogeneity. However, edge states may allow leakage current or promote charge injection into WSe₂, as revealed in the MoS₂ FET, where the electrical conduction starts from the edges before emerging in the MoS₂ bulk [10].

Our conclusions regarding metallic formation of step edges are quite different than those reported previously by Park *et al.*, who argued that air exposure resulted in passivation and an *increase* in the size of the band gap at the step edges [1]. However, it is important to note that that prior work employed a different means of displaying the data, in which the “normalized conductance” is computed as a ratio of the differential conductance, dI/dV , over the total conductivity, I/V (with the latter quantity being averaged over a voltage interval of about 1 V). While this normalized conductance is useful for many purposes [22,58], it tends to emphasize the largest density-of-states features of the spectra, *i.e.* the ones above (below) the conduction (valence) band edges. In contrast, the smaller features that lie within the band gap appear only as relatively weak “tails” in the normalized spectra of Park *et al.* However, if plotted on a logarithmic scale as employed in the present work (or, using a linear scale but over a narrow range of dI/dV that strongly emphasizes the gap region), then such tails in the spectra are much more visible, producing the substantial features within the gap as seen in the present work in Figures 1-3.

The Supporting Information is available at

http://iopscience.iop.org/2053-1583/5/2/025017/media/Supplementary_Information.pdf

AUTHOR INFORMATION

Corresponding Author

E-mail: addou@utdallas.edu and rmwallace@utdallas.edu

Acknowledgment

The authors thank Prof. Christopher Hinkle (UT-Dallas), Prof. Andrew Kummel (UC-San Diego), and Dr. Luigi Colombo (Texas Instruments) for useful discussions. This work is supported in part by the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA. It is also supported by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research

Initiative and NIST. JN was supported by National Research Foundation of Korea by Creative Materials Discovery Program (2015M3D1A1068062). CMS was also supported in part by NSF Award No. 1407765 under the US/Ireland UNITE collaboration.

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