Thermodynamics of vapor-surface equilibria in *ab initio* modelling of semiconductor growth processes

Paweł Kempisty[1,2], **Paweł Strąk**[1], **Konrad Sakowski**[1,2,3], **Yoshihiro Kangawa**[2,4] **and Stanisław Krukowski**[1]

[1]*Institute of High Pressure Physics PAS, Sokolowska 29/37, 01-142 Warsaw, Poland*
[2]*Research Institute for Applied Mechanics, Kyushu University, Fukuoka 816-8580, Japan*
[3]*Faculty of Mathematics, Informatics and Mechanics, University of Warsaw, Banacha 2, 02-097 Warsaw, Poland*
[4]*CIRFE, IMaSS, Nagoya University, Nagoya 464-8601, Japan*

Thermodynamic foundations of *ab initio* modelling of vapor-solid and vapor-surface equilibrium are presented. It is demonstrated that the chemical potential change during vaporization process could be divided into enthalpy and entropy part. These two contribution have to be calculated using different paths. The entropy path avoids singular point at zero Kelvin temperature overcoming solid-vapor transition at standard state conditions (T=298.15 K, p=1 bar), where standard evaporation entropy is defined. The enthalpy path includes *ab initio* term at T=0 K. Then, to examine the system state at a given temperature, thermal changes have to be calculated from these reference points. The chemical potential difference contribution of the following terms: vaporization enthalpy, vaporization entropy, the temperature-entropy related change, the thermal enthalpy change and mechanical pressure is obtained. The latter term is negligibly small for the pressure typical for epitaxy. The thermal enthalpy change is two orders of magnitude smaller than the three first terms, which have to be taken into account explicitly. The configurational vaporization entropy change is derived for adsorption processes. The same formulation is derived for vapor-surface equilibrium using various vapors at GaN(0001) and AlN(0001) surfaces as the useful examples. The critical factor is dependence of enthalpy of evaporation (desorption energy) on the pinning of Fermi level bringing drastic change of the adsorption energy value. In summary, a complete and exact formulation of vapor-solid and vapor-surface equilibria is derived and presented [1].

The aforementioned studies have used SIESTA software for the calculations based on Density Functional Theory (DFT) [2]. To investigate the thermal properties of surfaces the first-principles phonon calculations in harmonic approximation were carried out. Both total energies of systems and phonon dispersion relations were determined using DFT within general gradient approximation (GGA) with PBE-WC parametrization of exchange-correlation (XC) functional.

[1] P. Kempisty, P. Strak, K. Sakowski, Y. Kangawa, S. Krukowski *Phys. Chem. Chem. Phys.* **19**, 29676–29684 (2017).
[2] SIESTA web page: *http://departments.icmab.es/leem/siesta*