Electronic Band Structure of ALD $MoTe_2/TiO_2$ Heterostructures

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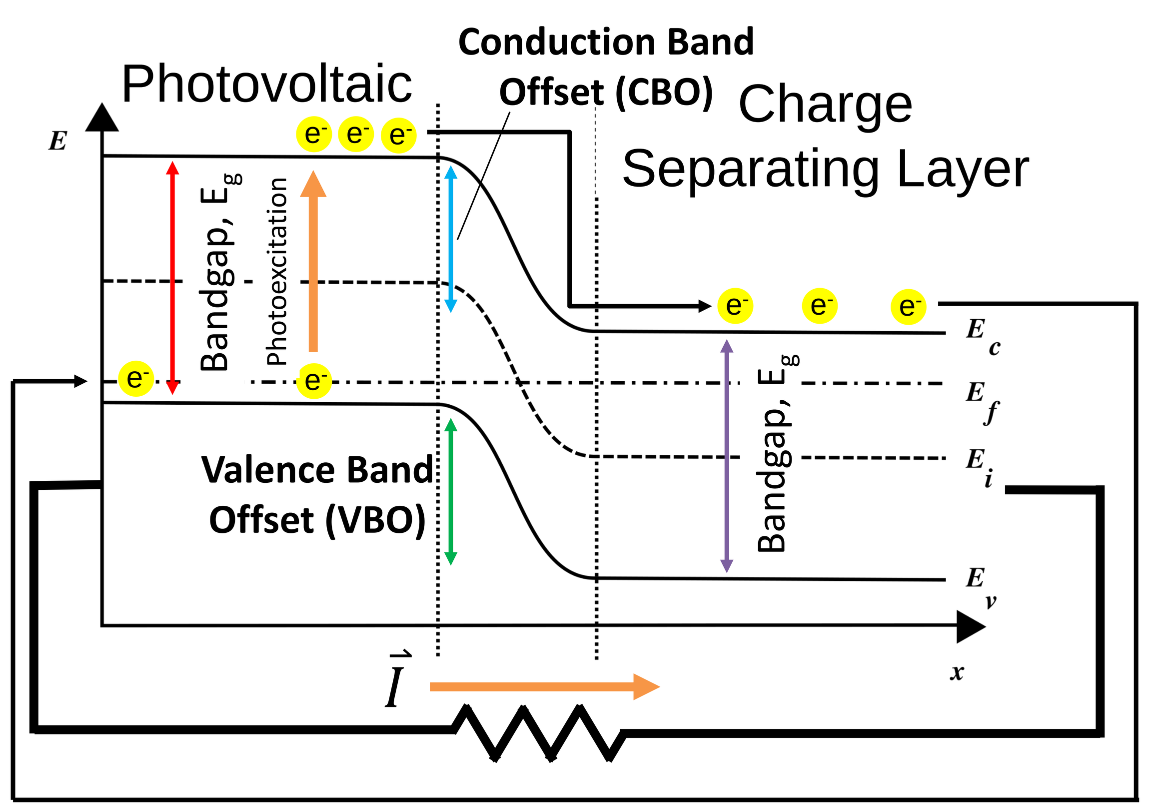
Background

Solar Cell Operations

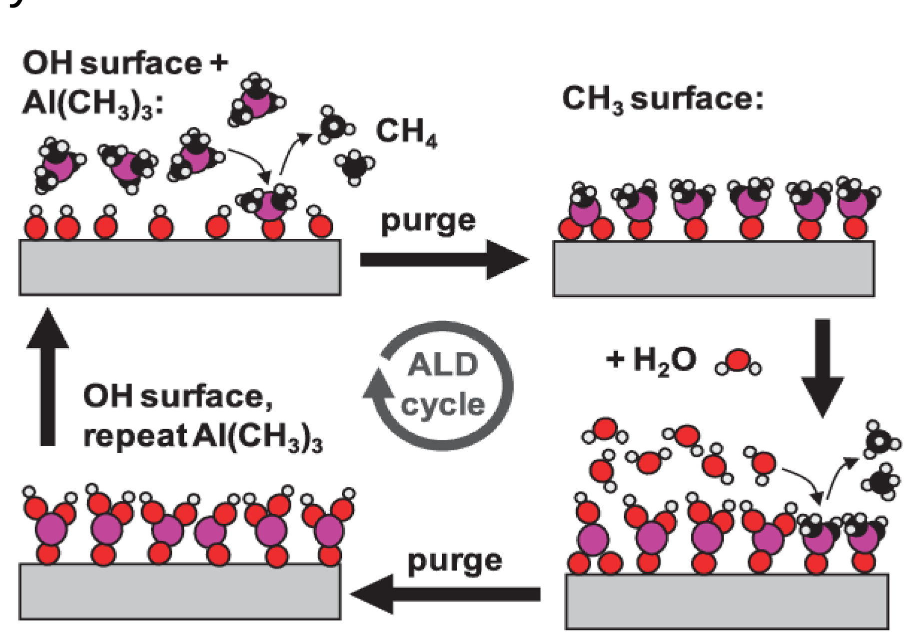
A solar cell absorbs photons to excite electrons, then pass these through a circuit to generate electrical power. This requires a photovoltaic and a layer to separate out excited electrons before they decay.



The diagram above shows the alignment of the valence bands (EV, valence electrons' "ground state") and conduction bands (EC, first excited state) in such a device. Important parameters for the operation of the device are labeled.

Atomic Layer Deposition

In Atomic Layer Deposition (ALD), a substrate is alternately exposed to low-vacuum pressures of two precursors, which react to form a desired surface species in a self-limiting way. Films can be made as thin as one atom



Schematic of one of the most common ALD Processes, for Al_2O_3[1]

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This work

Characterizing the chemical and electronic properties of ALD $MoTe_2/TiO_2$ heterostructures

- Observe alignment of E_V and E_C
- Observe chemical effects at interface

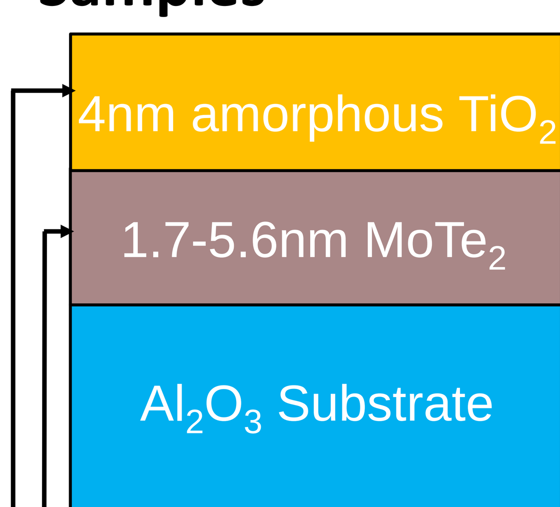
$MoTe_2$

$MoTe_2$ is a promising photovoltaic which very strongly absorbs visible light (films a few nanometers thick appear black). It also has unique properties as a 2D material. A single atomic layer of $MoTe_2$ has a direct E_g = ~1.15 eV, while thicker films have an indirect E_g = ~1.00 eV[2]

TiO_2

TiO_2 is a transparent insulating oxide with E_g = ~3.2 eV used as an e^- collecting layer for $MoTe_2$. Amorphous TiO_2 can be deposited using a well studied and effective ALD process[3]

Samples



- Prepared heterostructures w/ and w/o TiO_2 at a range of $MoTe_2$ thicknesses

Commercially Available single-crystal sapphire substrate

- 15, 25, 50, 80, or 120 cycles of MoO_x deposited via ALD
- Annealed in Te vapor atmosphere at 500°C[2]

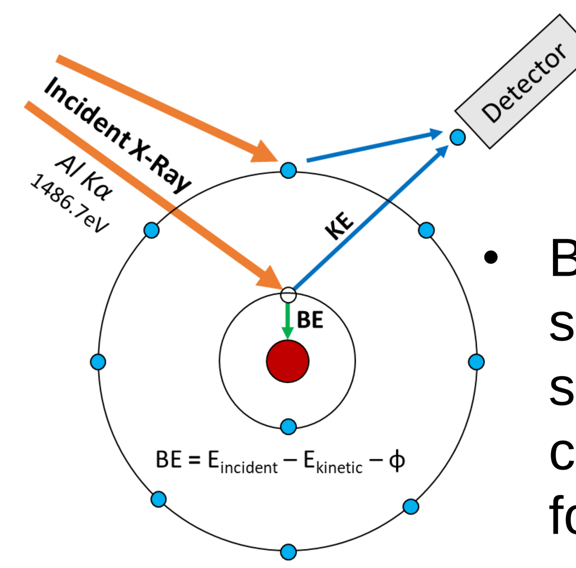
- Deposited 89 ALD cycles of TiO_2
- Constant thickness of 4nm used[4]

Future Work

- Repeat experimentation on more samples to confirm findings
- Knowledge of Energy levels in $MoTe_2/TiO_2$ heterostructures will be used to inform further study of excitons in $MoTe_2$
  - Applying Transient Absorption Spectroscopy, a pump-probe method identifying energy levels and lifetimes of excited states

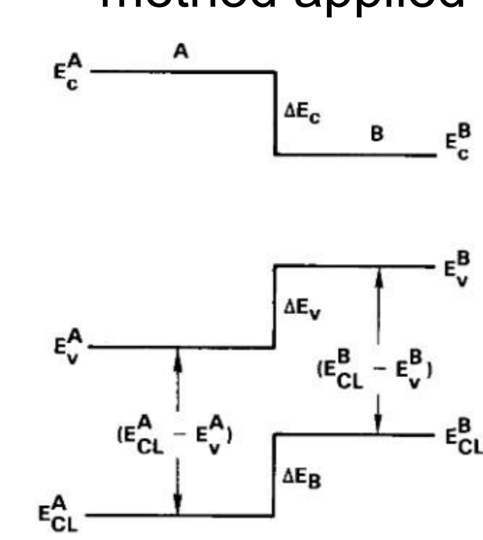
Methods

X-ray Photoelectron Spectroscopy (XPS)



- Measures e^- binding energy (BE)
- BE of core levels sensitive to chemical state of atom, characteristic peaks seen for different species

- Can identify valence band energy relative to sample core levels
- XPS spectra taken of Mo3d, Te3d, Te4d, VB edge, and Ti2p on post deposition samples
- Used to analyze chemical structure, Kraut method applied to find VBO's:

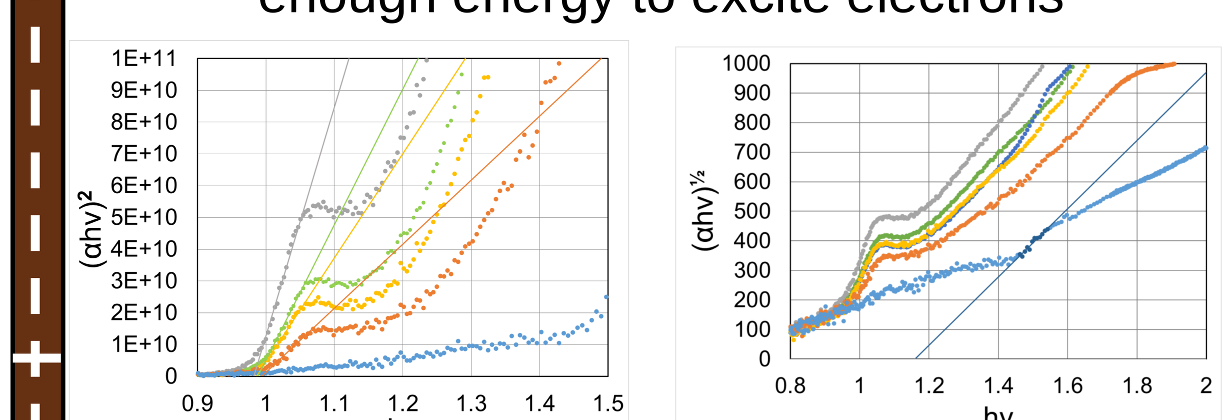


- ΔE_B, $E_{CL}{}^B - E_V{}^B$, and $E_{CL}{}^B - E_V{}^B$ measured directly,
- ΔE_V follows from these
- ΔE_C follows from ΔE_V and E_g

Schematic of energy levels at thin film interface[3]

UV-Visible Spectroscopy

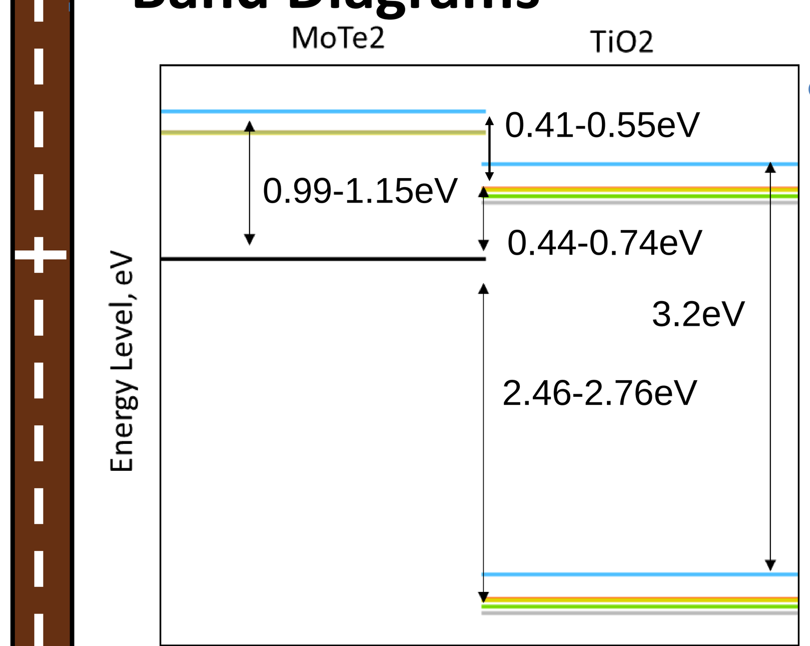
- Determines absorption coefficients
- Used to measure bandgap of $MoTe_2$
  - Absorption drops off at hv < E_g, not enough energy to excite electrons



- Tauc Plots used to identify bandgap: characteristic linear features appear for hv vs different powers of αhv, extrapolating to y=0 gives bandgap
- Direct E_g= 1.15 eV seen for thinnest $MoTe_2$ sample, indirect E_g= 0.99 eV for others
  - Consistent with typical behavior of $MoTe_2$ as a 2D material

Results

Band Diagrams

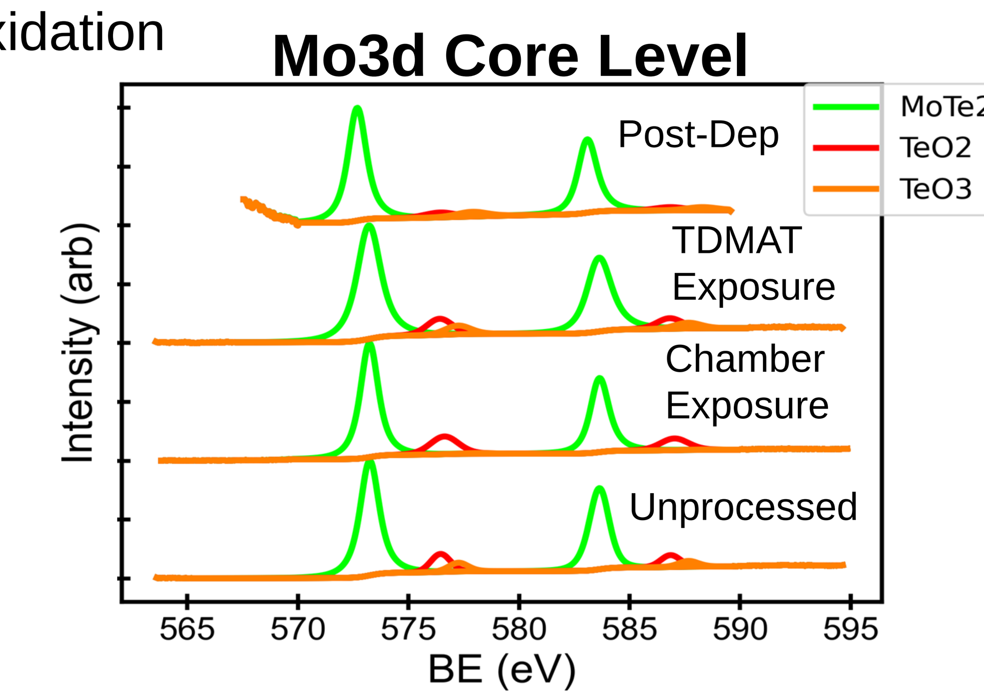


- Combined E_g and VBO data to determine alignment E_C and E_V

- TiO_2 electron selective layer for all thicknesses
- VBO decreases significantly as E_g increases for monolayer $MoTe_2$, 15 cycle

Film Chemistry

- Oxide forms on surface of $MoTe_2$
- Exposure to TiO_2 precursor found to reduce oxidation



- Performed XPS on one $MoTe_2$ sample after exposure to ALD chamber conditions, exposure to precursor, and deposition, oxide seen to reduce after precursor exposure and deposition

References

1. Hyde, G. K., et al. (2011). Atomic layer deposition of titanium dioxide on cellulose acetate for enhanced hemostasis. *Biotechnology Journal*, *6*(2), 213–223. https://doi.org/10.1002/biot.201000342
2. Hynek, D. J. et al. (2020). CM²-Scale Synthesis of $MoTe_2$ Thin Films with Large Grains and Layer Control. *ACS Nano*, *15*(1), 410–418. https://doi.org/10.1021/acsnano.0c08069
3. Waldrop, J. R., Grant, R. W., Kowalczyk, S. P., & Kraut, E. A. (1985). Measurement of semiconductor heterojunction band discontinuities by x-ray photoemission spectroscopy. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, *3*(3), 835–841. https://doi.org/10.1116/1.573326
4. Sivaramalingam, A., Thankaraj Salammal, S., Soosaimanickam, A., Sakthivel, T., Paul David, S., & Sambandam, B. (2021). Role of tio2 in highly efficient solar cells. *Metal, Metal-Oxides and Metal Sulfides for Batteries, Fuel Cells, Solar Cells, Photocatalysis and Health Sensors*, 147–168. https://doi.org/10.1007/978-3-030-63791-0_5

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