Summary

Nanotechnology refers to the understanding and controlling of materials on the nano (10^{-9} m) scale. Nanowires are a beautiful example of nanotechnology, with dimensions of ∼5-100 nm in diameter and up to several microns in length. They have a large aspect ratio of 1000 or more and therefore nanowires are referred to as 1-D structures. Due to the dimensions of the nanowires interesting optical and electrical properties are found that are not seen in bulk (3-D) materials. The crystal structure, defect density and morphology are important parameters that determine the quality of the nanowires. This thesis reports in detail on the formation and control of these parameters during the Vapor-Liquid-Solid (VLS) growth mechanism of nanowires with Metal Organic Vapor Phase Epitaxy (MOVPE).

In chapter 2 we have investigated the morphology of heterostructured GaP-GaAs nanowires grown by metal-organic vapor-phase epitaxy as a function of growth temperature and V/III precursor ratio. The study of heterostructured nanowires with transmission electron microscopy tomography allowed the three-dimensional morphology to be resolved, and discrimination between the effect of axial (core) and radial (shell) growth on the morphology. A temperature- and precursor-dependent structure diagram for the GaP nanowire core morphology and the evolution of the different types of side facets during GaAs and GaP shell growth were constituted.

In these wires many planar defects (twin planes) are present in the zinc-blende nanowire crystal structure, which are generally positioned in a random fashion along the nanowire length axis. However, under certain conditions twin pairs are formed, as described in chapter 3. In such pairs the first twin plane is formed at a random position, rapidly followed by the formation of a second twin plane of which the position is directly related to that of the first one. We show that the triangular $\{11\bar{2}\}$ morphology of the nanowire is a key element in the formation of these twin pairs. We have used our kinetic nucleation model, and show that this describes the development of the nanowire morphology and its relation with the formation of single and paired twin planes.

In chapter 4 we have investigated the formation of twinning superlattices in InP nanowires. We show that we control the crystal structure of Indium Phosphide (InP) nanowires by impurity dopants. We have found that zinc decreases the activation barrier for 2D nucleation growth of zinc-blende InP and therefore promotes the InP nanowires to crystallize in the zinc-blende, instead of the commonly found wurtzite crystal structure. More importantly, we demonstrate that we can, once we have enforced the zinc blende crystal structure, induce twinning superlattices with long-range order in InP nanowires. We can tune the spacing of the superlattices by the wire diameter and the zinc concentration, and we present a model based on the distortion of the catalyst droplet in response to the evolution of the cross-sectional shape of the nanowires to quantitatively explain the formation of the periodic twinning.

Twinning superlattices are predicted to give rise to a direct bandgap in normally indirect materials. Control in the segment length between two successive twin planes is crucial in order to manipulate the band structure. In chapter 5 we show for the first time that we are able to synthesize GaP twinning superlattice nanowires. Moreover by controlling the Ga pressure during growth we can alter the segment length independently from already known parameters like the nanowire diameter, Zn-concentration and temperature, which are found for InP and InAs. From the experimental data we are able to extract the effect of the chemical potential on the superlattice segment length and compare this with our quantitative model for InP superlattices. We find that the effect of surface energies rather than the chemical potential has a major effect on the superlattice segment length.

The crystal structure is an important parameter that determines the morphology of the wire. As shown for the paired and superlattice twins the droplet dynamics are affected by the morphology. In chapter 6 we report on an *in-situ* surface X-ray diffraction study of liquid AuIn metal alloys in contact with zinc-blende InP $(111)_B$ substrates at elevated temperatures. We observe strong layering of the liquid metal alloy in the first three atomic layers in contact with the substrate. In the first atomic layer the alloy has a higher indium concentration than in the bulk. In addition, in this first layer we find evidence for in-plane ordering at stacking fault positions. This can explain the typical formation of the wurtzite crystal structure in InP nanowires grown from AuIn metal particles.

Finally in chapter 7 a generic process has been developed to grow nearly defect free arrays of (heterostructured) InP and GaP nanowires. Soft nanoimprint lithography has been used to pattern gold particle arrays on full 2 inch substrates. After lift-off organic residues remain on the surface, which induce the growth of additional undesired nanowires. We show that cleaning of the samples before growth with a piranha solution in combination with a thermal anneal at 550 °C for InP and 700 °C for GaP results in uniform nanowire arrays with 1% variation in nanowire length, and without undesired extra nanowires. Our chemical cleaning procedure is applicable to other lithographic techniques such as e-beam lithography, and therefore represents a generic process. The patterned structures that can be made in this way are extremely useful for future experiments. The control in positioning eliminates fluctuations in nanowire diameter and density on the substrate. This ensures an equal mass transport and diffusion between the nanowires and thus an increased control in the nanowire growth compared to growth from colloids or thin film.

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