In this chapter an overview of the work described in the previous chapters will be given. Chapter 1 gives a general introduction to the subject of this thesis: the real-space analysis of colloidal epitaxy. Colloidal particles are macroscopic particles with a size ranging from several nanometers to a few micrometers, that, due to their Brownian motion, can explore phase space in thermodynamic equivalence with atoms and molecules. This, together with the fact that colloidal systems are easily accessible from an experimental point of view, e.g. by light microscopy, makes colloids an important model system for the study of phenomena like crystallization. The technique of confocal microscopy together with the use of a model system that consists of fluorescently labeled colloids with a core-shell morphology, allows for a three-dimensional (3D) analysis of particles in a suspension.

Apart from the theoretical interest in the colloidal model system, colloids are also an important building block for applications in many diverse areas of research. For most of these applications either the functionality of the application or its production process relies on the ability of colloids to self-assembly. In colloidal epitaxy a patterned substrate surface, or template, is used to direct colloidal self-assembly. This technique can on the other hand also serve as a model system for studying the influence of boundaries and substrate potentials on (epitaxial) crystal growth. In this research we have explored the technique of colloidal epitaxy, both concerning its use as a model system in the study of epitaxial crystallization, as well as its use in manipulating colloidal crystallization.

The lithographic techniques that we have used for patterning substrates for colloidal epitaxy are described in Chapter 2. With electron-beam lithography templates can be created by direct writing of a pattern in a poly(methylmethacrylate) (PMMA) layer. In Chapter 2 examples are shown of templates consisting of regular arrays of holes in the PMMA-layer, with lattice distances varying from about 100 nm to a few micrometer. The subsequent transfer of these patterns to solid substrates like glass, quartz or silicon using wet etching or plasma etching is demonstrated as well. These solid substrates can, among other things, be used as a master for soft-lithography. In soft-lithography an elastomeric mold is created with which the original pattern can be easily and in a comparably cheap way replicated. The use of soft-lithography in making polyurethane relief structures is demonstrated in Chapter 2. Furthermore, we show the chemical patterning of glass substrates using an elastomeric mold and a sol-gel mixture that contains a silane-coupling agent.

Apart from lithographic techniques, a method was devised for positioning colloidal particles on surfaces in any designed pattern. This method is described in Chapter 3. These colloid-patterned substrates can be used in various applications, but can also serve as a template in colloidal epitaxy, complementary to the lithographically made templates that were described in Chapter 2. In this technique optical tweezers are used to bring particles from a reservoir to the substrate where opposite surface charges immobilize particles on the surface. Both chemical surface modification and polyelectrolyte coating of either substrate or colloids make the method generally applicable. We demonstrate that using this technique large, two-dimensional patterns can be created that can be dried without distortions by critical point drying. As an example we
demonstrate the positioning of particles with a diameter ranging from 80 nm to 700 nm. The application of these 2D patterns in 3D epitaxial crystal growth is demonstrated as well.

In **Chapter 4** epitaxial growth of colloids that interact via a hard-sphere like potential is described. We have found that it is possible to grow metastable hard-sphere hcp and ‘double hcp’ (dhcp) crystals by using a surface pattern that directly dictates the stacking sequence. A detailed 3D analysis based on real-space measurements was performed on crystal structure as a function of template-crystal mismatch. Perfect template-induced hcp-crystal growth was found to occur at an isotropically deformed template, which is a strong indication for prefreezing at the template. At stretched and compressed lattices we observed growth of a non-close-packed superstructure and of a perfectly layered and (100)-aligned fcc crystal. Small mismatches led to increased out-of-plane displacements followed by a structural breakup in ‘crystal’ grains where particle positions in successive layers are strictly periodic and ‘defect’ grains where these positions are displaced with respect to each other. At an anisotropically stretched surface pattern, increasing the hexagonal c/a-ratio, these displacements as well as the mutual orientation of these grains were directed perpendicular to the stretched direction.

Apart from the study of colloidal epitaxy in a system with hard-sphere like interaction, the use of colloidal epitaxy in a model system with long-ranged repulsive interaction was examined as well. In this system the role of gravity was eliminated from the epitaxial growth process by density matching colloids and solvent and using a set-up in which the resulting small gravitational field is directed away from the template.

In **Chapter 5** we describe how a simple 1D pattern of repulsive, charged lines was found to direct 3D crystallization in this system. At volume fractions where the bulk phase behavior led to bcc crystallization, the 1D template was found to induce formation of a metastable fcc crystal. At lower volume fractions and different line spacing, bcc crystals were oriented with the (100)- or the (110)-plane, with two-fold twinning, parallel to the template. The template further induced prefreezing of the (100)-plane. At a large mismatch between template and interparticle spacing, 1D strings formed in the surface layer of a 3D crystal.

The research described in Chapters 4 and 5 mostly focused on the study of colloidal epitaxy under equilibrium conditions, which is important for a fundamental understanding of (colloidal) crystallization and for the use of colloidal epitaxy as a model system for molecular epitaxy. The ability to create crystal structures that are metastable in bulk crystallization is however also a promising development for the use of colloidal crystals in applications. Many techniques to make (functional) colloidal assemblies rely on particle ordering directly during the evaporation of the solvent liquid, so called controlled drying techniques.

In **Chapter 6** the use of templates in directing colloidal crystallization in controlled drying techniques is examined. Template-induced colloidal crystallization is demonstrated in a tilted-horizontal setup of the templated substrate for crystals that are both a few layers as well as more than 100 layers thick. Furthermore, at templates that possessed a mismatch with respect to the colloidal dimensions, a reconstruction in surface orientation of the crystal took place. The strain relaxation phenomena observed on these mismatched templates are similar to those observed in
epitaxial crystal growth in suspension during slow sedimentation. For vertical controlled drying, where in general there is more control over crystal thickness and uniformity, template-induced growth was examined for silica colloids ranging in diameter from about 100 nm to over 1 µm. Our results indicate that the ability to form a templated crystal is crucially dependant on the surface topography of the template. For a square symmetric fcc(100)-template, 2D crystal growth was only observed on a pillar-shaped template.

In the last two chapters in this thesis, crystallization of colloids that are subjected to a relatively large gravitational field (i.e. large Peclet numbers) on a flat bottom wall is investigated. Where crystallization of colloids without gravity or in a weak gravitational field has often been examined, the role of the gravitational field has so far hardly been addressed. Apart from this fundamental interest, the study of colloidal crystallization in such a system at a flat wall also provides a first step towards an understanding of crystallization at a patterned wall, like for instance for the system studied in Chapter 4.

In Chapter 7 a real-space study on the crystallization process in a system of sedimenting colloids is presented. During sedimentation a gradient in particle concentration develops at the bottom of the sample container. The presence of the lower boundary wall induces layering in the liquid and, upon increasing sediment thickness, crystallization occurs in these liquid layers. Crystallization in the first layer was found to proceed via a first-order transition. The formation of small crystalline nuclei in this layer, induced epitaxial crystal growth in the second layer on top of these crystallites, which resulted in both layers undergoing the phase transition simultaneously. The critical osmotic pressure for crystallization at a plain wall, as well as for epitaxial crystallization on an already crystallized layer, was determined. The nucleation-and-growth mechanism leads to a poly-crystalline end-state. Due to this polycrystallinity we could not determine whether the crystallization process involved an intermediate ‘hexatic-like’ phase. Our results regarding the nature of the transition in the first two layers are in agreement with recent computer simulations.

Finally, the structure of colloidal crystals formed by sedimentation was examined, focusing especially on the occurrence of stacking faults. The results that are presented in Chapter 8, indicate that the equilibrium crystal structure for these colloids is an fcc-crystal, with the number of stacking faults determined by the interplay between sedimentation and crystallization kinetics, irrespective of the softness of the interaction potential. The number of stacking faults was found to decrease with decreasing initial volume fraction. These results thus provide a way to grow fcc-crystals of hard-sphere particles by slow sedimentation. There is an increased probability for stacking faults to occur in the first few layers above the bottom wall, which is due to the crystallization kinetics on a plain wall in a gravitational field. A patterned bottom wall that favored a specific hexagonal orientation was found to drastically reduce the number of stacking faults in the crystal.