Point Defects in CVD-grown Monolayer WSe₂ studied by STM/STS and DFT Modeling

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Motivation

• Single layer (SL) WSe₂ 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 WSe₂ at the atomic scale.

Methods

• Growth: SL-WSe₂ was grown by chemical vapor deposition (CVD)
• Atomic-scale Imaging: Scanning Tunneling Microscopy/Scanning Tunneling Spectroscopy
  • Operated at ~77 K under ultrahigh vacuum conditions (10⁻¹³ 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)
  • 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 WSe₂ and SL-WSe₂ supercell and 0.05 eV/Å for WSe₂/graphite supercell
• Tersoff-Hamann approximation for simulation of STM images
• Workflow
  • CVD-grown SL-WSe₂ 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-WSe₂.
• 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 WSe₂).
• However, O substitution and O insertion defects increase the chemical activity of WSe₂ (not shown).

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