Manipulation and control of the growth of magnetic iron nitride films
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Chapter 7. On the growth mechanism of Fe₄N on Cu(100)

7.1. Introduction

The growth of epitaxial layers of binary compounds starting from fluxes of the constituting atoms (or molecules containing these atoms) is an interesting topic of research. Although many examples of the growth of such layers are described in literature, there is still a lack of insight what is happening at the atomic scale during growth. Important ingredients determining the growth are the mobility of the atomic species, as well as of the molecules of the formed compound, and the creation of nucleation sites where the new species is formed. Especially the interaction of the atoms arriving at the surface with the substrate is a decisive factor for the further growth of a perfectly crystalline layer. Another important factor to understand is how to grow one particular phase out of a number of possible other phases that could be formed from the same atomic species. The complexity of the combination of such questions may well be the reason that relatively few works exist in which it is tried to unravel the growth mechanism of binary compounds. Such work was mostly done on the growth of metallic alloys and of semiconductors like GaAs [see, for example, 1-3]. The mechanism of growth of oxides and more complex compounds like high-temperature superconductors is not known in detail, although recipes were developed and are used for the growth of perfectly crystalline layers [4].

In this chapter we study the growth of epitaxial layers of γ'-Fe₄N on a substrate of Cu(100). STM was used as the major tool for the investigation of the early stages of the growth of Fe₄N on Cu(100) as well as for the study of the surface structure of deposited layers with a thickness up to 200 ML. Also AES and LEED provided information about the composition and the symmetry of the surface. With these methods we were able to understand many aspects of the growth process. We found two types of reconstruction, p4g(2x2) and c(2x2), depending on the amount of N atoms incorporated in the first layer. The c(2x2) reconstruction is also called in literature \( r(\sqrt{2}x\sqrt{2})R45^0 \), but here we will stick to the c(2x2) denomination. The p4g(2x2) reconstructed surface is shown schematically in figure 7.14. Finally we produced thick samples on Cu(100). These samples were studied with RBS/Channeling, XRD and CEMS to determine the phase, the crystalline structure and the defect density in the grown layers. In this way we were able to show that the grown layers are epitaxial and consist of the pure γ'-Fe₄N phase.

As a starting point of this study we used the method found in our group for the growth of epitaxial layers of pure γ'-Fe₄N on substrates of MgO(100). In this method Fe is deposited at a low rate (~50s/Å) in the presence of a flux of atomic N (~1x10^{12} atoms/s cm²) plus H on a MgO(100) substrate kept at 400 °C. In the rest of this paper we refer to these conditions as “standard conditions”. The epitaxial layers grown on MgO were found to have a low density of defects. RBS/channeling, XRD, CEMS and AFM were employed for the study of the properties of these samples. The admixture of H was found to be crucial in order to obtain the
pure $\gamma'$-Fe$_4$N phase. Here it has to be mentioned that other Fe-nitride phases can be formed using the same method without H, namely the hexagonal $\epsilon$ phase (Fe$_{2-3}$N) and the $\gamma''$ plus $\gamma'''$ phases (FeN). These last phases can only be formed at substrate temperatures below 200 °C [5]. They also have the Fe atoms arranged in a fcc configuration like in the $\gamma'$ phase, but with all 4 (instead of 1) of the tetragonal sites occupied with N. We were able to get some insight into the mechanism of growth (see Chapter 5). An important conclusion related to the growth mechanism was that both Fe and N atoms can cover long distances over the surface of the growing layer before being incorporated into the phase formed.

Other important ingredients used as a starting point for the present study are the structures formed after deposition on Cu(100) at 400 °C of pure Fe and of pure N separately, as discussed in the previous chapter. Here it was concluded that both species are very mobile at this high temperature. Both species form islands. The Cu-N islands are observed at the surface; the Fe islands are buried with one or several Cu layers, forming islands of Cu. In some cases, copper islands with a c(2x2) superstructure were observed. We interpreted these reconstructed areas as Fe islands covered with 0.5 ML of Cu. It was also found that the Fe-Cu intermixing is prevented if the Fe deposition takes place in the presence of a flux of atomic N.

### 7.2. The early stages of growth

When atomic N and Fe arrive at the surface of Cu(100) at the same time, the appearance of the surface as observed with STM is not anything like the surface covered with only one of the atomic species. Figure 7.1 shows a set of STM images taken from a sample grown at standard conditions. The amount of deposited iron was equivalent to 0.7 ML’s. The LEED pattern showed a c(2x2) reconstruction of the surface. The surface consists of flat terraces and depressed islands. These terraces must be Cu terraces, unaffected by the deposition of Fe and N. The amount of islands increases when more Fe + N is deposited. The depressed areas must then consist of the new growing phase, since both Fe and N are present at the surface, according to the Auger spectra taken. The level of the islands seen with STM is lower than the level of the flat terraces by an amount that varies in the range of 0.3-1.4 Å with applied voltage on the STM tip. As will be shown later, thick samples grown under these conditions consist of pure Fe$_4$N.

The STM signal is determined by the density of electron states (DOS) near the Fermi level and, of course, by the distance of the tip to the surface. When two different chemical species are present at the same actual height at the surface, they may be seen with STM at different heights. This effect, also called chemical contrast, is the cause for the typical depressed appearance of N adatoms on metal surfaces [6, see also Chapter 6]. The difference in DOS for different species at the surface causes also the change of their apparent height with applied voltage. This is readily seen in figure 7.2, where the islands appear to be flat and almost level with the surrounding area in one image and show a much larger contrast when taken with a different voltage. This points to a different electronic structure and, therefore, different chemical composition of the islands in comparison with the surrounding flat areas, the difference being the presence of Fe plus N in these regions. The conclusion is that the surface of these islands is probably close to level with the topmost layer of the flat terraces surrounding them.

Figure 7.3 shows the appearance of the surface after deposition of 0.6 ML of Fe plus N at standard conditions. The LEED pattern taken from this sample reflected the p4g(2x2) reconstruction of the surface. The c(2x2) and/or the p4g reconstructions were seen with LEED on all our samples when Fe$_4$N is formed. Neither iron nor nitrogen form this type of reconstruction on a Cu(100) surface as was shown in the preparatory study of Chapter 6.
On the growth mechanism of Fe₄N on Cu(100)

**Figure 7.1.** 0.7 MLs of Fe + N were deposited on Cu(100) at standard conditions. The reconstruction of the surface is c(2x2). The depressed islands form the growing phase. The apparent depth of depressed islands changes with the voltage applied, the actual height of the islands may be level with the surrounding copper terraces. For more details see text.
Obviously, the surface of the islands of the growing phase gives rise to these LEED patterns. This is confirmed by the observation of atomic arrangements with both types of symmetries on Fe-N surfaces with atomic resolution STM (see figure 7.6e). Also in this case the islands of the growing phase appear darker than the flat terraces, pointing to a chemical contrast. An obvious difference in the appearance of the surface of these two samples is the presence of protrusions (white dots) inside the area of depressed islands of the sample with a c(2x2) reconstruction. The height of the protrusions varies with applied voltage in the range of 0.8-2.8 Å, their typical size is 10-20Å. In many cases these protrusions are higher than the level of flat terraces. They again show a chemical contrast with the rest of the surface of the islands.

Figure 7.2. STM images taken with voltage of −0.09V and +0.09V. The contrast, seen in the right image, has nearly disappeared in the left frame.

In both samples, meandering steps are visible on the otherwise flat Cu terraces. Such features are not visible on a freshly cleaned and annealed Cu(100) surface. These steps, most clearly visible in figure 7.3, point to the formation of Cu islands possibly formed by surface diffusion of Cu adatoms. These adatoms must be created in the process of nucleation of Fe-N islands.

A very low deposition rate of Fe resulted in a different picture of nucleation. The STM images in figure 7.4 were taken from a sample grown with a deposition rate of Fe of the order of ~1000 s/Å (instead of ~100s/Å). A typical p4g(2x2) LEED pattern was observed confirming that the islands consist of Fe₄N. The surface is covered with rather ordered, self-organized arrays of islands of square or rectangular shape with their edges aligned along <001> directions. The degree of long range order is remarkable. The presence of both Fe and N at the surface is independently confirmed by AES. The lateral size of the islands is 40 nm on the average. The surface surrounding the islands is homogeneous without signs of inclusions. Since increasing the exposure increases the density of islands, we assign the area in between the islands to clean Cu and the islands to Fe-N. The islands of the growing phase do not look depressed but slightly (1-2 MLs) protruding in this case. Nevertheless, the ratio of the Auger peaks indicates that the FeN islands must be several (3 or 4) layers thick in order to be consistent with the morphology revealed with STM. This implies that the islands extend deep into the substrate. Inside the islands, white blobs (with a height depending on the tunneling parameters) appear randomly distributed [7].
Figure 7.3. 0.6 ML of Fe + N were deposited on Cu(100) at standard conditions. The reconstruction of the surface is p4g(2x2). The depressed islands are the growing phase. Steps of copper islands made of emerging Cu adatoms are marked with arrows. For more details see text.

Figure 7.4. Patterning of Fe-N islands obtained after a very slow deposition of Fe.
It is interesting to compare the arrangement and appearance of the islands visible in the figures 7.4 with those observed in ref. [8] (see figure 7.5). Here a Cu(100) substrate was bombarded with low-energy nitrogen ions and then annealed (figure 7.5). A particular arrangement of CuN islands appears at the surface after this treatment. When Fe is deposited subsequently at RT the Fe nucleates in between these Cu-N islands.

The appearance of a thicker film 2.3 ML’s as seen with STM is shown in figure 7.6. The deposition resulted in the full coverage with the growing phase and no terraces of copper were observed at the surface. A flat and continuous film is formed. However, the terraces of the Fe-nitride contain two types of areas, which are clearly seen everywhere at the surface. We will call these areas white and gray regions. The height difference (0.2-0.5 Å) is too small to be caused by a step. Again the different appearance of the two regions must be due to a chemical contrast of the two areas. The STM image in figure 7.6e reveals the atomic arrangement of the gray area. A close look at the white grid in the gray area reveals a weaving pattern (follow the black guide lines), which has a p4g(2x2) symmetry in accordance with the LEED pattern obtained for this sample. The black spots, which appear as holes in the grid, are interpreted as N atoms. They occupy every second 4-fold hollow site in the plane of iron (white grid) as it occurs in N containing planes of Fe₄N. It seems that the white regions contains no N atoms, which makes them look featureless in the majority of STM-images. Figure 7.6f resolves the cubic symmetry of the white area. It looks as if this area also has a p4g(2x2) symmetry, although we do not have enough data to prove that all white areas have this type of reconstruction. We believe that the presence of N atoms introduces the difference between white and gray regions and that the actual height level of both regions is the same.

The bulk-terminated (100) surface of Fe₄N has a c(2x2) symmetry with respect to the surface of a Cu(100). This is illustrated in figure 7.8. There are two planes of Fe₄N parallel to the (100) plane: N-containing and N- free planes. These planes can be the two possible surface terminations of bulk Fe₄N, which we will call N-terminated and Fe-terminated. Strange enough, we see no other appearance of surfaces of all produced Fe-N layers (including thicker films) than terraces with white and gray regions. This points to a mixed
On the growth mechanism of Fe₄N on Cu(100)

Figure 7.6. STM images taken from a sample after deposition of 2.3 MLs of Fe plus N on Cu(100) at standard conditions.
termination, whereby both Fe-terminated and N-terminated surfaces of Fe₄N adsorb N atoms, regardless of the occupation with N of the second layer. Also for thicker layers we observed only the white and gray areas, and no terraces with a different termination.

Figure 7.9. AES intensity ratio of peaks of Fe and N for a set of produced samples. On average the amount of N at the surface is higher for samples with p4g(2x2) reconstruction of the surface.
An image with atomic resolution of a surface with the c(2x2) structure is also observed with STM (figure 7.8). The image shows a square arrangement of atoms as expected for the c(2x2) reconstruction. The LEED pattern for some samples shows bright spots of c(2x2) and, at the same time, faint spots of p4g(2x2) proving the presence of areas with both reconstructions.

The ratio of intensities of Auger peaks of Fe and N changes from one sample to another. These ratios are plotted in a graph shown in figure 7.9. The average value of this ratio for samples with c(2x2) reconstruction of the surface is higher than that for samples with p4g(2x2) reconstruction. However, there is a large spread in the data points. The correlation between the reconstruction and the concentration of N at the surface was established in the following experiment.

**Figure 7.10.** Manipulation of the reconstruction of the surface by changing the concentration of nitrogen at the surface. The sequence of LEED patterns was taken from the same sample after certain treatments. See text for details.

A sample with a thickness of 20 MLs with a c(2x2) reconstruction of the surface was produced by the standard procedure. The surface of this sample was exposed to a flux of N from the RF-source at 400 °C for 5 minutes. After this exposure the LEED pattern had changed from c(2x2) to p4g(2x2) as seen in figure 7.10b. The ratio of Auger signals of Fe and N changed from Fe99/N379=3.37 to 1.80. This experiment proves that the cause of the p4g(2x2) reconstruction is extra nitrogen at the surface. In order to reduce the concentration of N at the surface of this sample, we deposited 4 ML’s of iron at RT onto this sample. The iron to nitrogen ratio changed to 2.47 and the LEED pattern changed back to the c(2x2) pattern, although with relatively diffuse spots (figure 7.10c). The same behavior was observed when only 2 ML’s of iron are deposited on a p4g(2x2) reconstructed surface. A mild annealing at 200 °C improved the surface structure and a sharp c(2x2) LEED pattern was
obtained (figure 7.10d). Thus, the change of the reconstruction turned out to be reversible and directly dependent on the concentration of N at the surface. With this knowledge, we are able to control and manipulate the reconstruction.

After deposition of 4 MLs of iron at RT (figure 7.10c), the surface still contained a lot of nitrogen according to AES. It implies that N floats on top of the growing layer of iron even at RT. This effect we observed earlier when we grew Fe on top of a Fe$_3$N/Cu(100) structure (see Chapter 6).

We also noticed that the c(2x2) reconstruction of a freshly produced hot sample can change to p4g(2x2) during cooling down the sample to RT. The temperature of the transition was not well defined and was estimated to be between 200 °C and 300 °C. We found that this change of the surface reconstruction is reversible. If the p4g(2x2) reconstruction is induced by the stress in the layer, which increases at lower temperature due to a possible difference in the expansion coefficients of Cu and Fe$_3$N, the transition temperature probably depends on the concentration of N at the surface.

Figure 7.11. Films with a thickness of 7MLs. There are terraces of only 3-4 levels present at the surface suggesting the growth and coalescence of islands. The black spots are believed to be holes created due to decomposition of Fe$_3$N.
Figure 7.11 shows the appearance of thicker films. The surface of the growing layer consists of flat terraces containing islands with a height difference of only 3-4 levels over an area of 0.5x1.5 µm². Such a small corrugation is seldomly encountered in growing films. The step heights correspond to the Fe₄N phase. Also for thicker layers we observed with LEED the two types of reconstruction of the surface. We conclude that the growth of thicker films proceeds by growth and coalescence of islands.

The formation of holes was observed in thick layers (figure 7.11). These holes can be as deep as the layer thickness. The holes can be related with the decomposition of Fe₄N layers. The temperature of decomposition of Fe₄N estimated in our earlier experiments is 460 °C. At 400 °C fractional decomposition of this unstable phase is possible, which results in the formation of N₂ and pure Fe. The Fe atoms would diffuse at the high temperature of 400 °C to be included elsewhere in the growing Fe₄N layer.

![Graph](image)

**Figure 7.12.** The CEMS spectrum of a 250Å thick Fe₄N sample grown on Cu(100). The solid line is the fit of the spectrum with components as indicated by the dashed lines. The peaks are much broader than in case of a MgO(100) substrate. The fitting parameters are listed in table 7.1.

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<td>-</td>
<td>1.39</td>
<td>0.40 0.4</td>
</tr>
</tbody>
</table>

**Table 7.1.** The parameters used to fit the spectrum in figure 7.12.

In Groningen we have grown a series of relatively thick samples (~250Å) on a Cu(100) substrate, using the same standard conditions. The layers were characterized with CEMS and XRD. LEED showed the c(2x2) reconstruction of the surface, which is expected for bulk-terminated Fe₄N. A CEMS spectrum is shown in figure 7.12. Again, as in the case of the films grown on a MgO(100) substrate, the pure Fe₄N phase was formed. However, the peaks in the CEMS spectrum are noticeably broader, and the hyperfine field parameters are slightly smaller (see table 7.1). This must be due to a variation of hyperfine parameters due to
Chapter 7

defects. Channeling in the film was not observed, which again points to a higher density of defects than present in films grown on MgO(100).

The XRD examination showed the epitaxial nature of the film with no tilting of the film lattice with respect to the substrate lattice. The orientation relationship between the film and the substrate is the following:

\[ [100]_\gamma \parallel [100]_{Cu}, (001)_\gamma \parallel (001)_{Cu}. \]

Figure 7.13a represents the area-scan of (113) reflections from the film and from the substrate in reciprocal space. The region of reciprocal space, which was scanned, is depicted in figure 7.13b. By definition, the [113] directions for all cubes regardless the size should be parallel. The line drawn on the experimental scan crosses the origin of the coordinates. It also crosses the maximum of the (113) reflection from the copper single crystal. The reflection from Fe\(_4\)N is not precisely located on this line, showing that the film is stressed and tetragonally distorted. However, the fact that \(k_{\parallel}\) of the film is not equal to the one of the substrate implies that the film is partly relaxed and the in-plane lattice parameter of the film and the substrate are different. From the values of \(k_{\parallel}\) and \(k_{\perp}\) we deduced the lattice parameters of the tetragonally distorted Fe\(_4\)N phase:

- in-plane \(a = 3.781\ \text{Å}\),
- out-of-plane \(c = 3.806\ \text{Å}\).

We conclude that Fe\(_4\)N grows epitaxially on a Cu(100) substrate although with a slight tetragonal distortion and with a relatively high density of defects.

![Figure 7.13](image)

**Figure 7.13.** a) An XRD scan of reciprocal space. b) Illustration of the region of reciprocal space, which was scanned.

7.3. Summary and discussion

The features we observed with STM and other techniques contain a wealth of information about the surface processes. In this section we will use this information for the development of a model of nucleation and growth of Fe\(_4\)N on Cu(100). The arriving species to be considered here are iron, nitrogen and hydrogen atoms. Hydrogen is not expected to play a role in the nucleation process of Fe\(_4\)N since in does not stick well to a hot copper...
On the growth mechanism of Fe₄N on Cu(100) surface [9]. The observed depressed islands contain all the Fe and N atoms deposited to the surface since the flat copper terraces visible in STM images are continuous and unaffected by these species. We concluded already that these islands are about level with the copper terraces; the depressed appearance is due to the fact that the Cu and the Fe-N phase have different DOS near the Fermi level. We know that arriving iron atoms (in the absence of nitrogen flux) are incorporated into the copper surface, and form clusters of iron atoms, which are finally covered with a copper island with a thickness of one or more ML’s (see Chapter 6). The same process can occur here during the very early stage of nucleation when both Fe and N are deposited. It seems that N atoms have a much higher affinity to Fe atoms than to Cu atoms at the substrate temperature of 400 °C. This leads to migration of the N atoms to the (maybe buried) Fe clusters and to chemisorption of N at these Fe clusters. In this way the Fe nitride is nucleated as an island at the same height as the surrounding Cu. The presence of a possible layer of Cu on top of the Fe clusters would hardly impede this process. As in the case for deposition of Fe only, the number of islands increases with coverage, which corroborates our view of the nucleation process. When the compound is formed, the layer of Cu on top will diffuse away. Apparently, the surface free energy of Fe₄N is lower than that of iron and of copper. The fact that the depressed islands are not covered with copper is confirmed by the different appearance in comparison with copper terraces in STM images and also by Auger spectroscopy. The white protrusions seen in figure 7.1 might be copper atoms covering a region of iron that has not yet reacted with nitrogen. A different interpretation of these protrusions, namely as being small islands of Fe growing as a next layer on top of the Fe-N islands cannot be excluded.

The nucleation process may be different if the flux of Fe is very low compared to the flux of N. In that case the surface, partially covered with Fe-N islands, reveals a self-organized pattern of these islands. As in the case of a higher Fe flux, the FeN islands extend into the substrate. The patterning is similar to the patterning observed after bombarding plus annealing of a Cu(100) surface to a flux of N only (figure 7.5 [8]). This fact makes it probable the N patches formed are the nucleation centers for the growth of the Fe-N phase. The phenomenon of the creation of a (probably ferro-magnetic) Fe-N phase as islands with dimensions of about 40 nm with a certain degree of self-ordering is in itself very interesting. We concluded, that the thickness of these islands is several layers. If the patches are ferromagnetic, then such a configuration could be used for high-density storage of information. This is a reason for a lot of research activities with the aim of producing such nano-structures [10, 11].

As mentioned we observe meandering steps on Cu surfaces covered with “depressed islands” of Fe-N. The appearance of such steps of copper terraces is quite different in comparison with a clean copper surface before deposition (see figure 7.3). We interpret the formation of meandering steps as a result of diffusion of copper adatoms created in the formation of depressed Fe₄N islands.

A higher amount of deposited Fe plus N results in the formation of a smooth, continuous film. Two types of reconstruction of the surface are observed with LEED in this case, dependent on the growth conditions: c(2x2) and p4g(2x2). The c(2x2) reconstruction can be explained by the bulk termination of the surface of the Fe₄N. A complete layer of Fe₄N shows a characteristic pattern of two regions at the surface: white and gray as described earlier. These regions are on the same level. We interpret these regions as a (100) iron plane of Fe₄N with chemisorbed N atoms in every second 4-fold hollow site (the gray region) and the same plane with no N (the white region). Both types of reconstruction can also be recognized in STM images (see figures 7.6 and 7.8 ) as square or as distorted-square patterns.
Both the c(2x2) and p4g(2x2) reconstructions of the surface were observed before in different systems. The adsorption of C, N or O on metal surfaces with square symmetry often causes the surface to change its symmetry. For example, in case of O on Cu(100) and Ni(100) the surface undergoes a c(2x2) reconstruction [12, 13]. In the case of N or C on Ni(100) the reconstruction can be p4g(2x2) [13, 14]. The schematic positions of atoms in the c(2x2) and p4g(2x2) reconstructed surface is drawn in figure 7.14. In this scheme iron atoms turn around the closest N atom clockwise or counterclockwise. This picture of the displacement of atoms can explain the weaving pattern appearance of the surface in figure 7.6e. Pairs of iron atoms move closer to each other, forming a “bridge”. There are two types of white regions that can be distinguished: the small areas surrounded by gray patches and large white islands (see figure 7.6). It would be logical that the arrangement of iron atoms in small white patches would be the same as in the surrounding gray area. This arrangement can even be observed (or rather guessed) in figure 7.6f. The height level in the middle of large white islands is 0.2-0.5 Å higher than that at the edges. This means that these islands are stressed. The p4g(2x2) reconstruction of the surface is one of several ways to release the stress in the layer. Iron atoms in such a surface are packed closer than in a cubic arrangement. The curvature of the island is another way of the stress relief. We were not able to resolve the atomic arrangement of large islands.

In spite of two possible terminations of the bulk Fe₄N crystal, we see only one appearance of the surface, that is white and gray areas at the same level. This points to a mixed termination whereby both Fe-terminated and N-terminated surfaces of Fe₄N adsorb N atoms, regardless of the occupation with N of the subsurface layer. At the growth temperature used here the mobility of N atom in Fe₄N is sufficient for the re-arrangement of N atoms to form the Fe₄N structure with alternating N-containing and N-free planes. We suppose that this happens during the growth of thicker layers.
The two reconstructions of the surface were correlated with the concentration of N at the surface of the sample. The p4g(2x2) reconstruction occurs at higher concentration of N. In the experiment described above we showed that the c(2x2) reconstruction can be transformed into the p4g(2x2) reconstruction by admitting more nitrogen to the surface. The p4g(2x2) reconstruction can be changed back to the c(2x2) by depositing iron without offering any nitrogen. We also noticed that the deposition of a large amount of Fe on the p4g(2x2) reconstructed surface at RT does not result in the burying of the Fe$_4$N under an iron layer but in the floating of nitrogen on top of the surface. Nitrogen induces a c(2x2) reconstruction in this case.

At higher thickness the growth proceeds by the growth and coalescence of islands. This results in large flat areas with only 3-4 monolayer height difference over an area of at least 1 µm$^2$. This is an exceptionally high flatness of a growing layer. The holes in the film can be as deep as the thickness of the layer. They can be created due to the decomposition of Fe$_4$N since the substrate temperature was close to the decomposition temperature of 460 °C.

The role of H+H$_2$ during the growth process on Cu(100) was not investigated. We assume that the presence of H prevents the formation of Fe-nitrides containing more N (like the $\gamma''$, $\gamma'''$ and $\varepsilon$ phases). This assumption is based on our experience with the growth of Fe$_4$N on MgO(100) where the excess nitrogen is removed from the surface in the presence on H, probably by the formation of NH$_x$ compounds (x=1-3) or the decrease of the barrier for the recombination N atoms into a N$_2$ molecule.

7.4. References

5. D.M. Borsa, private communication.