Chapter 9. Summary and outlook

The title of this thesis presumes an answer to questions like “How to grow nitrides, how does Fe₄N form, how does it develop, what are the properties of it?” We have to conclude that the content of the thesis answers these questions only partly. Instead, it opens new ones. The answers a reader can find in this thesis, a possible use of these answers and a set of new questions to be answered will be summarized below.

The growth mechanism of different compounds is a broad subject of research, which is still expanding. This fact is related to a rising need in new materials and compounds in many fields of human activity, and especially in the field of electro-magnetic, optical or magneto-optical devices based on thin films and multilayers. The detailed knowledge of the mechanism of the nucleation and growth serves as a basis in the quest for new materials. The shining illustration of this statement can be our own research. Actually, there is a lot of knowledge and experience that has been collected by people for many years of research in this field and we started basing on the known phenomena and facts. The orientation of the research in our group was the interaction of gases with metals and we have a lot of experience in dealing with this type of physics. These skills allowed us to develop new methods for the production of nitrides and uncover new processes or to put the known phenomena (like exchange mechanism, for example, mentioned in chapters 6 and 7) in the context of the mechanism of nucleation.

The growth of epitaxial films is a specific branch of the field of growth. The use of monocrystalline substrates can cause the nucleation of a phase, which inherits some properties of the substrate. These include the orientation of the crystallites, the orientation of the surface with respect to crystallographic planes and maybe more. In an ideal case, the use of this method allows to produce monocrystalline films with an extremely low density of defects. Such films might have specific properties and represent a useful model system, where the influence of imperfections can be neglected.

The aim of this work was to develop a method for the growth of epitaxial monocrystalline films of magnetic iron nitrides, to study the mechanism of nucleation and growth of produced phases and to investigate the (mainly crystalline) properties of the produced films. We can conclude now that many anticipated aims of this research have been fulfilled.

As a first trial, we attempted to use a published recipe of the production of the α”-Fe₁₆N₂ phase by depositing Fe in an NH₃ atmosphere (the maximum pressure of ammonia we applied was 10⁻⁴ mbar). Soon we realized that the dissociation of ammonia at an iron surface is quite slow and the growth of nitrides is not possible with a reasonable speed. Instead of this, we developed and tested two new methods for the production of Fe-N films by MBE assisted with a source of atomic N. We used a hot (>900°C) iron nozzle as an outlet for a mixture of N₂ and NH₃ gases while depositing Fe. This method resulted in a high enough uptake of N by the growing sample and we could grow nitrides with a speed of ~0.02 Å/s. Obviously, the iron surface of the nozzle served as a catalyst for the decomposition of one or
both of the gases. This resulted in a flux containing N atoms. These atoms of nitrogen form
the reactive reagent, which is needed for the reaction with iron at the surface. In the second
method, we used a radio-frequency electro-magnetic field for the creation of a plasma in
which molecules of an N-containing gas could be effectively cracked. The output of the RF-
source of N atoms was led to the surface of the growing film by a Teflon tube. We used pure
N\textsubscript{2} and mixtures of N\textsubscript{2} and H\textsubscript{2} as a working gas. The production of Fe-N films was achieved
with both mixtures. This method seemed to be easier to use and to control. Further on we
concentrated on the production of the films with this method.

In order to take control over the output flux of the RF-source and to improve its
efficiency in the production of N atoms, we have undertaken an investigation of the properties
of the source with several methods. We monitored the efficiency of the source with optical
spectroscopy of the plasma. The contribution of atomic transitions into the complicated
optical spectrum of the plasma was found and used in fine adjustments of the parameters of
the source. The distribution of the flux behind the exit of a long, narrow tube was simulated
with the Monte-Carlo method. This calculation gave us a total flux at the surface of the
sample and let us estimate the efficiency of the source. Assuming that the sticking coefficient
of N atoms to Fe and Fe-N surface is unity, the actual flux of N was derived from the nitrogen
content of produced samples and then compared with the calculated flux. The efficiency of
the source estimated in this way amounted to ~2%. A treatment of the plasma container with
boric acid improved the performance of the RF-source. This is due to the coating of the walls
of the plasma container with boron, which reduces the recombination rate at the walls.

A study of the mechanism of the growth of Fe\textsubscript{4}N on a MgO(100) substrate was
undertaken. We investigated samples that contained an insufficient amount of N for the
formation of pure Fe\textsubscript{4}N. To our surprise, the α′ phase with a lower nitrogen content did not
form. The samples grown consisted of pure α-Fe and Fe\textsubscript{4}N. Moreover, both phases were
growing epitaxial on the MgO(100) substrate at the temperature of 350 °C. When grown at
RT, the sample consisted of a nanocrystalline Fe-N material as was shown with XRD. The
uptake of N in this two cases was the same. This fact led us to the conclusion that the sticking
coefficient of N atoms to the surface of the growing Fe-N sample is equal to unity. Otherwise
it would depend on temperature. If the flux of N is not high enough and only a small (<30%)
amount of Fe\textsubscript{4}N can be formed, the growth mode changes. In this case the formation of four
crystallites of Fe\textsubscript{4}N tilted by ~6.5° with respect to the <001> direction of the substrate was
observed. This fact was assigned to a competing mechanism of nucleation of the phase where
the formation of Fe\textsubscript{4}N takes place via nitridation of epitaxial film of α-Fe. Further, we
investigated the role of hydrogen in the production of the films. We showed that the presence
of hydrogen in the source increases the efficiency of it roughly by a factor of three in case the
source is not properly coated with boric acid. This is due to the reduction of the
recombination rate at walls of the plasma container by passivation with hydrogen. Hydrogen
also influences the growth itself. It supplies an escape root for extra nitrogen, so that the pure
Fe\textsubscript{4}N with better crystalline properties is formed when hydrogen is admitted to the gas
mixture. The optimal substrate temperature was found to be 400 °C. At a slightly higher
temperature (~460 °C) the decomposition of the nitride phase occurs and a pure iron film was
obtained. Using optimal conditions of growth we managed to obtain a excellent
monocrystalline film with very low density of defects.

We continued the study of the growth of Fe\textsubscript{4}N on a different substrate. A Cu(100)
single crystal was used. In-situ STM technique was employed to study the morphology of
samples of sub-monolayer thickness. As a preparatory study, we exposed the Cu(100) surface
kept at 400 °C to a flux of N from the RF-source. This action resulted in the sticking of N
atoms to the copper surface. High-resolution STM images taken at RT allowed us to see
separate atoms of N, which were changing their configuration at the surface from one scan to
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Another. The quantitative analyses of the amount of moving and steady atoms allowed us to
determine the diffusion barriers for isolated atoms (it amounted to \(E_{\text{is}}=(0.88\pm0.05)\ eV\)) and
for those in clusters. When Fe was deposited at the Cu(100) surface kept at 400 °C with no
flux on N present, the formation of copper islands was observed. Apparently, these islands
were covering the clusters of iron, which were embedded into the surface layer of the
substrate. This process is driven by the difference in the surface energies of copper and iron.
When a somewhat thicker (1.3 ML) layer of iron was deposited, the formation of pinholes in
the center of the Cu islands was observed. This is also a part of the segregation process. On
the bases of the observed morphology of the samples produced and of available literature, a
model of the segregation process was proposed.

This study and the developed model were useful to understand the growth of an iron
nitride on a Cu(100) substrate when both Fe and N were supplied to the surface kept at 400
°C. The first observation was the suppressed intermixing between iron and copper when
nitrogen was admitted. The formation of an iron nitride is most probably the cause of the
reduced intermixing. The formed nitride is not covered with copper, probably, because it has
a lower surface energy than Cu. The nucleation of Fe-N islands occurs in (and not on) the
surface layer of the copper substrate. Thicker layers of Fe-N cover the surface completely and
the growth proceeds in the layer-by-layer mode. The films have an exceptionally low surface
roughness. The XRD study of thick samples has proven that epitaxial films of Fe\(_4\)N(100) are
formed. This phase can have two types of termination of the surface: with planes that contain
N and that are free of N. However, none of these were observed with STM. Instead, flat and
continuous areas were present at the surface. This surface contained an iron grid of Fe\(_4\)N
partly occupied with N. In regions where nitrogen was present, N atoms occupied every other
4-fold hollow site. The LEED pattern taken from our samples revealed a c(2x2) or a p4g(2x2)
reconstruction of the surface depending on the growth conditions. As we found in a series of
experiments, the p4g(2x2) reconstruction of the surface is related with a higher concentration
of nitrogen at the surface. When Fe was deposited at a slow speed (~1000s/Å) in the same
flow of N, rectangular patches with a size of ~150 Å forming a regular pattern at the surface
were obtained. This pattern resembles very much the structure obtained at the Cu(100) surface
by exposing it to a flux on N ions. The main difference is that our array consisted of a
magnetic Fe\(_4\)N compound. The formation of the patchwork is the result of the nucleation of
highly stressed islands inside the copper matrix.

Finally, the two reconstructions of the surface of Fe\(_4\)N were investigated with LEIS.
The LEIS scans were fitted with simulated spectra calculated for model structures. The
measured angular scans of scattered and recoiled atoms taken from samples, which had a
c(2x2) reconstruction of the surface, were fitted using a slab representing a bulk-terminated
[100] surface of Fe\(_4\)N containing N atoms slightly shifted away from the surface. For both
samples grown on MgO(100) and on Cu(100) substrates the same arrangement of atoms at the
surface was used. A characteristic feature of an Fe-terminated surface was observed in the
experimental spectrum, indicating that a part of the surface is nitrogen-free. We confirmed
that the c(2x2) reconstructed surface contains less nitrogen than the surface with the p4g(2x2)
reconstruction. The p4g(2x2) reconstruction appeared to be a “clock” reconstruction, which
has been seen at the surfaces of other metals (O on Ni(100), for example). The fits gave the
positions of the atoms with an accuracy of 0.05 Å.

The perspective use of the results presented is manifold. Further research could answer
some open questions. First of all, the presented method of the production of Fe\(_4\)N films can be
employed for the production of other nitrides. At present, several laboratories (including ours)
are already using such method for the growth of Cu\(_3\)N.

Epitaxial films of Fe\(_4\)N themselves are considered to be a good candidate for the
substitution of other ferromagnetic conductors in electro-magnetic devices. A main reason is
that these films are expected to have little intermixing at interfaces. Some work in this
direction has been already done in our group. An attempt to grow an epitaxial all-nitride
magnetic tunnel junction made of Fe$_4$N/Cu$_3$N/Fe$_4$N multilayer has been accomplished. Here,
the knowledge of the mechanism of growth of Fe$_4$N is very important for the control of the
properties of interfaces between the layers. Also, the Fe$_4$N phase can be used in spin valves
then consisting of a sandwich of layers of Fe$_4$N and non-magnetic metal layers. A reduced
intermixing as observed between copper and the iron-nitride is exploited in this case.

The research described in this thesis resulted in the production of a self-assembled 2D-
array of islands of Fe$_4$N. The density of these islands was as high as 4x10$^{11}$ cm$^{-2}$. Such an
array of magnetic islands can be used as a high-density magnetic memory medium. Further
research on the formation and properties of such array is underway.

The precise structure of the surface of Fe$_4$N can be used in theoretical calculations to
determine the electron band structure at the surface, which should depend on the surface
reconstruction. For this purpose, the position of atoms in deeper layers can also be determined
by LEIS experiments in a special geometry.

Certainly, this is not the complete list of further use and perspectives of the
accomplished work. There is always more behind the closed doors of Nature than we can
think of. And we are to open them.