Predicting Surface Phase Diagrams in Realistic Atmospheres

Phase diagram of Si(100) in H_2 gas phase including anharmonic effect

***Y. Zhou, M. Scheffler, and L. M. Ghiringhelli**, Fritz Haber Institute of the Max Planck Society*

In Short

- Hydrogenated silicon surface is often used as prototypical semiconductor adsorption system.
- We apply a new methodology to the reliable *ab initio* calculation of the temperature-pressure phase diagram of Si(100) surface in contact with a H_2 atmosphere at realistic $T - p$ conditions.
- We optimize our massively parallel code for performing Replica-Exchange Grand-Canonical sampling, `FHI-panda`.

The processes that occur at surfaces play a critical role in the manufacture and performance of advanced materials. As prototypical example, the hydrogen adsorption on and desorption from Si surfaces are of great technological relevance for, e.g., the etching and passivation of Si surfaces or the growth of Si crystals. Furthermore, hydrogen on silicon is a promising model system for studying general aspects of chemical reactions on covalent surfaces. Despite extensive experimental and theoretical investigation, the nature of the reconstruction of the Si(100) surface in the hydrogen atmosphere, for instance as depicted in Fig. 1, is still subject to debate.

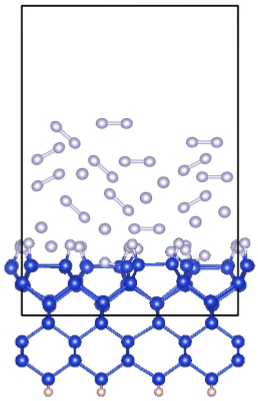

***Figure 1:** The schematic representation of the Si(100) surface in contact with H_2 gas phase characterized by defined temperature T and pressure p_{H_2}. Pink atoms are the hydrogen atoms terminating the dangling bond of Si atoms in the bottom layer. Blue atoms are the Si atoms in the slab. Grey atoms are the hydrogen atoms including physicall/chemically adsorbed on Si surface and floating like gas in the vacuum.*

Phase diagrams of surfaces in a reactive atmosphere provide detailed information on surface composition and structure at realistic conditions (e.g., temperature and pressure of the reactive gas). This is a prerequisite to understand and control electronic properties and function of surfaces.

For decades, *ab initio* atomistic thermodynamics (aiAT) [1,2] has been very successful in predicting phase diagrams for surfaces at realistic T, p conditions. However, aiAT phase diagrams reply on a pre-determined list of possible structures (local minima of the potential-energy surface), compiled by means of informed guess by researchers. In contrast, an unbiased sampling of the configurational and compositional space could reveal unexpected (metastable) structures. Furthermore, aiAT usually describes the relative free energy neglecting vibrational contributions of the substrate and adsorbate or at most approximation them at the harmonic or quasi-harmonic level. These approximation do not always yield accurate phase diagram, especially at high temperature and/or coverage. If the unbiased configurational sampling is rigorously conducted in the grand-canonical ensemble, all vibrational contributions can be accounted for accurately.

Recently, we have developed a Replica-Exchange (RE) Grand-Canonical (GC) approach [3] implemented within the python package `FHI-panda` [4]. The REGC method enables the calculation of complete temperature-pressure phase diagrams including anharmonic effect of surfaces or clusters in contact with reactive gas atmospheres. The RE and GC steps of the algorithm are formulated in the Metropolis Monte Carlo framework, while the canonical sampling of configurations (diffusion) is supported via *ab initio* molecular dynamics. In the case of surface in contact with a gas phase reservoir, the gas molecules can physi-/chemisorb on the surface, while adsorbed molecules or single atoms can desorb from the surface to the gas phase. At thermodynamic equilibrium, the number of desorbed molecules/atoms balances the adsorbed one, so that on average a constant number of molecules/atoms is present on the surface. We specifically target thermodynamically open systems in the GC ensemble, aiming at describing (nano)structured surfaces in a reactive atmosphere at realistic T, p_{H_2} conditions, so that the surfaces can exchange particles with the gas reservoir. The idea of RE is to allow for an efficient sampling of the configurational space by shuttling configurations from regions of low T or high chemical potential μ_{H_2} to regions of high T or low

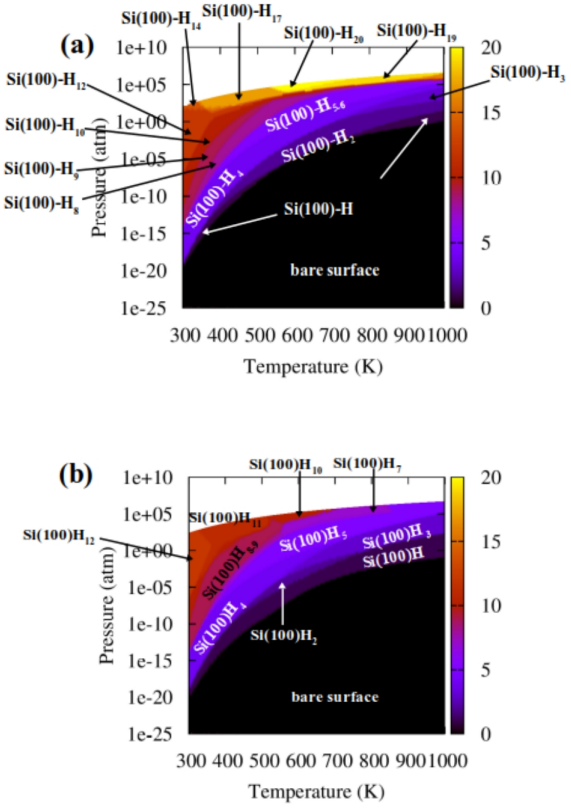

Figure 2: *(a) Phase diagram of Si(100)-(3×3) surface in a H_2 gas phase. (b) Phase diagram of chemically adsorbed hydrogen on Si(100)-(3×3) surface in a H_2 gas phase.*

μ_{H_2}.

After the unbiased sampling by REGCMD (the only limitation being having to deal with a fixed cell volume and shape throughout the whole sampling), equilibrium samples are obtained from each of the sampled thermodynamic states within the grand-canonical ensemble. For each sample, a wide range of observable values can be collected, starting from the potential energy, the number of particles, and going to properties that are not related to the sampling rules, for instance the HOMO-LUMO gap or the Si-H radial distribution function. In order to calculate the phase diagram, the partition function (and therefore the free energy) of the phases defined by the number of particles is evaluated at each temperature (T) and chemical potential (μ_{H_2}). For each (μ_{H_2}, T) state, the most stable phase is the one with lowest free energy. Notice that p_{H_2} is determined by T and μ_{H_2}. To the purpose, a Boltzmann reweighting of the statistics of the observables collected at each sampled (μ_{H_2}, T) state is performed. For this, we employ the multistate Bennett acceptance ratio (MBAR) [5] approach, as implemented in the `pymbar` code [6]. Then, it is feasible to calculate free energies and expectation averages of observables at any thermodynamic state (T, μ_{H_2}).

As shown in Fig. 2, the procedure has been already applied, as preliminary investigation of the system, to calculate the phase diagram of Si(100)-(3×3) surface in contact with a H_2 gas phase. The reconstruction of Si(100) surface varies with different lateral periodicities such as p(2×1), p(2×2) and c(4×2), which indicates that the choice of supercell size and shape has an effect on the reconstruction patterns. Therefore, larger supercell (4×4, 6×6) of Si(100) surface need to be taken into account, so that the size effect can be taken into account and carefully assessed. The investigation of these larger supercells is the aim of the current proposal.

Finally, we like to give an outlook. The proposed application of our REGC algorithm to the Si(100) surface in a reactive H_2 atmosphere is a first step. In the next stage, more than one species of adsorbed particles will be taken into consideration (controlled by more than one independent chemical potentials), so that one can treat more challenging and technologically relevant problems, such as the thermodynamics of adsorbed polymetallic nano-particles.

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`http://www.fhi-berlin.mpg.de/`

More Information

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