Growth chemistry and interface properties of III/V-silicon semiconductors studied by DFT

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Chemical growth processes of III/V semiconductor vapour deposition were investigated by density functional theory (DFT). These optically functional materials are multi-component mixtures of group 13 and 15 elements and are grown by chemical vapour deposition (CVD) techniques under highly specific conditions. Often, the materials are metastable which challenges successful growth and crystal quality.
I will focus on the epitaxial growth of gallium phosphide (GaP) on silicon Si(001) substrates. As the two materials have almost identical lattice constants the strain energy is negligible and GaP-Si(001) can serve as a model system for more complex III/V-IV combinations. Although both materials are indirect semiconductors and therefore irrelevant for optical applications, GaP-Si is applied in solar cells, lasers and transistor devices as a structural buffer layer enabling the integration of active materials (e.g. Ga(NAsP), (InGa)(AsSb)) into Si-based superstructures.
The processes under investigation can be classified in five phases of CVD growth as sketched in Figure 1. In metal-organic vapour phase epitaxy (MOVPE), the materials to be grown are transported into the growth reactor as precursor molecules which chemically decompose dissipating any alkyl groups in the gas phase or on the substrate surface. One important reaction class for many precursor species was found to be beta-hydrogen elimination which exhibits the lowest decomposition barriers for hydride acceptors (i.e. metal compounds) as well as proton acceptors (i.e. saturated pnictogen/group 15 compounds). This new chemistry was discovered by DFT-based analysis of the reaction mechanism, the bonding character and the reaction dynamics of representative tert-butyl compounds. The insights gained can be utilized to further increase the precursor performance by addressing the bottleneck decomposition channel with ligand design: the beta-hydrogen elimination rates range within four orders of magnitude for constitutionally isomeric butyl ligands.

In a second phase, the precursor fragments reach the substrate and interact with the surface. As the surface is typically passivated by hydrogen, adsorption and activation need to be addressed alongside further side group decomposition of adsorbates. The chemical effects of the surface towards the established decomposition mechanisms is one aspect of the research presented. Next to surface-assisted molecular reactivity, the mechanisms of nucleation and growth were investigated as sketched in Figure 1. Growth is known to be dominated by lateral surface diffusion. Based on calculated hopping barriers for adatoms on Si and GaP(001) surfaces, kinetic Monte Carlo simulations unveiled that the GaP-Si(001) interface is not flat but rather atomically intermixed. This is in quantitative agreement with experimentally grown samples and observable in transmission electron microscopy images.

Finally, as a consequence of the intermixed GaP-Si morphology, periodic DFT calculations were performed in order to understand the relationship between atomistic structure at the interface and the electronic properties of these systems. It is of particular importance whether local electronic states arise at the interface donor and acceptor bonds (i.e. Si-P, Si-Ga) and how these influence the performance of devices grown under similar conditions.

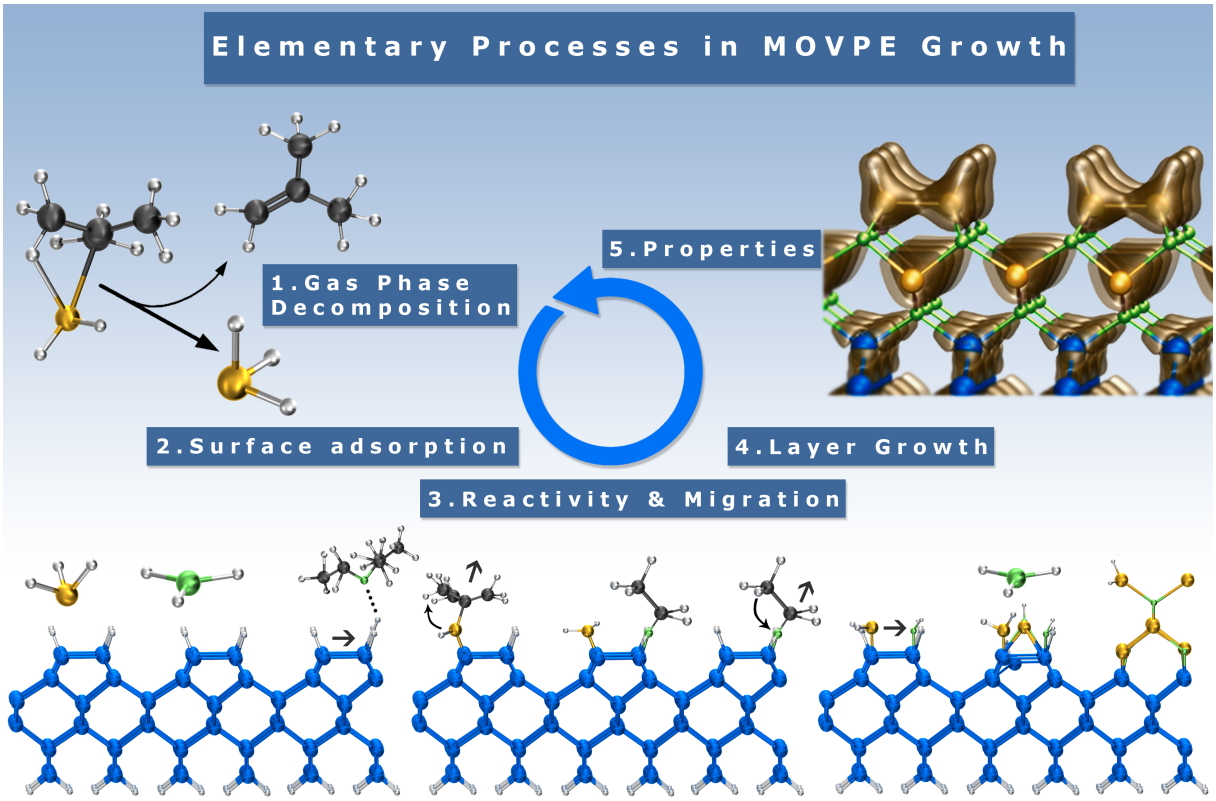

Figure 1: Schematic of elementary processes during MOVPE growth of III/V materials on IV substrates.

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