Summary

Two relatively new materials have been investigated in the research that led to this thesis: hexagonal boron nitride (*h*-BN) and graphene. They have a similar structure, namely that of a film with a thickness of precisely one atomic layer, in which the atoms are arranged in a honeycomb lattice. They both come with appealing physical properties and have the potential for being applied, for example in electronics, touch screens, sensors and as coatings (for a list, see 1.3.2.). In spite of their extremely small thickness, *h*-BN and graphene remain intact under ambient conditions, in liquids, and at high temperatures. The high appeal of graphene makes it today's "hottest" material.

The method used to produce these materials that is being reported in this thesis is called chemical vapor deposition (CVD). The basic principle is the same for both materials. A precursor gas is dosed onto a clean Rh surface, namely borazine (HBNH)$_3$ for *h*-BN and ethylene (C$_2$H$_4$) for graphene. The Rh acts as a catalyst for the decomposition of the precursor molecules. After decomposition, the H atoms desorb, while B and N or C atoms stay behind on the Rh substrate and form single-layer *h*-BN and graphene. Once the Rh surface is covered by *h*-BN or graphene, it is no longer reactive, and further precursor molecules landing on it simply desorb again. In this way, the *h*-BN or graphene stops growing by itself at a thickness of precisely one atomic layer.

Growth of these overlayers on Rh(111) is used as a model system for the growth of *h*-BN and graphene on metal surfaces in general, which is considered as one of the candidate approaches towards mass production of these materials. Even though the formation of these materials on metal surfaces is, by now, fully established, the quality of the grown layers is not optimal. Non-idealities, such as lattice defects deriving from the finite grain size, variations in thickness (i.e. combinations of single-, double- and multi-layer structures), incomplete coverage and impurity problems, all make that realistic films do not have the special physical properties that have been measured for microscopic flakes. These non-idealities are a direct consequence of the atomic-scale nucleation and growth phenomena that are active during the formation of the monolayers. In this thesis, I report on the direct visualization of these phenomena in an attempt to understand the physics behind them, and to construct new 'recipes' to optimize the quality of CVD-grown *h*-BN and graphene.

Like most chemical reactions used in practical applications, CVD of *h*-BN and graphene is carried out at elevated temperatures. The most straightforward way to investigate such reactions would be to directly 'see', with full time resolution (ps) and full spatial resolution (pm), how the impinging molecules decompose and re-assemble into new combinations, and thus follow all relevant steps in extreme detail on the atomic scale. This dream scenario can be realized partly by using a so-called scanning tunneling microscope (STM), a powerful tool with which atoms and molecules can be imaged at material surfaces. Gerd Binnig and Heinrich Rohrer (at IBM Zürich) have been honored with the 1986 Nobel Prize in Physics, only a few years after their invention of this wonderful instrument. The working principle of an STM is to scan the contour of a surface, line by line, with a macroscopic metal wire that has a typical length of several millimeters and ends in a sharp tip, with a final radius of curvature of a few tens of nanometers. The tip is held at a fixed distance to the surface, in the order of half a nanometer, by applying a modest voltage between tip and surface and keeping the small electrical current constant that results from the quantum-mechanical tunneling of electrons between the two. When this is done with sufficient precision and stability, individual atoms and molecules can be visualized. How difficult this is, can be illustrated by the simple observation that the ratio between the millimeter size of the metal wire and the sub-nanometer distances between the atoms that are imaged is as extreme as that between the height of the Eiffel tower and the thickness of a human hair. Imaging surfaces and reaction steps with an STM at elevated temperatures is very challenging, because at high temperatures the atoms are very mobile. We could extend the above analogy by comparing high-temperature STM observations to an attempt to use the tip of the Eiffel Tower to image a single human hair, while both are subjected to a strong wind! This level of difficulty explains why STM measurements are performed usually only at or below room temperature. In case of chemical reactions and other high-temperature processes, one usually first runs the high-temperature process and then cools the specimen down, before inspecting its surface in detail with an STM. Although this type of "post-mortem" measurement can yield very relevant information on the reaction that took place, this information is rather indirect, which makes it very difficult to infer the detailed, atomic-scale processes that have been at work at the high temperature. Yet, it is precisely this type of insight that is crucial for a full understanding of and, eventually full control over the reaction. After years of optimization and experimentation, we now can perform STM measurements during the growth of materials at temperatures up to 1300 K. This is a wide temperature

range that encompasses many industrial chemical processes, as well as the new processes of CVD of *h*-BN and graphene, investigated in this thesis.

For both systems, the effect of temperature is explored by first exposing an atomically clean Rh(111) surface at room temperature to a sufficiently high dose of precursor molecules to form a saturated layer of adsorbed molecules, after which the Rh substrate is heated up. During all these stages, the surface is continuously imaged with the STM. Both borazine and ethylene are found to initially form molecular clusters on the Rh surface that ripen into larger sizes as the temperature rises. At sufficiently high temperatures, between 762 and 806 K for borazine, the images indicate that the molecules decompose, resulting in the formation of *h*-BN patches. The first stage of decomposition of ethylene, namely into CH_x clusters, takes place at room temperature, while the transformation into graphene starts around 808 K. When the temperature reaches 1000 K, the orientation of the graphene islands becomes rather similar (within 5°), while the *h*-BN islands exhibit two domain orientations, with 180° rotational difference. In both cases, the Rh(111) lattice underneath dictates the preferred orientation of the overlayer. For both overlayers, the small mismatch in lattice constant between the overlayer and the substrate leads to a moiré pattern, in the form of a modulation in the height of the overlayer with a long period. For *h*-BN on Rh(111), this corrugation is known as the 'nanomesh' structure.

In experiments where clean Rh is exposed to ethylene directly at elevated temperatures, between 750 and 980 K, rhodium carbide is observed to form instead of graphene. Luckily, a narrow temperature window can be identified, in which only graphene is stable. Deposition of ethylene in this temperature window indeed produces well-ordered graphene. Unfortunately, when the specimen is cooled down to room temperature, the overlayer structure degrades dramatically, which is due to the segregation of carbon that wasdissolved into the Rh substrate at the high growth temperature. The strategy that we adopt to avoid both the formation of carbides and the dissolution of significant amounts of carbon, is to first 'seed' the Rh surface with small graphene islands, by low-temperature ethylene exposure and slow heating, followed by further ethylene deposition at the regular growth temperature. In this way, graphene can be produced of a relatively high quality. In a way, one can consider our seeding approach as the introduction of an extra combination of parameters, namely the initial density of nuclei and the nature of

these nuclei – graphene – that is added to the conventional growth parameters of deposition temperature and gas pressure.

We also demonstrate that we can use the segregation of dissolved carbon to make graphene islands grow, by slowly cooling down the specimen after stopping the ethylene exposure. At lower temperatures, we are confronted with the problematic phenomenon that this type of growth leads to the spontaneous formation of double-layer Rh islands. The Rh atoms involved in these structures originate from the retraction of Rh steps, an effect that we nick-named "anti-step flow". The mechanism behind this type of flow is that when the growing graphene overlayer 'colonizes' the area that is temporarily vacated by a spontaneous fluctuation in the local position of a Rh step, this step can no longer return to its original configuration; in this way, the graphene growth biases the step fluctuations of the Rh surface in the direction of an effective retraction. For Rh adatom islands, this process leads to their shrinkage. The Rh atoms that are released at the edge find themselves trapped on top of the island, where they eventually nucleate a new layer of Rh, thus leaving their mark in the form of double-layer Rh structures. With respect to the growth of graphene at its free edges, the anti-step flow mechanism of graphene growth becomes more important as the temperature is lowered. This behavior disqualifies lower-temperature deposition of graphene as a practical growth recipe.

At the end of the thesis we combine the insight obtained in our studies of graphene growth on Rh(111) into a single, qualitative picture, in which the competition between the formation and growth of graphene and carbide is described in terms of the equilibrium between dissolved carbon, carbon adatoms and islands of graphene or carbide, based on the formation energies of these overlayers and the activation energies for their nucleation. This qualitative picture also applies to graphene growth on other transition metal systems than Rh(111).

The STM growth movies of graphene and nanomesh also enable us to analyze the kinetics of the growth process in detail. For both overlayers, we find that the basic growth unit corresponds to one complete unit cell of the moiré pattern between the overlayer and the Rh substrate. From measurements of growth rates at various sites, we conclude that the growth proceeds in two steps. The first and more difficult step is the creation of a kink, with a size corresponding to a full unit cell of the moiré pattern. After this, the new kink rapidly advances, again in units of the moiré structure. In the graphene growth process, it is easier to create a kink at concave corners than on a straight edge, and we

observe a significant preference for 60⁰ corners. In the case of *h*-BN, the edges of *h*-BN islands are terminated by either B or N atoms, which gives rise to different edge energies. The kink creation rate is higher on high-energy edges and the kink advancement rates are equal for the high- and low-energy edges. We use these observations to obtain detailed information on formation energies of new growth units, on the formation energies of boron- or nitrogen-terminated edges, and on the corner energies of the *h*-BN overlayer.

Measurements of the speed at which voids (vacancy islands) in the overlayer fill up have formed the basis for a description of precisely how precursor molecules contribute to the growth of the film. As these molecules do not decompose on the areas that are already covered by graphene/*h*-BN, the rate at which precursor molecules reach the vacancy island is directly known from the area of the vacancy island and the gas pressure of the precursor. From these measurements we learn that borazine has to land on the Rh surface close to an *h*-BN edge in order to become incorporated in the overlayer. During ethylene exposure, we find that carbon atoms dissolve into the Rh substrate when (or where) the graphene coverage is low and the surface is populated only by separate graphene islands. Under the same conditions carbon is found to segregate back to the surface when (or where) the graphene covers a larger fraction of the surface and the uncovered Rh regions are enclosed by graphene. This interesting conclusion is explained by the observation that it is easier to create a kink at concave corners than on a straight edge. As the kink creation rate is the limiting factor for graphene growth, the average growth rate at the inner perimeter of vacancy islands in the graphene overlayer is much higher than that at the outer perimeter of compact graphene islands. This difference results in different carbon adatom densities on Rh surface even when the temperature and gas pressure are the same, which affects the flux of carbon dissolving into or segregating out of the Rh substrate.

We investigate whether it is possible to improve the quality of overlayers, in particular for *h*-BN, after they have formed on the Rh substrate. If domains can be made to ripen to much larger sizes, by diffusion and annihilation of domain boundaries, this would enable one to separate the stage of deposition from that of film quality control. Our observations show that large-angle domain boundaries are removed when temperature is increased sufficiently. But the boundaries between domains with nearly equal orientations and translational domain boundaries remain stable all the way up to the temperatures at

which the *h*-BN overlayer evaporates and the graphene overlayer dissolves. This means that a large fraction of the structural defects that are introduced during the growth of these layers cannot be removed by a simple, high-temperature procedure.

Combining all the above insights into the atomic-scale mechanisms, we arrive at optimal recipes for the growth of high-quality *h*-BN and graphene films on Rh(111). In the case of *h*-BN, the message is extremely simple: the quality of the film is completely defined by the density of domain boundaries, which is dictated by the density of *h*-BN nuclei, formed in the early stages of the growth. Keeping this density low, by combining a low borazine pressure with a high deposition temperature, one can grow *h*-BN films with excellent quality. In the case of graphene there are conflicting requirements connected to the reduction of the nucleation density, the avoidance of carbide formation and the reduction of the dissolution of carbon into the Rh substrate, which would otherwise lead to multilayer growth and deterioration of film quality. In order to reasonably satisfy all requirements, we developed a two-step deposition recipe, in which we separate the stages (and conditions) of nucleation and subsequent growth.

This thesis presents two examples of atomic-scale microscopy at high temperature. The observations made here, under actual process conditions, enable us to draw detailed conclusions that go beyond the interpretations that one could reasonably obtain from post-process, room-temperature imaging. In this approach I have tried to follow the great example set by Heike Kamerlingh Onnes, the initiator of the field of low-temperature physics after whom our laboratory is named, and who has introduced the famous motto: "Door meten tot weten" (Through measurement to knowledge).