Point Defects in CVD-grown Monolayer WSe_2 studied by STM/STS and DFT Modeling

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Motivation

- Single layer (SL) WSe_2 has potential applications in nanoelectronics, gas-sensing, and other applications.
- Defects can change the electronic and chemical properties of any material.
- Important to understand defects in WSe_2 at the atomic scale.

Methods

- **Growth: SL-WSe_2 was grown by chemical vapor deposition (CVD)**
- **Atomic-scale Imaging: Scanning Tunneling Microscopy/Scanning Tunneling Spectroscopy**
  - Operated at ~77 K under ultrahigh vacuum conditions (10^{-10} mbar).
  - STS acquired by a lock-in amplifier with a sinusoidal modulation of 40 mV at 625 Hz.
  - Bias voltage (V_{Tip}) is applied on the STM tip respect to the sample.
  - Electrochemically etched tungsten tips were used in all measurements.
- **Modeling: Density Functional Theory (DFT) Calculations**
  - VASP code, PBE exchange-correlation functional with Grimme's correction for van der Waals interactions
  - Energy cutoff: 400 eV
  - Force convergence criterion: 0.01 eV/Å for graphite, bulk WSe_2 and SL-WSe_2 supercell and 0.05 eV/Å for WSe_2/graphite supercell
  - Tersoff-Hamann approximation for simulation of STM images
- **Workflow**
  - CVD-grown SL-WSe_2 was deposited on graphite substrates
  - STM and STS were performed
  - DFT calculations on many atomic models were performed, including vacancies, antisite defects, intercalation or adsorption of W, Se and O
  - STM images and densities of states were simulated to compare with experiment
  - Only atomic structures involving O substitution, O insertion, and O adsorption were consistent with experiment

Conclusion

- Point defects have been observed in atomic-scale STM images of CVD-grown SL-WSe_2.
- Extensive DFT modeling of different structures strongly suggests that these point defects are all related to the presence of atomic oxygen (O substitution, O insertion and O adsorption)
- It is likely that these defects are due to the dissociation of molecular oxygen on Se vacancy sites
- These defects do not have a large impact on electronic structure close to the valence and conduction band edges (their STS and PDOS are similar to pristine WSe_2).
- However, O substitution and O insertion defects increase the chemical activity of WSe_2 (not shown).

Acknowledgements

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Results

WSe_2 on graphite

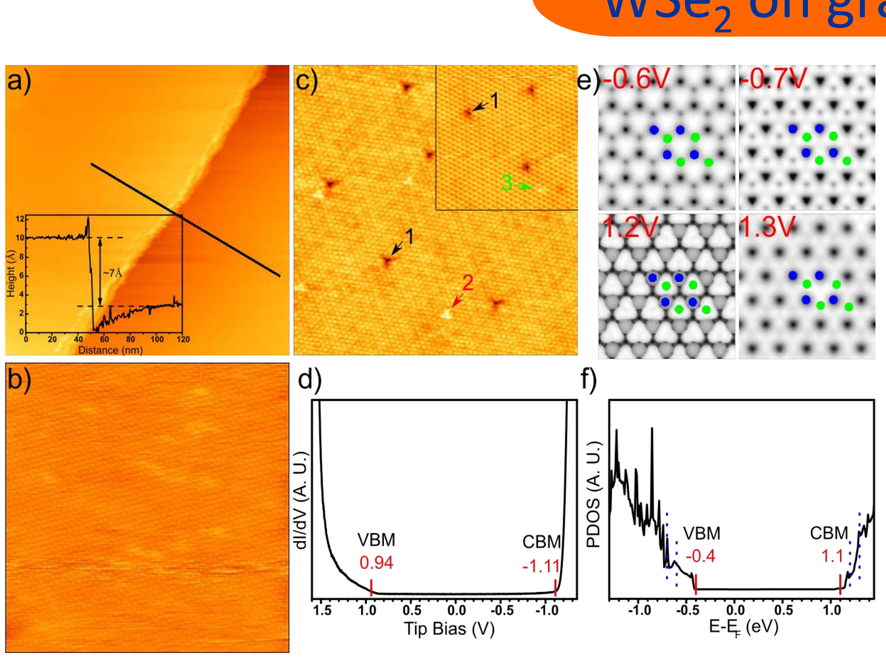

Figure 1. a) (V_{Tip}= -1.5V; 150nm×150nm) and **b)** (V_{Tip}= -1 V; 50nm×50nm) Images of SL-WSe_2 layer on graphite substrate. Inset: lateral profile corresponding to the dark line in panel **a)** reveals a height of 7Å for SL-WSe_2. **c)** STM image showing 3 types of point defects labelled by black, red and green arrows (V_{Tip} = 1 V; 20 nm×20 nm, Inset: 10 nm×10 nm). **d)** STS spectrum reveals a 2.05±0.10 eV bandgap for SL-WSe_2 (V_{Tip}=1.3 V, 68.5 pA). **e)** Calculated bias-dependent STM images of pristine SL-WSe_2 on graphite (overlaid green spots: Se, blue spots :W.) **f)** PDOS of SL-WSe_2 reveals a 1.5 eV DFT PBE bandgap.

Proposed models for the three defects

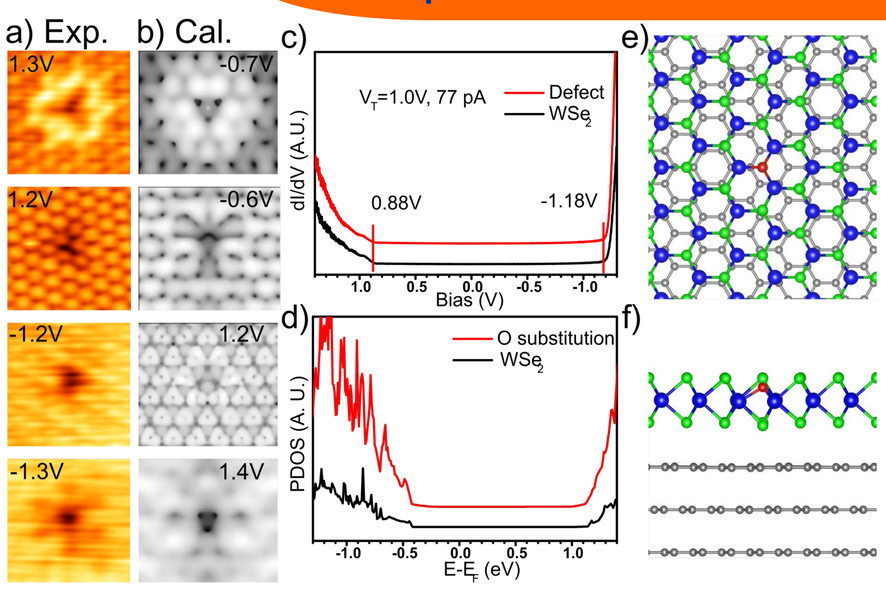

Figure 2. O substitution at Se site (triangular depression, black arrow) in WSe_2. **a)** Bias dependent STM images (2.5 nm× 2.5 nm) of the defect. **b)** Calculated STM images of the O substitution defect. **c** STS on defect sites and sites far from defects (> 2 nm). **d** PDOS of WSe_2 with and without O substitution. **e)** and **f):** top and side views of the proposed atomic structure (Red: O, Blue: W, Green: Se and Gray: C.)

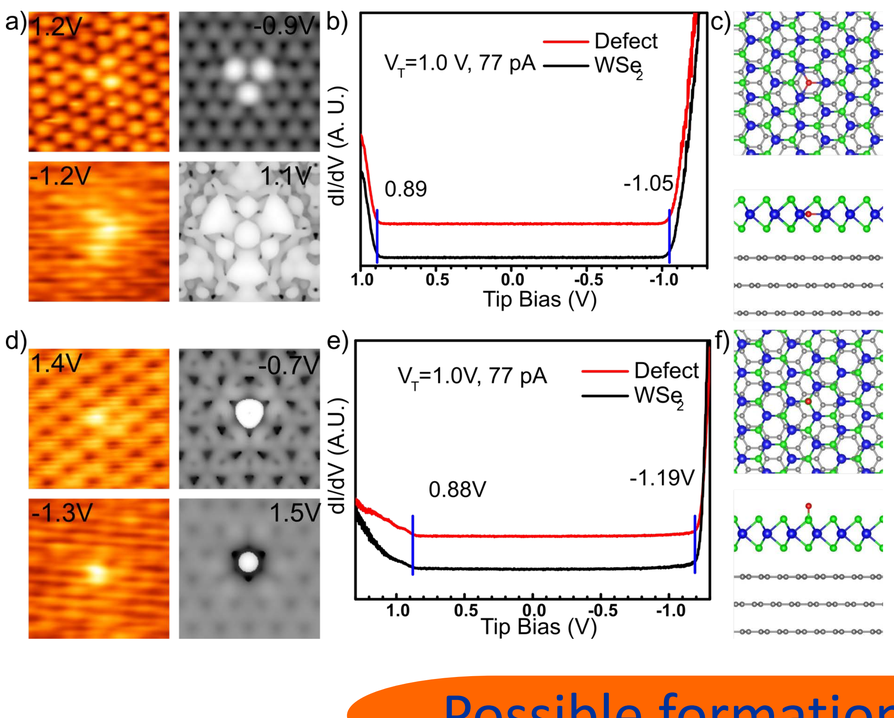

Figure 3. O insertion (bright triangular cluster, red arrow) and O adsorption (bright dot, green arrow) in WSe_2. **a)** and **d)** Bias dependent experimental (2.5 nm× 2.5 nm) and simulated STM images of O insertion and adsorption, respectively. **b)** and **e)** STS on defect sites and sites far from defects (> 2 nm) for O insertion and adsorption, respectively. **c)** and **f)** Top and side views of the structure of O insertion in, and O adsorption on WSe_2 layer on graphite substrate, respectively.

Possible formation mechanism

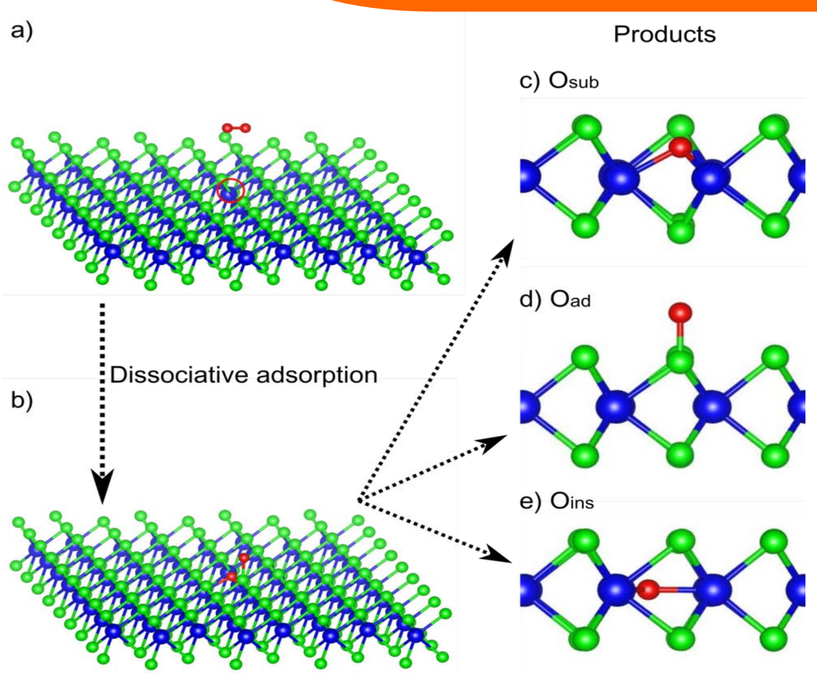

Figure 4, Schematic illustration of the formation of the O-related defects. **a)** O_2 far away from WSe_2 (with Se vacancy). **b)** O_2 dissociative adsorption on WSe_2 (substitution + adsorption). **c-e)** Products. (O substitute Se, another moves to most stable configurations (adsorption + insertion).