Self-limited growth of a thin oxide layer on Rh(111): A DFT study

L. Köhler, G. Kresse,[1] J. Gustafson, E. Lundgren,[2] and P. Varga[3]
[1]Institut für Materialphysik and Center for Computational
Materials Science, Universität Wien, A-1090 Wien, Austria
Lukas.Koehler@univie.ac.at
[2]Department of Synchrotron Radiation Research,
Lund University, Box 118, S-221 00, Sweden
[3]Institut für Allgemeine Physik, Technische Universität Wien, A-1040 Wien, Austria

Oxidation is often associated with corrosion, but under the right conditions it can lead to oxide layers which can be applied e.g. as protective layers against corrosion, as insulating layers in microelectronic devices and as catalytic devices[1, 2]. For late transition metals and noble metals (e.g. Pd and Ag), it is now understood that the oxidation proceeds through ultra-thin oxide layers, which are thermodynamically stable at intermediate oxygen potentials and can exhibit astonishing complexity[3–6]. It is still unclear whether the same holds for transition metals and to this end the Rh (111) surface was studied extensively experimentally [7]. To supplement these experimental studies, we performed density functional calculations with the Vienna Ab Initio Simulation Package (VASP) [8] using plane waves and the PAW method [9] as well as generalized gradient approximations [10].

The experimental studies show a Moiré like pattern in STM, indicative of a (8×8) oxide layer on a (9×9) supercell of the Rh(111) substrate. This phase is formed at intermediate oxygen pressures, whereas thick corundum-like Rh_2O_3 is only formed at significantly higher pressures and temperatures. The theoretical calculations indicate that the Moiré phase can be rationalised by an ultrathin O-Rh-O trilayer surface oxide. Contrary to the experimental observation, the bulk Rh_2O_3 oxide is however thermodynamically more stable than ultra-thin layers. This discrepency can be understood by the surface phase diagram shown in Fig. 1(a). It indicates that a single oxygen trilayer on Rh(111) is in fact only metastable, as the trilayer forms only under conditions, where bulk Rh_2O_3 is already stable (to the right of the thick grey line in Fig. 1(a)). Hence the trilayer is only *kinetically* stabilised, contrary to the situation on Pd(111) where a Pd_5O_4 ad-layer is *thermodynamically* stable for intermediate oxygen potentials [4]. An important hint to the reason of the kinetic stability of the O-Rh-O trilayer is given by the results for the three and four layer thick oxides. Four (three) layer oxides have a lower stability than the single trilayer for oxygen potentials $\mu_O < -0.99$ eV ($\mu_O < -0.78$ eV) corresponding to 10 mbar (1 bar) at 800 K. The formation of the bulk oxide must however proceed through thicker oxide layers that present a kinetic barrier for the formation of the bulk oxide at too low chemical potentials.

The most favorable structures for 2, 3 and 4 oxygen layers are depicted in Fig. 1(b). In contrast to oxygen atoms on the clean metal, the oxygen atoms at the oxide/metal interface are located preferentially on top of the surface Rh atoms (shifted slightly towards the bridge site). Remarkably, the trilayer termination remains favorable even for thicker oxides. For three oxygen layers (3L) the topmost surface layer contains three Rh atoms, and a fourth single Rh atom is located in the second oxide layer. For four oxygen layers (4L), the trilayer is found at both sides of the oxide, and a single Rh atom interlinks the two O-Rh-O layers.

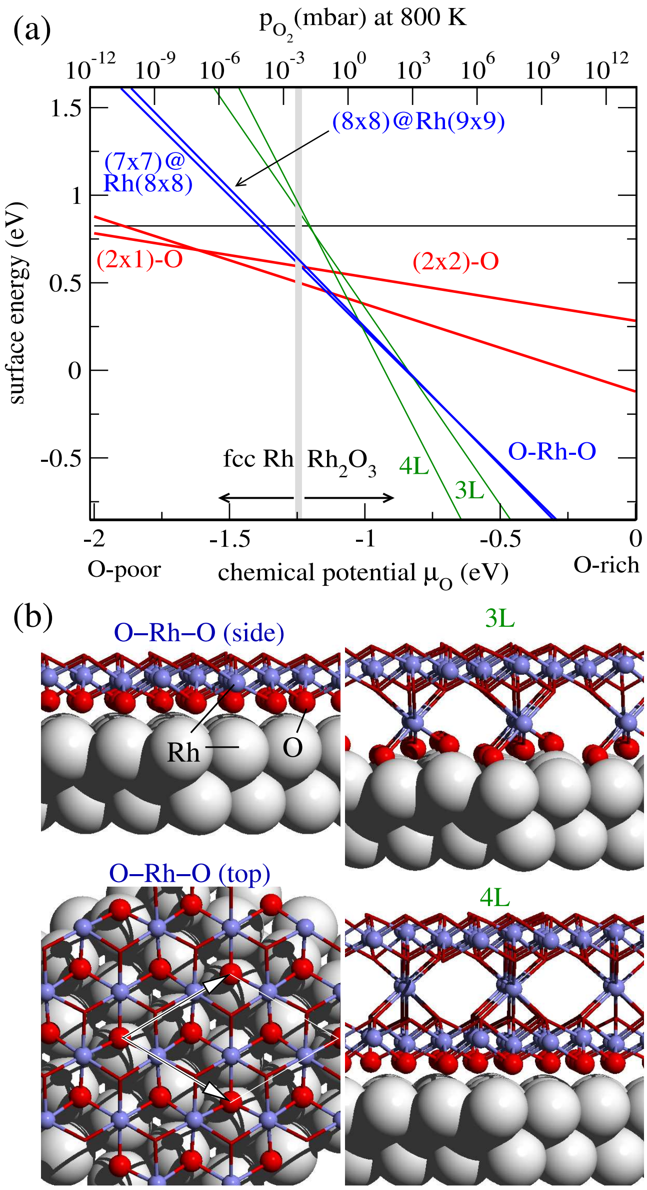

FIG. 1: (a) Calculated phase diagram and (b) lowest energy structures for oxides with 2 (O-Rh-O), 3 and 4 layers (L) of oxygen on a Rh(111)(2×2) supercell. In the phase diagram results for large supercell calculations (Rh(8×8) and Rh(9×9)) limited to two oxygen layers are included. Oxygen atoms are not shown as balls but bonds only except for the bottom oxygen layer. The chemical potential can be related to the temperature and the oxygen partial pressure p through the ideal gas equation $\mu_O(T,p) = \mu_O(T,p_O^0) + 1/2 k_B T \ln(p/p^0)$ [11].

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