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# First-principles study of the polar O-terminated ZnO surface in thermodynamic equilibrium with oxygen and hydrogen

B. Meyer
*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany*
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Using density-functional theory in combination with a thermodynamic formalism we calculate the relative stability of various structural models of the polar O-terminated (0001)-O surface of ZnO. Model surfaces with different concentrations of oxygen vacancies and hydrogen adatoms are considered. Assuming that the surfaces are in thermodynamic equilibrium with an $O_2$ and $H_2$ gas phase we determine a phase diagram of the lowest-energy surface structures. For a wide range of temperatures and pressures we find that hydrogen will be adsorbed at the surface, preferentially with a coverage of 1/2 monolayer. At high temperatures and low pressures the hydrogen can be removed and a structure with 1/4 of the surface oxygen atoms missing becomes the most stable one. The clean, defect-free surface can only exist in an oxygen-rich environment with a very low hydrogen partial pressure. However, since we find that the dissociative adsorption of molecular hydrogen and water (if also the Zn-terminated surface is present) is energetically very preferable, it is very unlikely that a clean, defect-free (0001)-O surface can be observed in experiment.

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