DFT Investigations of Early Stages of Formation of Aluminium Oxide at Al Surface

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Abstract: We use the DFT and Verlet molecular dynamics to investigate the formation of aluminium oxide at the surface of Al. The model corresponds to the early stage formation of oxide; we monitor the evolution at temperatures close to RT for one or two oxygen atoms placed on top of the Al surface. The quantitative stability of the system is evaluated by calculating the free energy of the system as a function of the number of oxygen atoms and/or the type of Al surface. Out of this analysis we pin down the parameters that can favor the formation of oxide as a function of surface type as well as function of temperature.

Methods

The supercells have a size of 6×6 and respectively 8×8 Al atoms in the XOY plane and include 8 layers of atoms (a total of 288 Al atoms, and respectively 512 Al atoms). The cell length along the OZ axis was set to L Z = 40 Å, to avoid the interference of the electric charge from one cell to another. The bulk parameter for Al has a value of 4,045 Å (i.e. the experimental value).

For each system we did 1500 timesteps of Verlet molecular dynamics at 300 K with a timestep length of 4.5 fs.

Expected data

Quantum mechanical

- The hybridization of Al-O orbitals at interface
- Role of geometry: e.g. O on Al(111) may hybridize different compared to O on Al(100)
- Role of O coverage:

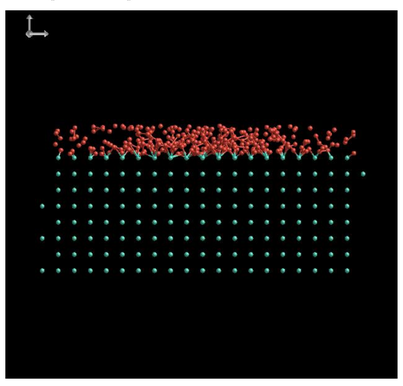
  (sub-monolayer → monolayer→ multilayer)
- The formation energy of Al – bulk at Al2O3 interface

Thermodynamics

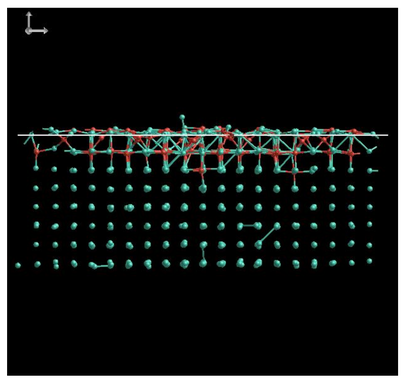
- Entropy, other relevant parameters to predict the Al2O3 formation on Al bulk – come from molecular dynamics
- Predict the role of temperature in Al-Al2O3 stability
- Vibrational density of states → entropy → free energy

Results and discussions

Surface formation Al(100) + O

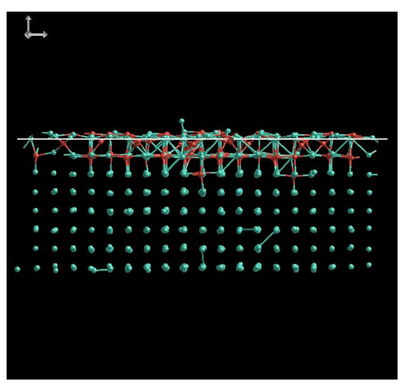


Initial system (Al100 + O)

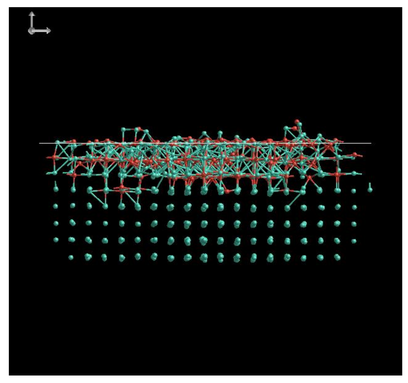


System after relaxation

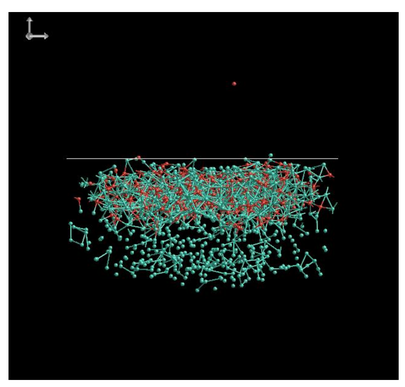
Al(100) + O role of O concentration



Al(100) + O (100%)

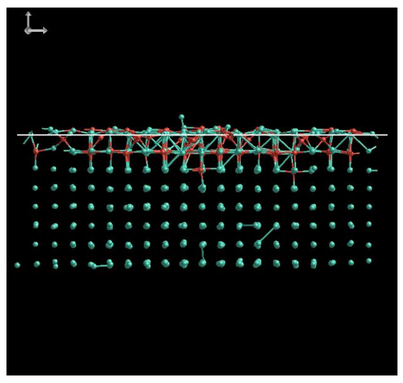


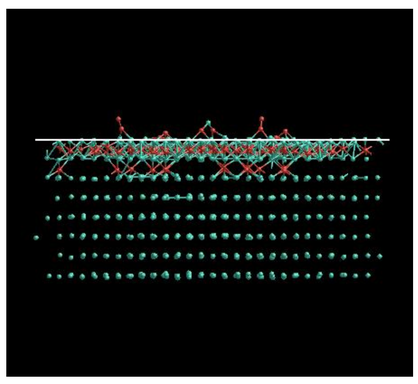
Al(100) + O (200%)



Al(100) + O (300%)

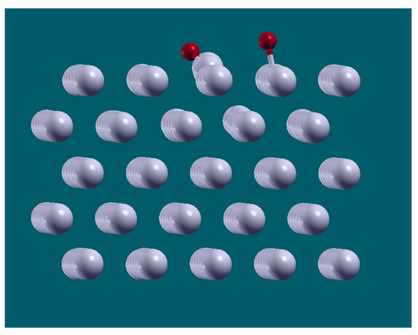
Surface formation Al(100) vs Al(111_

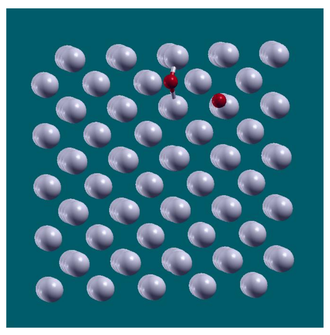


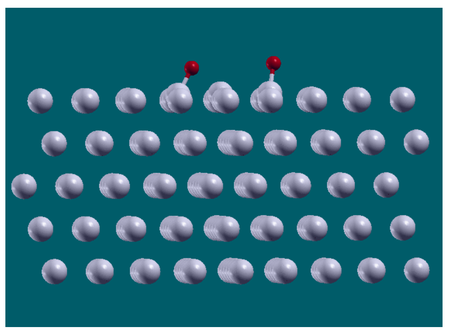


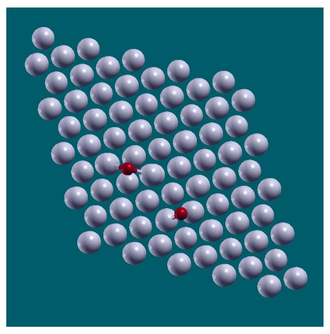
Al(100) + O

Al(111) +O

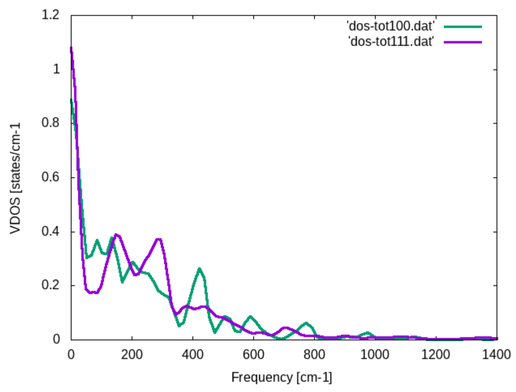




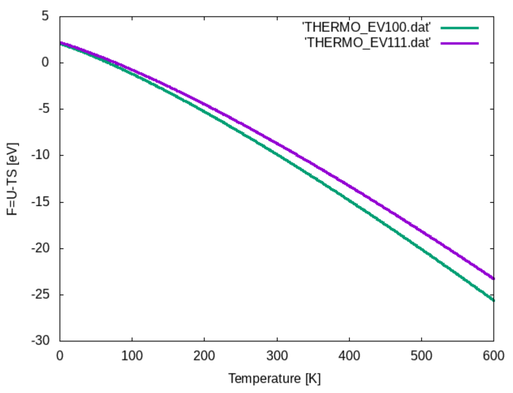




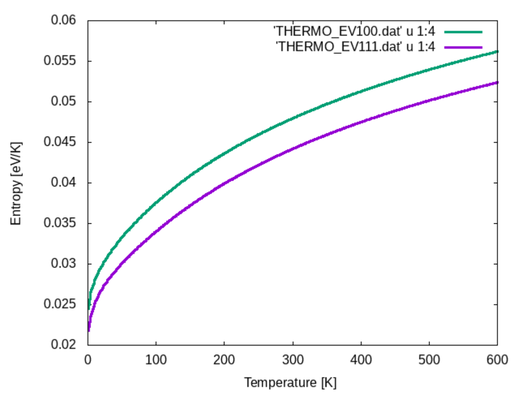
Thermodynamics



Vibrational density of states



Free energy



Entropy

Conclusions

- It can be seen that for Al111 the structure of the Al surface is more affected
- For Al111 the O atoms penetrate the surface, while for Al100 we do not see this to happen
- We need to get quantitative/numeric information on this effect on surface reconstruction
- The differences in the Entropy values indicate that the Al oxides seem to form easier of Al111 surface that on Al100

Acknowledgement

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