First-Principles Study for ALD of MoS_2

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1. Introduction/Background

Atomic layer deposition (ALD)

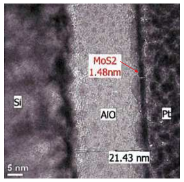
- ALD is a method for thin-film deposition with atomic precision.
- Volatile gas phase precursors allow lower reaction temperatures.
- Precursors are introduced sequentially and are self-limiting.

Molybdenum disulfide (MoS_2)

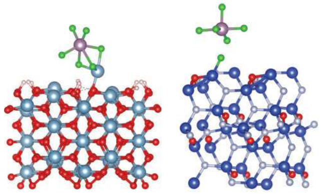
- 2D-MoS_2 is a semiconductor with a direct band gap of 1.8 eV [2].
- Applications in microelectronics, photovoltaics, and batteries [2].
- Deposited via ALD with molybdenum hexafluoride (MoF_6) and hydrogen sulfide (H_2S) precursors [1].

Challenges with ALD of MoS_2

- Difficult to study *in situ*.
- Relatively new and unknown chemistry.
- MoF_6-substrate interactions are unknown.



Above: Transmission electron microscope images of MoS_2 deposited on Al_2O_3 by ALD [1].
Below: Model of a single MoF_6 on hydroxylated Al_2O_3 (left) and Si_2N_2O (right) surfaces.



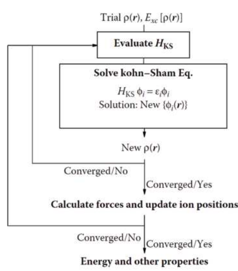
2. Project Goals and Methods

Project Goals

- Understand *role of hydroxyl groups* (OH) on Al_2O_3, Si_2N_2O, and TiO_2 substrates with a *single MoF_6 precursor.*
- Explain *bonding* and *reduction* mechanisms during first MoF_6 half-cycle.

Density functional theory (DFT)

- DFT is a first-principles computational modeling method (based on quantum mechanics rather than classical mechanics or empirical data).
- Calculates ground-state properties of a system.
- Less than 1,000 atoms in DFT modeled systems [3].
- We used the Vienna Ab initio Simulation Package (VASP) to implement DFT [4].



Above: Flow of DFT calculations [3].
Below: Example of Bader charge analysis.

Bader charge analysis

- Bader charge analysis creates Bader volumes from "zero-flux surfaces" around each atom [5].
- Using VASP output, it can determine the valence electron density within each Bader volume.
- Quantifies donation or acceptance of electron density for each atom in a system.

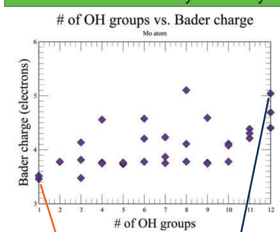
Atom #	Initial valence electrons	Bader charge	Δ valence electrons
Al11	3	0.56	-2.44

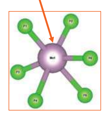
3. Results

Bader charge analysis of MoF_6 on hydroxylated Al_2O_3

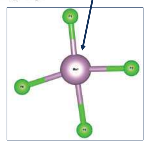
- A single MoF_6 was placed on Al_2O_3 surfaces at varying hydroxyl concentrations.

Observation:
OH groups increase the Mo atom's local electron density indirectly.





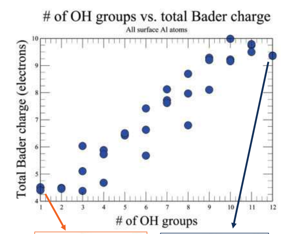
MoF_6 on Al_2O_3 with 1 OH group: minimal electron localization (small Bader charge) corresponds to +6 oxidation state.

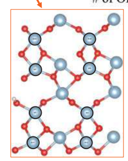


MoF_4, 12 OHs: Large Bader charge corresponds to +4 oxidation state.

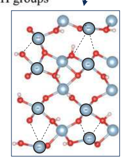
- A change in the oxidation state of Mo from +6 to +5, +4, and +3 is evident by increased local electron density [6].

How?
OH groups break Al-O bonds.





Top-down view of Al_2O_3 surface with 1 OH. Surface Al atoms outlined. MoF_6 omitted for clarity.



Same surface with 12 OH. Dashed lines represent Al-O bonds broken by OH.

- This frees up Al electrons so they can form Al-F bonds.
- Results in separation of F atoms from MoF_6.
- Electrons from broken Mo-F bonds then localize to the Mo atom.

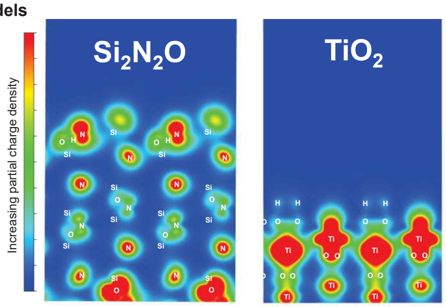
Legend

Mo	F	Al	O	H	N	Si

Si_2N_2O and TiO_2 surface models

Surface Energies	
Substrate	**Surface Energy (eV/Å)**
TiO_2 (100)	0.0237
TiO_2 110)	0.0433
TiO_2 (111)	0.0566
Si_2N_2O (100)	0.1972
Si_2N_2O (110)	0.2815
Si_2N_2O (111)	0.1181

Surface formation energies of non-hydroxylated TiO_2 and Si_2N_2O surfaces cleaved from bulk at various Miller indices: (100), (110), and (111).



Partial charge densities of Si_2N_2O 110 (left) and TiO_2 110 (right) surfaces, fully hydroxylated.

4. Analysis

MoF_6 on hydroxylated Al_2O_3

- Reducing Mo to an oxidation state of +4 may increase reaction favorability.
  - We predict that the oxidation state of Mo in the product, MoS_2, is +4.
  - However, the oxidation state of Mo in MoF_6 is +6.
  - Similar molybdenum sulfide reactions are proposed to be most energetically favorable when Mo does not change oxidation state during the reaction [1].
- Mo-O bonds were not observed on OH groups, so more OH → fewer Mo-O bonds.
  - Mo-O bonds are known to form in experiment [1].
  - Minimizing these bonds could make the film/substrate boundary cleaner.

Si_2N_2O and TiO_2 substrates

- On (110) and (111) Si_2N_2O, hydroxylation increases partial charge density of O atoms.
  - However, on (100) Si_2N_2O, hydroxylation decreases O atom partial charge density.
- Investigation of TiO_2 surfaces' partial charge densities is in progress.
  - Initial results show that hydroxyls affect these partial charge densities as well.

5. Conclusions/Future Work

Conclusions

- Based on our analysis, we predict increased reaction favorability and cleaner film/oxide interfaces by maximizing OH concentration because:
  - OH groups break Al-O bonds on the Al_2O_3 surface and reduce the oxidation state of a deposited Mo atom.
  - OH groups hinder Mo-O interactions.
- Hydroxylation changes Si_2N_2O and TiO_2 surface O chemistry in different ways depending on the surface: (100), (110), or (111).

Future work

- Determine if surface decomposition of Al_2O_3 has any effects on material properties.
- Bader charge analysis of two or more MoF_6 molecules on Al_2O_3.
  - Preliminary results indicate that surface chemistry may vary with more MoF_6.
- Add H_2S to various MoF_x species and calculate reaction energy.
  - This will provide insight on the relation between oxidation states and reaction energy.
- Simulate ALD of MoS_2 on Si_2N_2O and TiO_2 surfaces.
  - Investigate the mechanism by which hydroxylation increases O partial charge on some structures but decreases it on others.

6. Acknowledgements

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