Abstract

Layered boron nitride is one of the key materials in contemporary research on two-dimensional (2D) systems. Its atomically smooth surface free of dangling bonds, very wide bandgap, and excellent dielectric properties have made it a fundamental component of van der Waals heterostructures for many years, serving both as an insulating layer and as a substrate for the growth of other 2D materials. At the same time, recent studies indicate that boron nitride should not be regarded solely as a passive component, but rather as an active platform for engineering structural and functional properties.

The aim of this doctoral dissertation was to investigate the possibilities of modifying the properties of boron nitride grown by metalorganic vapor phase epitaxy (MOVPE), with particular emphasis on the influence of growth parameters on the crystal structure, defect environment, spin properties, and bandgap of the material. In the first part of the work, the epitaxial nature of BN growth on sapphire substrates was demonstrated, highlighting the crucial role of an intermediate g-C_3N_4 layer in enabling the transition from the three-dimensional structure of the substrate to a two-dimensional layered material while preserving crystallographic relationships. This was followed by a detailed analysis of growth in the flow modulation epitaxy regime, showing that the mechanism combines features of both reaction kinetics limitations and mass transport limitations. Based on this understanding, a set of technological parameters was proposed for achieving BN layers with the highest possible structural and optical quality.

The next part of the dissertation was devoted to the study of polytypism (polymorphism) in boron nitride grown by MOVPE. It was demonstrated that the luminescence of the C_BC_N dimer can serve as an effective probe of the local crystalline environment, enabling quantitative analysis of the relative contributions of hexagonal and rhombohedral phases in epitaxial layers. It was also shown that appropriate tuning of growth parameters allows control over the proportion of hBN and rBN, as well as spatial definition of triangular rBN domains embedded in an hBN matrix. For such domains, a piezoelectric response was demonstrated, along with the

possibility of obtaining oppositely oriented electric polarization depending on the stacking sequence of atomic layers, namely ABC or CBA.

In the subsequent part of the work, the possibility of controlling spin properties of epitaxial boron nitride through carbon defect engineering was investigated. It was shown that by modifying MOVPE growth parameters, it is possible to generate both ensembles of defects with spin S = 1/2 and individual centers with spin S = 1, which opens perspectives for applications of BN in quantum technologies.

The final part of the study focused on bandgap engineering through the formation of boron aluminum nitride alloys (BAlN). Efficient growth protocols for BAlN layers using MOVPE were proposed, and it was demonstrated that even a small concentration of incorporated aluminum leads to a significant modification of the absorption spectrum, including both bandgap narrowing and a change in the character of optical transitions from indirect to direct.

The obtained results demonstrate that boron nitride can be treated as a material whose properties can be deliberately engineered at the level of crystal structure, defect concentration and type, as well as alloy composition. This dissertation therefore establishes a coherent strategy for BN engineering, relevant for applications in photonics, 2D electronics, and more broadly in emerging quantum technologies.