# Ab initio thermodynamics and engineering of point defects in nanometric near-surface areas of III-nitride semiconductors

One of the key skills required for the development of semiconductor technologies is the ability to produce bulk crystals and layers of perfect structural quality and with specific electrical and optical properties. Unfortunately, like nothing is perfect in the real world, some defects are present in every crystallographic structure. Point defects occur where an atom is missing or in an irregular position in the lattice structure and also when there are any foreign atoms at the lattice site. All point defects in crystals obey basic thermodynamic rules. Therefore, a small number of foreign atoms (or vacancies) are always incorporated into the crystal lattice. To develop technology, we need to find a good way to manage these defects. Theoretical modeling and thermodynamic analysis are highly recommended and awaited by experimenters. The quantitative and sometimes even qualitative compliance of their concentrations predicted in theoretical models with the actual defect concentrations still requires improvement. It is commonly known that in the real experiment the concentrations of point defects are strongly dependent on the direction of growth, i.e. the crystallographic orientation of the surface on which the growth takes place. However, in the world literature equilibrium models based on bulk properties are dominant. The pioneering aspects of the project will involve determining the behavior of the selected point defects in the nanometric areas close to the surface, in the area where the symmetry of the crystal lattice is broken and where strong interactions between the quantum states of the defects and the surface states appear. This is definitely an unfilled niche that we see in the field of research on point defects behavior in the III-nitrides. The processes taking place in the first few atomic layers closest to the growing surface are definitely one of the key factors influencing the dopants incorporation and vacancy creation mechanism. The planned tasks will provide information which is not straightforwardly accessible in typical growth experiments of semiconductor layers, e.g. the relationship between the microscopic atomic state of a surface and the possibility of incorporating foreign atoms into the crystal.

The research will be carried out on the basis of quantum-mechanical calculations from first principles as well as statistical physics and thermodynamics. The planned tasks will provide information about the phenomena taking place at the atomic level. We want to determine the energy profiles of the dopant atoms and vacancies starting from the surface to the volume of the crystal. Additionally, we want to investigate the change of this energy as a function of temperature by determining the vibrational spectra of the defects at various temperatures. Then we will be able to determine the Gibbs free energy of each system and build a thermodynamic model of defect stability in the layer close to the surface. As part of the project, we intend to study the behavior of such technologically important dopants as Ge, Mg and C. Controlling these dopants is crucial for achieving high-quality n-type, p-type or semi-insulating material. An important part of the project will also be the research on the thermodynamics and electronic properties of GaN doped with atoms of group V elements: As and P, and their co-doping with Mg. The latter aspect is considered in the context of improving the hole conductivity in GaN doped with Mg. We want to identify the rules of preferential choice of the lattice site occupied by dopants near the surface, which may be different than the site in the bulk. Next, we plan to compare the formation energy and electronic properties the same point defects at various surfaces under growth conditions by different epitaxial methods.

We are convinced that the research proposed in this project will be an excellent extension to the existing models of point defects incorporation. Our research will provide results that can be used for preparing advanced models based on machine learning algorithms. After integrating all this knowledge, it can be usefully used in experiments, either to control the type and concentration of point defects during the growth processes or to plan more sophisticated post-growth annealing processes.