

DOI: <https://doi.org/10.24425/amm.2022.141076>EUNJEONG KIM<sup>1†</sup>, SANGYOEB LEE<sup>2†</sup>, YEONJIN JE<sup>3</sup>, DONG PARK LEE<sup>3</sup>, SANG JUN PARK<sup>3</sup>, SANGHYUN JEONG<sup>2</sup>, JOON SIK PARK<sup>2</sup>, BYUNGMIN AHN<sup>4\*</sup>, JUN HONG PARK<sup>1,3\*</sup>

## STRUCTURAL DEFORMATION OF TUNGSTEN DISELENIDE NANOSTRUCTURES INDUCED BY OZONE OXIDATION AND INVESTIGATION OF ELECTRONIC PROPERTIES CHANGE

Tungsten diselenide (WSe<sub>2</sub>) is one of the promising transition metal dichalcogenides (TMDs) for nanoelectronics and optoelectronics. To enhance and tune the electronic performance of TMDs, chemical functionalization via covalent and van der Waals approaches has been suggested. In the present report, the electric and structural transition of WSe<sub>2</sub> oxidized by exposure to O<sub>3</sub> is investigated using scanning tunneling microscopy. It is demonstrated that the exposure of WSe<sub>2</sub>/high-ordered pyrolytic graphite sample to O<sub>3</sub> induces the formation of molecular adsorbates on the surface, which enables to increase in the density of states near the valence band edge, resulting from electric structural modification of domain boundaries via exposure of atomic O. According to the work function extracted by Kelvin probe force microscopy, monolayer WSe<sub>2</sub> with the O<sub>3</sub> exposure results in a gradual increase in work function as the exposure to O<sub>3</sub>. Therefore, the present report demonstrates the potential pathway for the chemical functionalization of TMDs to enhance the electric performance of TMDs devices.

*Keywords:* Tungsten diselenide; Domain Boundary; Ozone Oxidation; Structural Deformation; Scanning Tunneling Microscopy

### 1. Introduction

Transition metal dichalcogenides (TMDs) have attracted great attention as potential electronic and optoelectronic platforms because of their thickness-dependent electrical and optical properties for diverse applications, such as high mobility nanoelectronics and 2D phototransistors [1-3]. Remarkably, the band structure of TMDs can be altered from indirect to direct bandgap as the number of layers decreases from multilayer to monolayer [4,5]. Furthermore, combining with molecular or atomic substitutional defects engineering, the electronic structure of TMDs can be modulated with phase deformation-induced bandgap engineering and direct/indirect doping schemes, resulting in a tunable electronic performance of nanoelectronics [6,7].

Tungsten diselenide (WSe<sub>2</sub>) is one of the most widely studied layered semiconductors due to its tunable electronic structure and intrinsic ambipolar behavior [8,9]. Since WSe<sub>2</sub> has high electron mobility and high stability for electric stress, a recent study of WSe<sub>2</sub> has focused on thin body channel materials; thereby,

atomic thickness allows efficient electrostatics and a high degree of vertical scaling [10,11]. Additionally, oxidation of WSe<sub>2</sub> via exposure UV-O<sub>3</sub> as an example of chemical functionalization has been demonstrated for hole-contact engineering at the interface of WSe<sub>2</sub> and metal [12-14]. In this work, we demonstrate the investigations of the structural and electronic properties of WSe<sub>2</sub> grown using molecular beam epitaxy (MBE) upon exposure to atomic oxygen. Using a scanning tunneling microscope (STM) and scanning tunneling spectroscopy (STS), WSe<sub>2</sub> oxidized by exposure to O<sub>3</sub> is atomically probed to elucidate the chemical transition of WSe<sub>2</sub> with the oxidization process. Therefore, the present report reveals that oxygen chemisorption induces the electronic/structural transition of domain boundaries as the initial reaction stage, and WSe<sub>2</sub> finally chemically transitioned into WSe<sub>2-x</sub>O<sub>x</sub> complexes. Moreover, the shift of the Fermi level position of WSe<sub>2</sub> is probed using Kelvin probe force microscopy (KPFM) to extract a work function on single and bilayer WSe<sub>2</sub>. Consequently, the present report elucidates the behavior of surface adsorption-induced chemical transition of WSe<sub>2</sub> at the atomic level.

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## 2. Experimental procedures

WSe<sub>2</sub> samples were grown on high-ordered pyrolytic graphite (HOPG) stabilized by the heating process. The growth was conducted based on prior MBE growth studies of WSe<sub>2</sub>. During a low W flux of deposition process, the Se flux is constantly exposed at an equivalent beam pressure of  $1.1 \times 10^{-7}$  Torr. The deposited sample was annealed with a Se flux at 773 K for 3 mins and then re-annealed at 873 K for 7 mins. The annealed sample was cooled to 263 K under a Se flux to deposit another Se layer (~60 nm) to protect against ambient air during the transportation from the furnace to the measurement system under ultra-high vacuum (UHV).

Using electrochemically etched tungsten tips, STM and STS were performed in the Omicron VT UHV chamber. After decapping the Se adlayers from the WSe<sub>2</sub>/HOPG samples, the mounted samples on the STM stage were cooled to 100 K by liquid nitrogen. The differential tunneling conductance ( $dI/dV$ ) of WSe<sub>2</sub> was probed by STS using standard lock-in modulation techniques (lock-in modulation voltage:  $\Delta V_{rms} = 20$  mV,  $f = 500$  Hz)

## 3. Results and discussion

After decapping Se adlayer from the WSe<sub>2</sub> surface, nucleation and growth of WSe<sub>2</sub> across the HOPG surface with

about 0.5 coverage. A large-scale image of WSe<sub>2</sub> on the HOPG substrate is observed using STM, as shown in Fig. 1(a). The WSe<sub>2</sub> is initially nucleated at the surface of HOPG; the islands of WSe<sub>2</sub> are formed by propagating from initial nucleation sites to form “sawtooth-shaped islands.” As denoted in Fig. 1(b), the hexagonal moiré pattern at the surface of the WSe<sub>2</sub> monolayer is observed in a high-resolution STM image [15]. As the WSe<sub>2</sub> monolayer stacks on the HOPG surface, the orbitals of WSe<sub>2</sub> are overlapped with the orbital of the topmost HOPG layer. Therefore, a hexagonal array of protrusions results from the periodic potential wells of orbital overlapping. The atomic-resolved STM image of WSe<sub>2</sub> captured at a sample bias ( $V_{sample}$ ) of  $V$  (80 pA) is obtained with periodic bright spots corresponding to the layer of Se atoms. The spacing between Se atoms measured is statistically about 0.33 nm, similar to the previously reported lattice parameters of WSe<sub>2</sub> [16,17].

After confirmation of bare WSe<sub>2</sub> surface, using STM, the WSe<sub>2</sub> samples are exposed to O<sub>3</sub> produced by UV-O<sub>3</sub> generator for 1 min in a separated dosing chamber. In contrast, the pressure of the dosing chamber maintains about  $2 \times 10^{-4}$  torr at 300 K. The exposure of the WSe<sub>2</sub>/HOPG sample to O<sub>3</sub> induces the existence of molecular adsorbates on the surface, as shown in the large-scale STM image in Fig. 1(c). It can be hypothesized that the adsorbates are mostly oxygen-containing complex or hydrocarbon. To elucidate the electronic effect of O<sub>3</sub>-induced

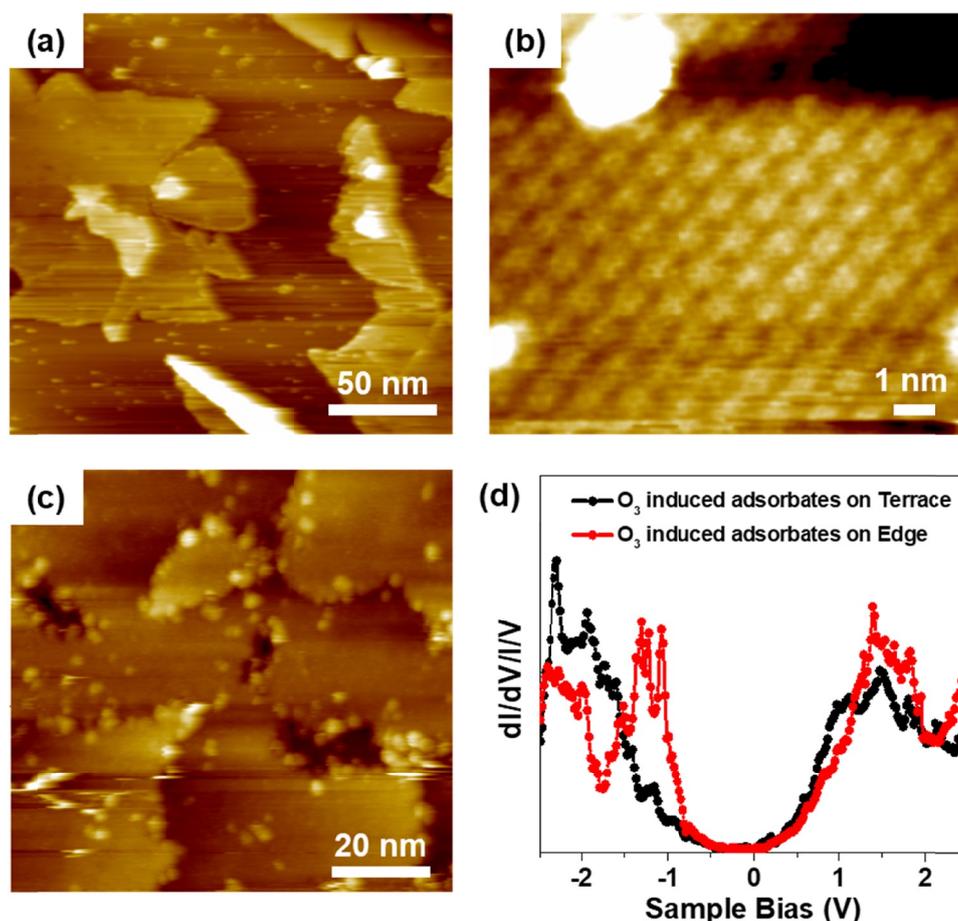


Fig. 1. (a) Large-area STM image of ML WSe<sub>2</sub> grown on the HOPG substrate ( $V = 2$  V,  $I_T = 20$  pA); (b) high-resolution STM image of WSe<sub>2</sub> ML ( $V = 1.0$  V,  $I_T = 80$  pA); (c) STM image of WSe<sub>2</sub> after the O<sub>3</sub> exposure ( $V = 2$  V,  $I_T = 20$  pA); (d) STS spectra of O<sub>3</sub> induced adsorbates

adsorption on  $\text{WSe}_2$ , STS is performed. In Fig. 1(d), the black spectra are assigned to the electronic structure of adsorbates on the  $\text{WSe}_2$  terrace, while the red spectra correspond to the electronic structure of adsorbates at the  $\text{WSe}_2$  edge. Although the narrow band structure is observed in both sites with a large band edge density of states (DOS), the  $\text{O}_3$  induced adsorbates at the  $\text{WSe}_2$  edges have larger DOS near valence band edge than adsorbates on the  $\text{WSe}_2$  terrace. The previous reports reveal that large DOS is associated with transition metal termination due to the incomplete structural configuration of atomic structure at the TMDC edge [18]. Therefore, as this defect associated DOS is mixed with DOS of adsorbates in tunneling signal, resulting in large DOS at the band edge in STS.

Exposure of  $\text{WSe}_2$  to  $\text{O}_3$  induces the electronic transition of domain structure in  $\text{WSe}_2$ , consistent with observable bias dependence of STM image. In Fig. 2(a), triangle-shaped domain boundaries are clearly shown with blight protrusion at a sample bias of  $-1.5$  V, consistent with the filled state image. Conversely, these domain boundaries are not observable in the empty state image of Fig. 2(b) obtained at  $1.5$  V. To bias dependence of domain boundaries at the atomic scale; the sample imaging bias decreases to  $1.0$  V to approach the STM tip to the surface. The filled state image obtained at  $-1.0$  V reveals Se atoms array in electrically brightened domain boundaries, as shown in the white arrow in Fig. 2(c). It is noted that although the empty state image of Fig. 2(d) also shows the triangular domain boundaries, it is less distinct than filled states. It can be hypothesized that the atomic O modified domain boundaries have donated electrons during tunneling between STM tips and samples. The local density of state (LDOS) of atomic O exposed ML  $\text{WSe}_2$  is measured using STS. The red circle is marked on the triangular domain boundaries, indicating the  $\text{O}_3$ -modified domain structures, while the black circle is marked internal domains. From the  $dI/dV$  spectra in Fig. 2(e), the red spectra obtained on triangle

boundaries has larger LODS at both valence band (VB) and conduction band (CB) edges, as shown in green arrows, compared to the black spectra measured at off the triangle boundaries. Thus, the atomic-scaled STS curves are consistent with the bias dependence of atomic O modified domain boundaries shown in Figs. 2(a-d).

To elucidate thermal stability of the  $\text{O}_3$  induced domain structure transition in  $\text{WSe}_2$ , the  $\text{WSe}_2$  samples are additionally exposed to  $\text{O}_3$  for 5 min under the same conditions, then are annealed at  $673$  K for 30 min under the ultra-high-vacuum ( $P: 2 \times 10^{-10}$  torr). Bias-dependent STM characterizations of triangular domain boundary in  $\text{WSe}_2$  can be observed in the STM image of Fig. 3(a). As shown in zoomed-in image of Fig. 3(b), triangle-shaped features along the domain are detected in the  $\text{WSe}_2$  samples, consistent with the high-thermal stability of  $\text{O}_3$ -induced domain transition. To elucidate the impact of  $\text{O}_3$  induced transition on the electronic structure of  $\text{WSe}_2$ , the band structure of the  $\text{WSe}_2$  monolayer (ML) is probed using STS, as shown in Fig. 3(c). The bare  $\text{WSe}_2$  ML has about  $2.09$  eV electronic bandgap, consistent with the previous reports [19]. After exposure of  $\text{WSe}_2$  to  $\text{O}_3$  for 1 min at  $300$  K, the bandgap of  $\text{WSe}_2$  ML decreases significantly to about  $1.16$  eV. With further exposure to  $\text{O}_3$  for 5 min, an additional reduction of  $\text{WSe}_2$  ML bandgap is observed about  $0.88$  eV. As shown in Fig. 2(e),  $\text{O}_3$  exposure induces the structural/electronic transition of the domain structure with an increase in DOS at VB and CB. As shown in previous reports [20], atomic oxygen atoms are produced by dissociation of  $\text{O}_3$  into  $\text{O}_2$  and O. Therefore, it can be hypothesized that as the atomic structure of  $\text{WSe}_2$  is exposed to atomic oxygen, initially, domain boundaries of  $\text{WSe}_2$  react with O. Afterwards, oxidization of  $\text{WSe}_2$  is propagate from domain boundaries to internal domains, consistent with the formation of  $\text{WSe}_{2-x}\text{O}_x$  complexes. Since the formed  $\text{WSe}_{2-x}\text{O}_x$  complexes have a large density of defects, the structural incomplete induces

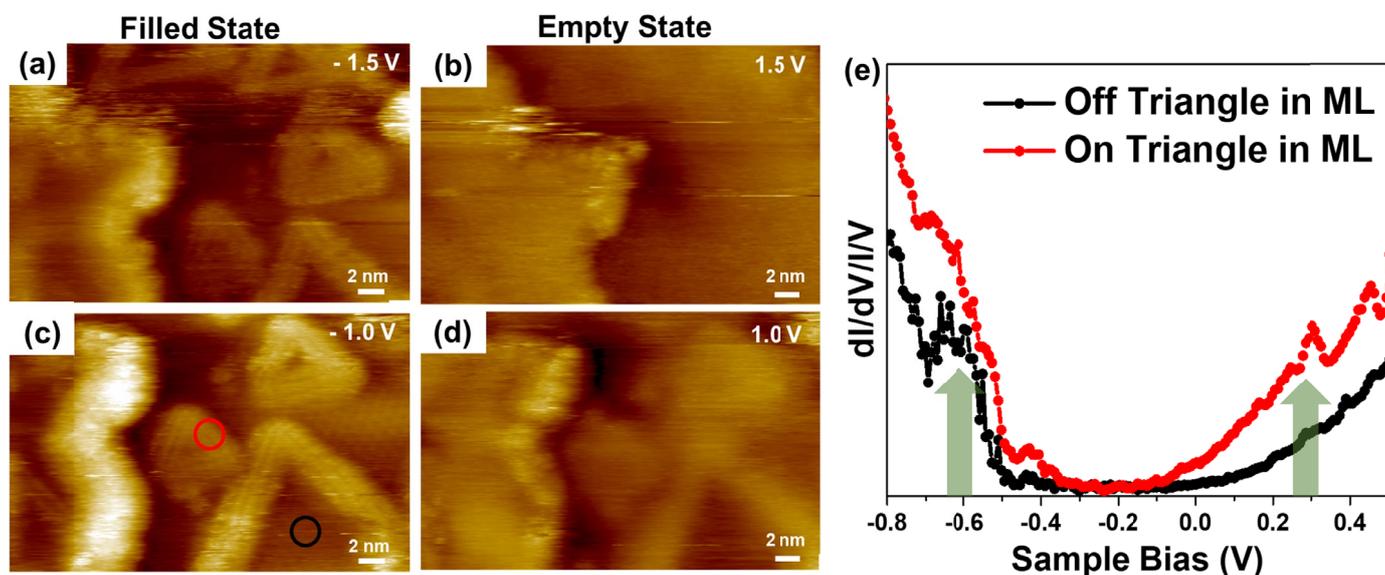


Fig. 2. (a) STM image of ML  $\text{WSe}_2$  in filled state at a sample bias of  $-1.5$  V ( $I_T = 100$  pA); (b) Empty state image obtained at  $1.5$  V ( $I_T = 100$  pA); (c) Filled state image obtained at  $-1.0$  V ( $I_T = 100$  pA); (d) Empty state image obtained at  $1.0$  V ( $I_T = 100$  pA); (e) STS spectra on the  $\text{O}_3$  modified domains boundary marked by a red-circle and the rest of the area marked by black-circle

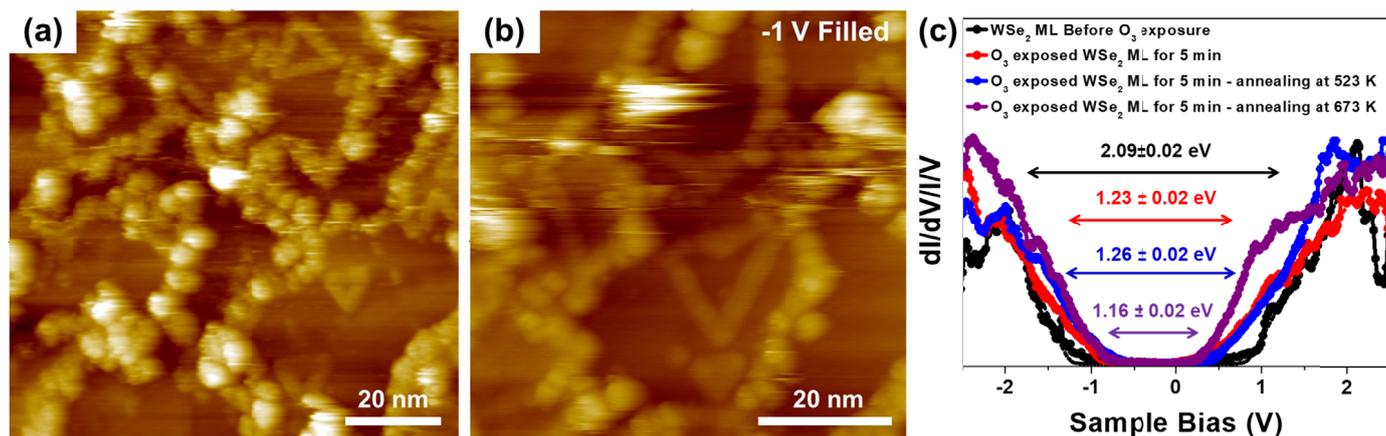


Fig. 3. (a) STM image of WSe<sub>2</sub> exposed to O<sub>3</sub> for 6 min ( $V = -1.5$  V,  $I_T = 20$  pA); (b) Zoomed-in STM image for the triangular domain ( $V = -1$  V,  $I_T = 80$  pA); (c) STS spectra of WSe<sub>2</sub> as exposure to O<sub>3</sub>

large defect states in the band structure, consistent with a narrow bandgap.

KPFM is employed to extract a work function on single- and bilayer WSe<sub>2</sub>. The WSe<sub>2</sub> is transferred by mechanical exfoliation of bulk WSe<sub>2</sub> onto thermally grown SiO<sub>2</sub> substrates. A topographical image of the entire WSe<sub>2</sub> flake is shown in Fig. 4(a). After confirmation of the position of the WSe<sub>2</sub> flake, KPFM images are obtained, as shown in Fig. 4(b). Contact potential difference images are displayed in Figs. 4(c) and 4(d), which corresponded to O<sub>3</sub> exposed for 2 min and O<sub>3</sub> exposed for 6 min, respectively. In order to track the Fermi level position upon exposure to atomic

oxygen, contact potential difference is measured by KPFM. Afterward, work functions of samples ( $\Phi_{\text{sample}}$ ) are extracted, as shown in the following equation [21],

$$V_{CPD} = \frac{\Phi_{\text{sample}} - \Phi_{\text{tip}}}{e}$$

where  $e$  is the elementary charge. The overall transition of work functions for each procedure are summarized in Fig. 4(e). After exposure of WSe<sub>2</sub> to O<sub>3</sub> for 2 min, the work function increases about 0.3 eV, consistent with STM/STS results shown above. Moreover, the O<sub>3</sub> exposure for 6 min induces the additional in-

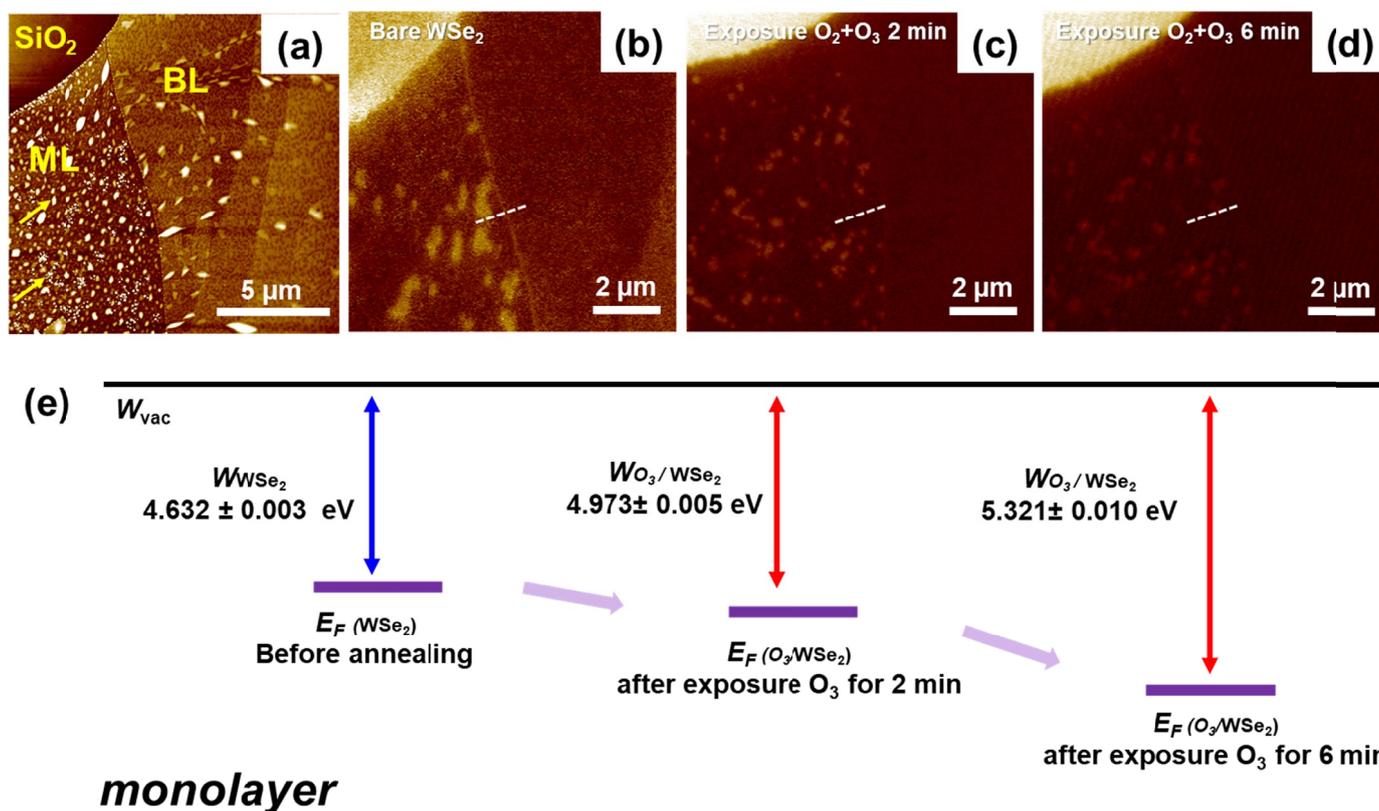


Fig. 4. (a) AFM topography image of entire WSe<sub>2</sub> flake consisting of single- and bilayer. KPFM images of (b) bare WSe<sub>2</sub>; (c) WSe<sub>2</sub> exposed to O<sub>2</sub> + O<sub>3</sub> for 2 min; (d) WSe<sub>2</sub> exposed to O<sub>2</sub> + O<sub>3</sub> for 6 min; (e) Summary of extracted work function of WSe<sub>2</sub> ML, as exposure to O<sub>3</sub>

crease of a work function to  $5.321 \pm 0.01$  eV. This suggests the Fermi level of WSe<sub>2</sub> shifts to the valence band with exposure O<sub>3</sub>, consistent with p-type behavior. It can be hypothesized that the exposure to O<sub>3</sub> results in a chemical transition to the formation of WO<sub>x</sub> with lattice distortion, consistent with previous reports [22].

#### 4. Conclusions

The electric and structural transition of WSe<sub>2</sub> oxidized by exposure to UV-ozone is investigated using surface probing. After confirmation of bare MBE grown WSe<sub>2</sub> surfaces, STM reveals that the WSe<sub>2</sub>/HOPG sample exposure to O<sub>3</sub> induces the existence of molecular adsorbates on the surface. It is noted that the O<sub>3</sub> induced adsorbates at the WSe<sub>2</sub> edges have larger DOS near valence band edge than adsorbates on the WSe<sub>2</sub> terrace due to the defect of the WSe<sub>2</sub> domain structure. As exposure of WSe<sub>2</sub> surface to atomic O, adsorption of atomic O induces the chemical/electric modification of domain boundaries, consistent with STM bias dependence. The electric transition of O<sub>3</sub> modified domain boundaries can be confirmed by STS, consistent with an increase of LDOS at both VB and CB. In addition, a work function on single- and bi-layer WSe<sub>2</sub> is extracted using KPFM. The extracted work function ( $\Phi_s$ ) of monolayer WSe<sub>2</sub> is increased with the O<sub>3</sub> exposure, resulting in the Fermi level shift to the valence band. Therefore, the present results suggest the elucidation of chemical and electric functionalization of TMDs, using molecular and atomic adsorption on the surfaces.

#### Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2021R1C1C1012209 and 2020R1A4A4079397).

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