Human knowledge and experience increases with enormous and permanently growing speed. This results in the production of huge amount of information. The need for storage carriers with large capacities and fast devices able to process this information rises accordingly. People used to use paper as an information carrier for ages. Nowadays this medium is being replaced partly by electro-magnetic, optical or magneto-optical devices, which have been successfully built and used and still are being developed all over the world. For these developments, monocrystalline films are of interest because of their fundamental importance and technological perspectives. This is especially true when a few monocrystalline layers are stacked together. These layers and multilayers can form a basis for unique electronic, optoelectronic, magnetic, and micromechanical devices of a future, which, in fact, already emerges. The fabrication of quantum wells, for example, has been achieved by stacking a thin semiconductor layer with a relatively narrow band gap in between two thicker semiconductive layers with wider band gaps [1]. Another example of the possible use of monocrystalline multilayers is a magnetic tunnel junction. The operation of a magnetic tunnel junction is based on a spin-polarized tunnel current between two magnetic conductors through a thin insulating barrier. The current can flow only through an extremely thin isolating barrier (a few nanometer thick). From a fundamental point of view, tunnel junctions consisting of monocrystalline films represent a useful model system, in which atoms in a defect-free compound are situated in perfect order. They can also be successfully used in technology and attempts are already on their way [2]. One more example of the use of epitaxial films is a surface array of nano-patches self-organized by the strain in the layer. They were obtained on Cu(100) by N-ion bombardment and consisted of a Cu3N-like surface phase [3]. In our research we obtained a similar array of nano-patches of Fe4N on Cu(100), which may be ferro-magnetic. Layers containing arrays of magnetic patches can be used as high density magnetic storage media.

The widely used method for the production of single crystalline films is epitaxy. The grown film is epitaxial on a substrate if the lattice of deposited film is aligned with the underlying substrate structure [4]. In fact, single crystals of some compounds can be obtained only by epitaxy. In order to produce a film of good crystalline quality as close to a single-crystal as possible, many difficulties have to be overcome. First of all, a very clean environment is needed, which can be supplied by ultra-high vacuum (UHV) conditions. By UHV a pressure of the rest gas of less than $10^{-9}$ mbar is implied. In this case, the bombardment of the surface with residual gas molecules is so low that it does not noticeably contaminate the film during the relatively short time of growth. Ultra-pure substances and fluxes must be used in combination with UHV conditions in order to be able to control the growth conditions. Another problem is epitaxy itself. If the material to be grown is different from that of the substrate (heteroepitaxial growth), then there is practically always a misfit between the lattice constants of the substrate and of the film. This fact gives rise to interface
stress, which finally gets (partly) released by the formation of misfit dislocations and other imperfections and causes the elastic deformation of the substrate and of the film. In many cases, which are almost never mentioned in literature for obvious reasons, a substance does not form an epitaxial phase on a substrate because the misfit is too big. This problem also appears at the interfaces between layers of a multilayer. In addition, interfaces can cause undesired intermixing, interdiffusion and roughening. The problem of the right stoichiometry rises when the compound to be grown consists of two or more elements. In this case the fluxes of the elements should be controlled very accurately. Also the components can escape to the vacuum. These undesired effects can be prevented or considerably reduced by changing the growth parameters like temperature, the fluxes of materials, or others. Thus, the search for the correct growth parameters is a broad subject of research.

The mechanism of epitaxial growth is a particularly valuable piece of knowledge, which would ease the quest for the growth parameters and open a new perspective in epitaxy. Many investigations were dedicated to the mechanism of epitaxial growth. This field became even more exciting since imaging techniques with atomic resolution such as scanning tunneling microscopy (STM) were developed. With STM a picture of the atomic arrangement can be taken in real-space by sensing corrugations in the electron density of the surface. These corrugations are related to the positions of surface atoms as well as to the chemical difference between the atoms. Nowadays, the growth of simple metals, some semiconductors and even more complicated systems is understood in considerable detail [5] and can be simulated by relatively fast computer codes. Also the potential-energy landscape of a number of simple well-ordered surfaces can be calculated and used to describe some surface reactions. The epitaxial growth of not only simple but also very complex chemical compounds (like high-temperature superconductors with accurate amounts of four elements) was successfully performed with impressing precision [6-8]. However, the epitaxial growth of complex compounds is described by very general models and the fabrication recipes were found by trial and error.

Molecular beam epitaxy (MBE) is one of several methods, that are used to grow an epitaxial film. It employs a thermal energy molecular beam of a vaporized material directed at the substrate. If gases, evaporated liquids or chemically gasified solids are used in the growth process, the method is called chemical vapor deposition (CVD). In CVD a chemical reaction takes place at the surface of the growing sample. Both methods are used in a very clean environment supplied by keeping the base pressure in the chamber at the UHV level (not counting the pressure created by the reacting species). The growth of metal oxides, for example, often occurs while evaporating a metal in an atmosphere of O_2, O_3, or NO_2 [8]. The partial pressure of the reacting gas is then in the 10^{-8} – 10^{-4} mbar range. In this work we used MBE assisted by a flux of atomic nitrogen and hydrogen, which thus also involves gases, or rather activated gases. In this respect the method we applied is close to the CVD method.

The work presented in this thesis is part of a project, which aimed to develop a fabrication method and to study properties of an epitaxial magnetic tunnel junction consisting of monocrystalline layers. At the time this work started, the layers in such devices were usually made of polycrystalline or amorphous materials. In order to characterize a polycrystalline film, so-called effective parameters had to be used. This made it difficult to predict the spin-dependent tunneling current through a junction because too many mostly unknown parameters to describe imperfections in the layers were needed. The properties of a junction made of monocrystalline materials can be modelled easier since the positions of atoms are known. Some theoretical work on this subject has been already published in the literature [9].

The materials of the multilayer were chosen to be an iron nitride (Fe_3N or Fe_{16}N_2, ferromagnetic conductors) and a copper nitride (Cu_3N, a narrow band gap insulator). This
choice was made for several reasons. First of all, these nitrides of iron and copper have a simple structure (cubic or tetragonal). The crystal structures of two layers of these compounds can be joined in only one unique way. This is not the case for compounds with larger unit cells, like Fe$_3$O$_4$. Here epitaxial layers can be shifted in a lateral direction over a length corresponding to half a unit cell, still being epitaxial. This feature causes the formation of structural domains in epitaxial layers. Second, the close match of the lattices of Fe$_4$N and Cu$_3$N allows for epitaxial growth of the epitaxial tunnel-junction structure with a low density of defects at the interface. Finally, the chemical bonding in these phases could prevent intermixing at interfaces between layers and between the bottom layer and the substrate.

In this work several methods to obtain the desired phase were tried. A recipe to produce the pure monocrystalline $\gamma'$-Fe$_4$N phase was found, and a certain level of understanding of the growth mechanism of Fe$_4$N on different substrates by MBE assisted by a flux of atomic nitrogen has been achieved. The growth of the Fe$_4$N compound illustrates all the difficulties described above. In general, the growth mechanism is dependent on the nucleation process on the substrate, on the mobility of the atom species, on the rates of chemical reactions occurring at the surface. The complication in the case of iron nitrides is the possibility to grow different phases with different stoichiometry. Another point of concern is the metastability of iron nitrides. They tend to undergo transitions from one phase to another, or even to decompose into pure iron and N$_2$ gas at elevated temperatures. All these problems had to be overcome in order to fabricate a single-crystal film and subsequently a multilayer.

In order to solve the difficult problems described we had to use various techniques developed in our laboratory as well as by other research groups in Groningen, Utrecht and in Madrid. The UHV setup we used was adapted for our purposes several times. In order to produce Fe-N films we used Knudsen-cells for evaporation of iron and a few types of sources of atomic nitrogen. After a sample was produced, we characterized it in-situ with low energy electron diffraction (LEED), low energy ion scattering (LEIS) techniques, Rutherford backscattering spectroscopy (RBS) and channeling. The phase composition was probed ex-situ with conversion electron Mössbauer spectroscopy (CEMS) and x-ray diffraction (XRD). To improve the sensitivity of CEMS measurements, most samples were grown using iron enriched with the “Mössbauer” isotope $^{57}$Fe. In special cases we used elastic recoil detection (ERD) and atomic force microscopy (AFM). Scanning tunneling microscopy (STM) was used in-situ in a special setup to uncover the morphology of a grown sample. The thickness of this series of samples was varying between sub-monolayer to up to tens of monolayers in order to see the progress of the growth. The setups used and the techniques utilized will be described in detail in Chapter 2.

The first trial to grow an epitaxial iron nitride film was made by following a recipe, that was published in literature. The epitaxial growth of $\alpha''$-Fe$_{16}$N$_2$ on a MgO(100) substrate by iron MBE deposition in an ammonia plus nitrogen atmosphere was reported by Sugita et al. [10]. In a series of experiments we showed, that the very slow nitridation of iron in ammonia does not allow the growth of an iron nitride at a reasonable speed even at ammonia pressure as high as $10^{-4}$ mbar. We successfully tried two other methods for the production of Fe-N layers. First, we deposited Fe in a flux of ammonia and nitrogen, which was led through a hot (>900°C) nozzle made of iron. It is known that a hot iron surface serves as a catalyst for the production of ammonia at high pressures [11]. The molecules of the mixture were hitting the inner iron surface of the nozzle and efficiently decomposed into atoms resulting in a flux containing N atoms. Another method to produce nitrogen atoms is to decompose N$_2$ (or NH$_3$) gas in a plasma. The plasma can be created by applying a radio-frequency (RF) electromagnetic field to a container with the working gas at low pressures (~$10^{-2}$mbar). The use of N$_2$ and a mixture of N$_2$ and H$_2$ as a working gas yielded a flux of N atoms high enough to grow Fe$_4$N films. The details of these developments will be given in Chapter 3 of the thesis.
Chapter 1

The RF-source turned out to be much easier to control than the hot iron nozzle and we concentrated on using the RF-source for the growth of nitrides. We monitored the efficiency of the RF-source with optical spectrometry of the plasma. We managed to detect the contribution of atomic lines in the spectrum and used it as a reference in adjustments of the RF-source parameters (the distance between the electrodes, the pressure, the gas mixture). The angular spread and the flux intensity (atoms plus molecules) behind the exit of the narrow tube directing the flux, was calculated by a Monte-Carlo simulation of atomic trajectories. We estimated the efficiency of the RF-source from the uptake of N atoms by the grown layer. Assuming the sticking coefficient of N atoms to a Fe or Fe-N surface is unity under certain conditions we have deduced the flux of N atoms at the surface and the efficiency of the RF-source, which turned out to be ~2%. This study of the RF-source will be described in chapter 4.

An extensive study of the growth mechanism of the Fe$_4$N phase on a MgO(100) substrate is presented in Chapter 5. We noticed that the uptake of nitrogen does not depend on the temperature of the substrate (in the range RT – 350 °C), when the flux of atomic nitrogen is not high enough to form a pure Fe$_4$N phase. From this fact we concluded that the sticking coefficient of a N atom to an iron surface is indeed equal to unity. Two phases formed in this case, namely α-Fe and γ'-Fe$_4$N, were both epitaxial. However, if the flux of N atoms is so low that only a very small amount of Fe$_4$N can be formed (<30%), the growth mechanism changes and the Fe$_4$N phase grows with four crystal directions, which are 6.5° tilted with respect to the <001> direction of the substrate. The role of hydrogen in the RF-source and at the surface was studied in a series of experiments. At a temperature as high as 460°C the Fe$_4$N phase decomposes and a pure iron layer was obtained. The optimal substrate temperature for the growth of epitaxial Fe$_4$N was found to be 400°C. At optimal conditions we have managed to grow a monocrystalline Fe$_4$N film with very low density of defects as was judged by the channeling in the crystal.

Chapter 6 is dealing with the preparatory study of N and Fe deposited on a Cu(100) substrate. We studied the adsorption at 400 °C and diffusion at RT of N atoms at the Cu(100) surface. Atomic-resolution STM allowed us to follow the change in the configuration of N adatoms at the copper surface and to determine diffusion barriers for isolated adatoms as well as for those in clusters. The deposition of Fe at a Cu(100) substrate at 400 °C resulted in the formation of islands of copper, which apparently covered the underlying iron clusters. When a relatively thick (1.3 ML) iron layer was deposited, the formation of pinholes was observed, which are also the result of the segregation of copper. A model of the intermixing process will be proposed. The deposition of iron in the presence of a flux of N at 400 °C resulted in the suppression of the intermixing between copper and iron. This is due to the formation of the Fe$_4$N phase.

Chapter 7 is dedicated to a scanning tunneling microscopy (STM) study of the growth mechanism of Fe$_4$N on Cu(100). Sub-monolayer thick layers were deposited at a substrate temperature of 400 °C in a flux of N and H from the RF-source. The nucleation process starts with the formation of depressed islands, which are about level with the copper terraces. Thicker films of Fe$_4$N (> 2 MLs) cover the substrate completely and the growth proceeds in the layer-by-layer mode. A c(2x2) or a p4g(2x2) LEED pattern is visible during all the deposition steps. The STM images with atomic resolution allowed us to recognize both reconstructions of the surface. A series of experiments showed that the p4g(2x2) reconstruction is related to a higher concentration of nitrogen at the surface of the film. In case of a very slow deposition rate of iron (~1000 s/Å) in the same flux of N, square-like patches of Fe$_4$N of a size of ~100Å are formed when a few MLs of Fe are deposited. These patches have about equal size and are arranged in a rather ordered way.
The surface structure of freshly grown Fe₄N films was investigated with low energy electron diffraction (LEED) and low energy ion scattering (LEIS). The measured angular scans of scattered and recoiled atoms obtained from samples both with a c(2×2) and a p4g(2×2) reconstruction of the surface. The p4g(2×2) reconstruction of the surface was obtained on a sample grown in excess nitrogen. LEIS scans from this sample were fitted with a slab where Fe atoms of the topmost layer occupied positions rotated in <100> directions around N atoms. The fits gave the positions of the atoms with accuracy of 0.05 Å. The details of this investigation will be presented in chapter 8.

In chapter 9 conclusions are drawn and an outlook for future studies is presented. It is concluded that many of the anticipated aims of this research are fulfilled. The complicated growth mechanism of Fe₄N has been unraveled in considerable detail. Ferromagnetic layers of Fe₄N can be grown on various substrates and may find useful applications in device technology.

References
