Microtutorial: Surface Phase Diagram

FHI-aims team

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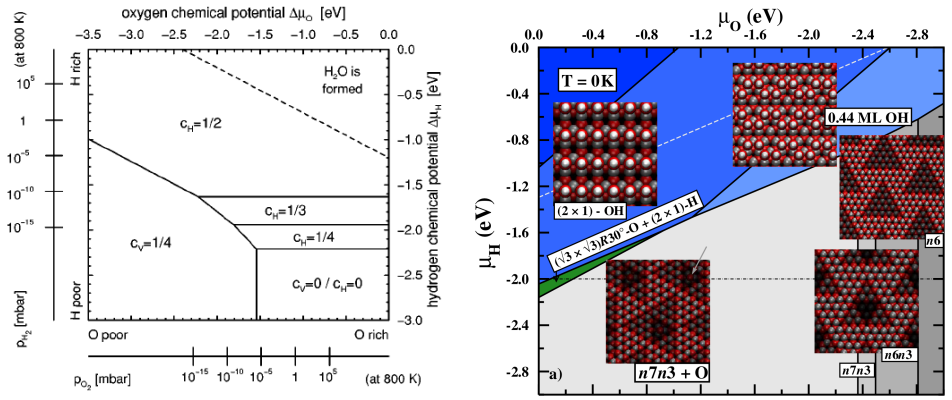


(a) ZnO (000-1) surface phase diagram from B. Meyer, PRB 69, -45416 (2004))

(b) ZnO (0001) surface phase diagram from Valtiner, Todorova, Grundmeier, Neugebauer, PRL 103, 065502 (2009)

Figure 1: Theoretical surface phase diagrams for ZnO (000-1)

The framework and tools to calculate a surface face diagram with FHI-aims are explained along the lines of the 2001 paper of K. Reuter and M. Scheffler: "Composition, structure, and stability of RuO2(110) as a function of oxygen pressure", Phys. Rev. B 65, 035406 (2001). As an example we will use the (000-1) O-terminated surface of ZnO, a very interesting system due to its many applications (LED, solar cell, catalysis,...). There is need for theoretical predictions due to the notorious difficulties to investigate ZnO with experimental techniques that rely on the conductivity of the sample, e.g., STM. We will try to reproduce the results of B. Meyer (B. Meyer, PRB 69, 45416 (2004)) (figure 1a) with very light computational settings. A more sophisticated surface phase diagram concidering more complicated reconstructions is depicted in figure 1b. The calculations for the final surface phase diagram should take altogether 90 Minutes on an 8-core machine.

Our case study: ZnO (0001) / (000-1)

Here just a few facts and figures about ZnO:

- Wurzite structure is the stable phase under ambient conditions

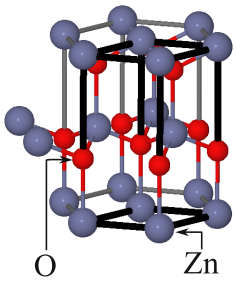
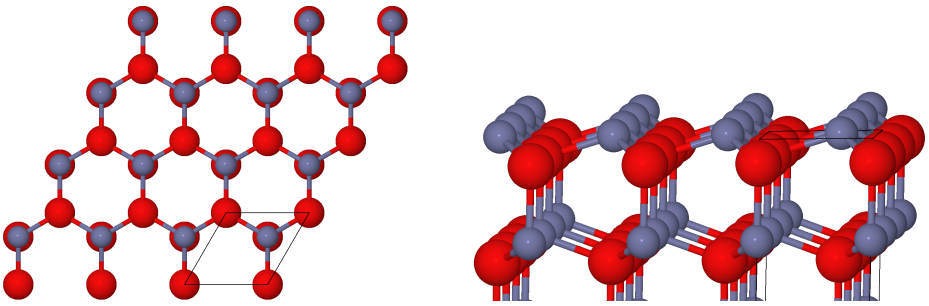


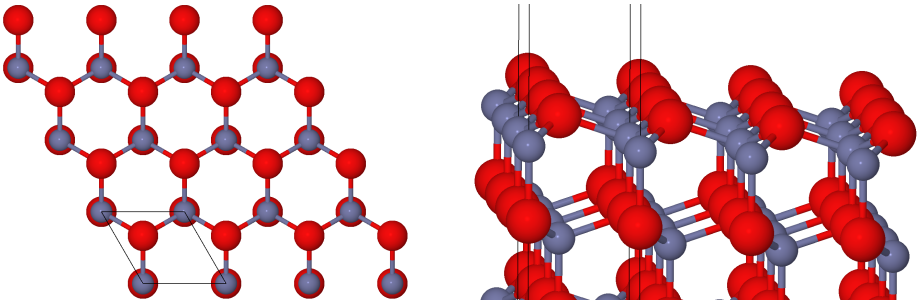
Figure 2: ZnO in its bulk wurzite structure

- experiment:a=3.250, c=5.207, u=0.38
- DFT-PBE: a=3.289, c=5.258, u=0.381
- Band gap: 3.3eV (Theory DFT-PBE: 0.76eV)
- Most studied surfaces: polar (0001), (000-1) and non-polar (10-10)
- Polar surfaces are stabilized through reconstructions and charge-redistribution



(a) ZnO (0001) surface - top view (b) ZnO (0001) surface - side view

Figure 3: ZnO (0001)



(a) ZnO (0001) surface - top view (b) ZnO (0001) surface - side view

Figure 4: ZnO (000-1)

Ab initio thermodynamics

We will start with a few formulas to find out what we have to calculate.

The Gibbs free energy

$$G(T,p) = E + p \cdot V + T \cdot S \tag{1}$$

- Experiments are performed under ultra-high vacuum (UHV) conditions $\Rightarrow p \cdot V = 0$.
- DFT ground state total energies are at $T = 0K$ and $p = 0atm \Rightarrow G(T,p) = G(T = 0K, p = 0atm) = E_{tot}$.
- Zero point corrections and vibrational entropy are neglected

The surface free energy

$$\Delta G_{ZnO}(T,p) = g^{bulk}_{ZnO}(T,p) - \frac{1}{2} g_{Zn}(T,p) - \frac{1}{2} g_{O_2}(T,p) \tag{2}$$

$$\Delta G_{ZnO}(T,p) \begin{cases} < 0 \ldots ZnO \text{ builds} \\ = 0 \ldots ZnO,\ Zn \text{ and } O_2 \text{ inequilibrium} \\ > 0 \ldots Zn \text{ and } O_2 \text{ form} \end{cases} \tag{3}$$

The Limits of the chemical potentials

From the definition of the Gibbs free energy:

$$\max(\mu_{Zn}) = \frac{1}{2} E^{bulk}_{Zn} \qquad \max(\mu_O) = \frac{1}{2} E_{O_2} \qquad \max(\mu_H) = \frac{1}{2} E_{H_2} \tag{4}$$

From the equlibrium condition $E^{bulk}_{ZnO} = \mu_{Zn} + \mu_O$:

$$\frac{1}{2} E^{bulk}_{ZnO} - \frac{1}{2} E^{bulk}_{Zn} \leq \mu_O \leq \frac{1}{2} E_{O_2} \qquad \mu_{Zn} = \frac{1}{2} E^{bulk}_{ZnO} - \mu_O \tag{5}$$

For convenience one uses:

$$\Delta\mu_{Zn} = mu_{Zn} - \frac{1}{2} E^{bulk}_{Zn}, \qquad \Delta\mu_O = \mu_O - \frac{1}{2} E_{O_2}, \qquad \Delta\mu_H = \mu_H - \frac{1}{2} E_{H_2} \tag{6}$$

What do we need?

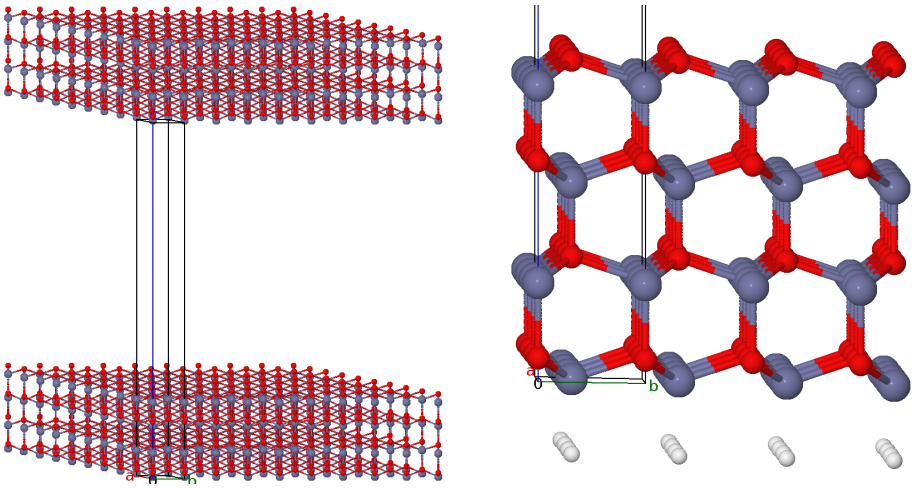
Total energies of bulk phases and molecules

- Bulk wurzite ZnO E_{ZnO}^{bulk}
- Bulk Zn E_{Zn}^{bulk}
- O_2 molecule E_{O_2}
- H_2 molecule E_{H_2}

You wild find the `geomtry.in` and `control.in` files the folder "files". You can try to generate everything by yourself, of course. The geometry.in and control.in files can be used to calculate the total energies (all light settings) on a desktop PC.

Approach to model surfaces

To calculate surface properties the slab approach is used. As for the previous calculations for bulk properties (ZnO, Zn) periodic boundary conditions in all three directions of space are used. In one direction the surface (here: ZnO 000-1) is introduced by putting a considerable amount of empty space (vacuum) between our cell and the next periodic replica in this direction. The unit cell is elongated in the direction containing the vacuum. The use of the local atom centred basis in aims has the advantage that vacuum costs almost no additional computational effort - use plenty of vacuum. Due to the polar nature of our system we have to passivate the dangling



(a) Model cell and first periodic replicant (b) slab passivated with hydrogen (white)

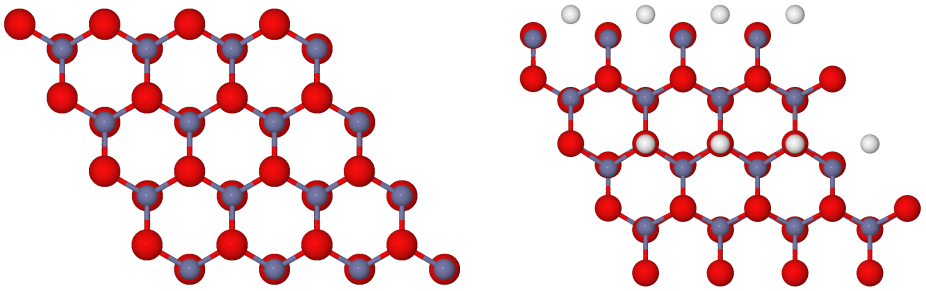
Figure 5: Modelling the surface

bonds on the back of our slab with hydrogen (pseudo-hydrogen). The hydrogens are placed at those positions that would normally be taken by the next layer. In experiments the substrate

or sample holder would do this job. We will see later what is the effect of passivation/no passivation on our phase diagram. The slab has to be thick enough to ensue bulk conditions at its center. We will also investigate the influence the thickness of the slab. Only the top most 2 layers of the slabs will be relaxed, the atom positions optimized to minimize the forces on the atoms. For productions calculations about 8 double layers should be used.

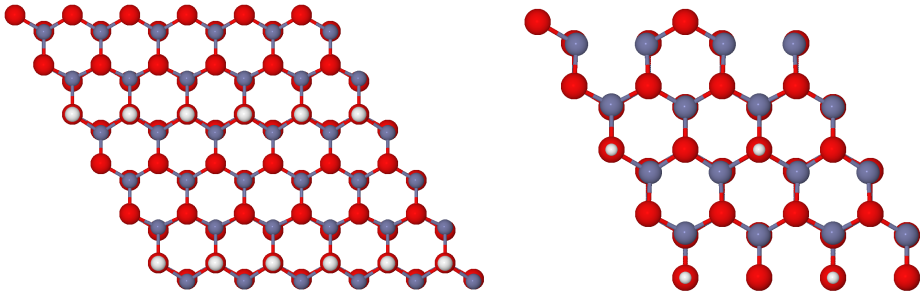
Candidate structures

Now we need to find structures that might appear in our phase diagram. We already have a good idea about those structures from previous works. The `geometry.in` file are created with a python script: `make_slab.py` in the folder "files". See the head of the script for the input parameters. In the folder you will also find control.in and geometry.in for structures with 3 layers (not double layers) of ZnO, 4 layers of ZnO and 3 layers of ZnO passivated with hydrogen.



(a) Clean surface (b) 1/2 coverage of H

Figure 6: Concidered structures



(a) 1/3 coverage of H (b) 1/4 coverage of H

Figure 7: Concidered structures

From chemical potential to pressure

The chemical potentials of hydrogen $\Delta\mu_H(T,p)$ and oxygen $\Delta\mu_O(T,p)$ have to be to related to a given temperature T and pressure p. We use the ideal gas law:

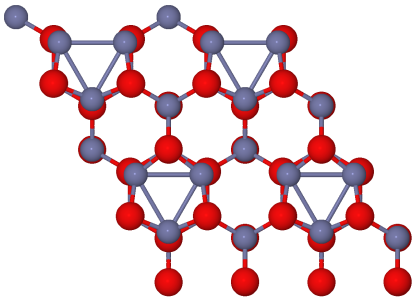


Figure 8: 1/4 of surface O missing

$$\mu(T,p) = \mu(T,p^0) + \frac{1}{2}kT\ln\left(\frac{p}{p^0}\right) \tag{7}$$

$$\mu_H(0K,p^0) = \frac{1}{2}E_{O_2} = 0 \tag{8}$$

$$\mu_O(0K,p^0) = \frac{1}{2}E_{O2} = 0 \tag{9}$$

With respect to this zero the chemical potential of hydrogen/oxygen is given by:

$$\mu(T,p^0) = \frac{1}{2}\Delta G_{H_2}(T,p^0) \tag{10}$$

$$= \frac{1}{2}\left(H_{H_2}(T,p^0) - H_{H_2}(0K,p^0)\right) - \frac{1}{2}TS_{H_2}(T,p^0) \tag{11}$$

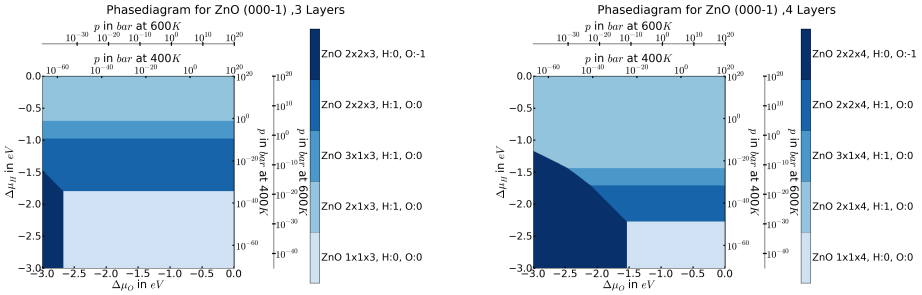
For $p_0 = 0.1MPa$ the missing values ($H_{H_2}(T,p^0)$, $H_{H_2}(0K,p^0)$, S_{H_2} are tabulated in thermochemical databases (http://kinetics.nist.gov/janaf/).

The surface phase diagram for ZnO (000-1)

After calculating the total energies for our candidate structure we can use the python script `phase_diagram_2d.py` from the "files" folder to plot our results. The script already contains the energies for all the structure. The 3 different cases (3 layer slab, 4 layer slab and 3 layer slab passivated with hydrogen) are selectable by invoking the script with the arguments 3L, 4L or 3L+H, respectively.

The calculations for the 3 layer slab, as well as for the 4 layer slab, are not converged with respect to slab size. About 16 layer (8 double layers) are necessary for appropriate convergence. The passivate slab calculation already look sufficiently converged with respect to slab thickness. One can observe the absence of the 1/3 hydrogen covered surface from the surface phase diagram as result of the passivation of the bottom of the slab.

Have fun!



(a) ZnO (000-1) surface phase diagram for 3 layer slabs

(b) ZnO (000-1) surface phase diagram for 4 layer slabsn

Figure 9: Surface phase diagram.

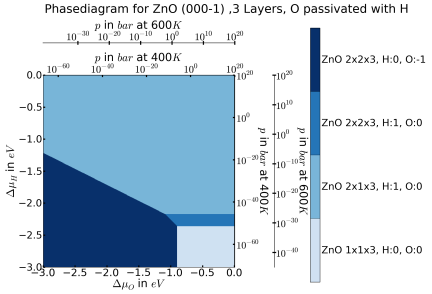


Figure 10: ZnO (000-1) surface phase diagram for 3 layer slabs passivated with hydrogen.