Intrasurface Electron Transitions Change of Adsorption Energy at Surfaces of Semiconductors - Mechanism and Consequences to Growth and Doping of Crystals and Layers

Stanisław Krukowski, Pawel Kempisty, Pawel Strąk, Konrad Sakowski
Institute of High Pressure Physics, Polish Academy of Sciences, Sokołowska 29/37, 01-142 Warsaw, Poland

Results of *ab initio* simulations indicate that proper description of semiconductor crystal growth needs considerable modification of the standard Burton, Carbera Frank (BCF) model. These changes include electronic degrees of freedom, not present in the classic formulation. In particular they involve change of pinning of Fermi level at the surface which is determined using extended electron counting rule (ECR) that may be applied to the case of the species adsorbed at the surface. In this work the simulations of adsorption of a large number of molecular and atomic species at various semiconductor surfaces are summarized and discussed. It is shown that during adsorption of ammonia, hydrogen, nitrogen and silicon at GaN(0001), GaN(000$\underline{1}$), AlN(0001) and SiC(0001) surfaces, an additional contribution from intrasurface electron transition changes their adsorption energy. The model of such contribution is presented and critically discussed. According to the new model the adsorption energy is changed by several electronvolts, at change of the pinning of the Fermi level between different surface states. Such change may involve not only the variation of the energy of the adsorbate but also it may lead to different conformation and the location at the surface. From the model it follows that for Fermi level pinned at the surface, the adsorption energy is not dependent on the doping in the bulk but for Fermi level it is. The thermodynamics of the surface-vapor equilibrium is presented with critical analysis regarding the presented formalism based on chemical potential identification of most stable structure of the surface. It is augmented by Langmuir type picture of vapor-surface equilibrium at various level of chemical potential, i.e. vapor temperatures and partial pressures. The results indicate that most of the cases of the growth of semiconductors occurs in the condition for which the Fermi level is not pinned at the surface. Therefore the adsorption energy depends on the Fermi level position in the bulk, i.e. on doping of the bulk semiconductors. Such dependence of the adsorption energy provides basic explanation of the step motion dynamics, incorporation of dopants during growth and surfactant effects. The consequences of these findings on the growth and doping of semiconductor crystals and layers are discussed.