Importance of the Study

The study investigates the mechanisms of the growth of magnetic iron nitride films, which are promising materials for magnetic data storage, magnetic sensors, and magnetic field generators. The growth of these films is influenced by various parameters such as temperature, pressure, and composition. The research also explores the control of the magnetic properties of these films, which is crucial for their applications.

Methodology

The study employs a combination of theoretical and experimental approaches. Theoretical calculations are used to predict the growth behavior of the films under different conditions. Experimental techniques, such as X-ray diffraction, magnetometry, and scanning electron microscopy, are employed to characterize the grown films and compare them with theoretical predictions.

Results and Discussion

The results show that the growth rate and the magnetic properties of the films can be controlled by adjusting the deposition parameters. The films exhibit a high magnetic anisotropy, which is essential for their use in magnetic data storage. The study also reveals that the magnetic properties can be tailored by modifying the composition of the films.

Conclusion

The research provides a comprehensive understanding of the growth and magnetic properties of magnetic iron nitride films. The findings have implications for the development of advanced magnetic materials. The study also opens up new avenues for future research on this fascinating class of materials.

References


A preparatory study: N and Fe on Cu(100)

Chapter 6. A preparatory study: N and Fe on Cu(100)

6.1. Introduction

As was shown in the previous chapter, under certain conditions Fe₄N can be grown epitaxially on MgO(100) in spite of the large mismatch between the lattices of these two compounds. Fe₄N crystallizes in a well-ordered single crystal with a low density of defects. The growth mechanism was partly clarified and described in the previous chapter. For a more detailed picture of the growth we needed a technique which could disclose the surface structure and topography of grown films. The scanning tunneling microscope (STM) is an excellent tool for this purpose. It provides a picture of the atomic arrangement of a surface by sensing corrugations in the electron density of the surface that arise from the positions of surface atoms. In order to make use of STM we have installed a radio-frequency (RF) source for atomic nitrogen on an UHV-chamber, which was supplied with STM, LEED and AES in the group of prof. R. Miranda at the Universidad Autonoma de Madrid (see chapter 2). The insulating properties of MgO made it impossible to perform in-situ STM scans of layers grown on MgO(100). Only in air we succeeded to establish an electric contact with the grown film and obtained STM images. A Cu(100) single crystal was used as a substrate to grow Fe₄N under the same conditions that were successful in the case of the MgO(100) substrate. In the preparatory study we investigated the adsorption at 400°C and the diffusion at RT of N atoms at a Cu(100) surface and the intermixing of Fe with Cu in the absence of the flux of N atoms. We imaged the intermixing process between Fe and Cu, occurring at 400°C, and we propose a model describing the process. Iron nitride Fe₄N was grown at temperatures in the range from 300 up to 400°C. As will be shown in this chapter the intermixing is largely suppressed when Fe is deposited in a flux of atomic N. That happens because the γ'-Fe₄N phase stabilizes on the substrate and this reduces the mobility of Fe atoms as well as shifts the thermodynamic equilibrium. These results were published in a number of papers [1-3] and will be extensively presented in this chapter.

6.2. The test sample: Fe₄N on MgO(100)

The first experiment done in Madrid was meant to check whether we can use the recipe obtained in Groningen to grow Fe₄N samples. We have grown a sample under the established conditions on a MgO(100) substrate. The LEED pattern showed diffused spots arranged in the c(2x2) symmetry. Unfortunately, we were not able to perform STM scans in-situ on this sample because we could not establish an electrical contact with the film. But we managed to do so in air, when the sample and the STM microscope were taken out from the vacuum.

This sample was taken to Groningen for examination of its bulk properties. The thickness of the sample was measured with RBS and amounted to 240Å. This corresponded to
a growth rate of ~45s/Å, which is comparable with the one we used in Groningen. Channeling (with a minimum yield of 60%) in the grown film showed that the film is epitaxial, although it was not as good as for the best sample produced thus far. XRD spectra also showed a strong texture confirming the epitaxial nature of the film. In the CEMS spectrum the three sextets of Fe$_4$N (82%) and the doublet of the surface oxide (18%) could be identified. All these data point to the reproducibility of the results we obtained in Groningen.

An STM-image of the oxidized surface of the sample is shown in figure 6.1. The surface roughness (rms) was found to be as low as 1.5nm on an area of 500x500 nm$^2$. The surface consisted of patches of the size of ~50 nm, which were very flat.

This preliminary test proved that the conditions in the two UHV chambers are similar and can be reproduced and that the results can be compared. It also showed that we could not make use of the STM microscope while using an insulating MgO substrate. This fact forced us to change the substrate to a conductive one. All further research described in this, and in following chapters, was done on a Cu(100) single crystal.

### 6.3. Adsorption and diffusion of N on Cu(100)

When a chemical compound is to be grown, the growth starts with adsorption and diffusion of the deposited reagents. The adsorbed species react with each other and with the surface, forming chemical bonds. The initial aggregation of the film material is called nucleation. The nucleation of the phase is driven by the surface diffusion, which is a very important determinant of the film structure. The experiment described in this paragraph was meant to determine the diffusion parameters of N atoms on a Cu(100) substrate.

The surface of an as-prepared Cu(100) single crystal (see chapter 2) contained no carbon or oxygen contaminations according to AES. The LEED pattern showed sharp spots with a low background. The surface of the substrate exhibited atomically flat terraces with a width of 200 Å, or more, separated by mono-atomic steps (figure 6.2). In a few cases rows of Cu atoms could be resolved in STM images which allowed us to calibrate the in-plane scale of the tip of the microscope. The out-of-plane scale was calibrated with mono-atomic steps of copper.
The sticking of N to the copper surface and the surface diffusion were studied in the following experiment. The Cu(100) surface, kept at 400°C, was exposed to a flux of N/N$_2$ plus H/H$_2$ from the RF-source for 8 minutes and then immediately cooled down. The total flux of atomic N arriving at the surface was estimated to be $\sim 10^{15}$ atoms/cm$^2$ for the total time of the exposure. This number corresponds to the density of four-fold sites at a Cu(100) surface and to the density of copper atoms in a 1 monolayer thick film. At a temperature of 400 °C H atoms and H$_2$ molecules are not expected to stick to a copper surface [4]. The LEED pattern appeared to be unchanged in comparison with the LEED pattern obtained for the bare Cu(100) surface. However, an Auger signal of nitrogen was clearly observed.

STM images further indicated the presence of N atoms at the exposed copper surface (see figure 6.3). N atoms show up as depressions. The atomic resolution allows to see rows of nitrogen atoms along <100> directions. N atoms also form bar- or cross-like clusters or appear as isolated atoms. The distance between closest N atoms in clusters is $\sim 3.6$ Å. This corresponds to the occupation of every second four-fold site and to a local c(2x2)
reconstruction of the surface inside a cluster of N atoms. Clusters with a cross-like shape are often seen, indicating that this structure is relatively stable. Also it is clearly seen that N adatoms decorate the steps of Cu(100) as well (see figure 6.3b). In principle, their presence at step edges can impede the emission of Cu adatoms from steps, which would occur at a temperature of 400 °C. In a sense the steps are stabilized by the decoration.

![Figure 6.4. N on Cu(100).](image)

The time delay between the images is 63 seconds. Black features represent adsorbed N atoms. The shape of the cross-like feature changes revealing the diffusion of N atoms (see text).

The sequence of frames shown in figure 6.4 was taken with a time interval of ~90s. One can see that the configuration of N atoms changes from one frame to another. This shows the surface diffusion of N atoms on a Cu(100) substrate at RT. N atoms jump from one fourfold symmetry site to another. The diffusion in two dimensions can be described by the random-walk theory [5]. The probability of finding an isolated adatom displaced by i,j lattice constants after time t is given by:

\[
P(i,j) = e^{-4ht} \times I_n(2ht) \times I_j(2ht),
\]

Here \(h=h_x=h_y\) is the hopping rate in case of isotropic diffusion of isolated atoms; \(I_n\) is the modified Bessel function of the first kind. The number four in the exponent accounts for four possible directions of hopping. In case one or more neighbors are present, this number should be reduced accordingly. \(P(0,0)\) is the probability of observing the adatom in the same site in the following frame, which can be found experimentally as \(P(0,0) = N/M\), where N is the number of observations where the adatom has not moved, and M is the total amount of observations. Thus we get the following equation for the hopping rate:
The hopping rate has an exponential dependence on the temperature: 

$$h = \frac{-\ln(P(0,0))}{4t}.$$ 

Here $v_0$ is the attempt frequency, $E$ is the diffusion energy barrier.

The coverage with N atoms amounts to 0.1 ML, although the amount of offered nitrogen was equivalent to ~1 ML. About 80% of the adatoms are in clusters, the rest appears as isolated adatoms. Isolated adatoms look much more mobile than those in clusters. We identified only two isolated adatoms, which apparently did not move during the time interval between the two scans, out of 60 observed. Then $P(0,0)$ must be of the order of 0.03 and the hopping rate $h=0.01$ s\(^{-1}\). Taking the attempt frequency equal to $10^{13}$ s\(^{-1}\) [6], the diffusion barrier for isolated atoms is equal to $E_{h}=0.88\pm0.05$ eV. The error of this estimation is the sum of the statistical spread $\sigma(P(0,0))=\sqrt{N(1−N/M)/M}$ and the uncertainty in the estimation of the attempt frequency. The significance of the error of the estimation of the attempt frequency is reduced because the energy is defined by the logarithm of the attempt frequency. It is apparent that adatoms with three and four closest neighbors move extremely rarely and no moves of them were observed. Adatoms with 2 closest neighbors move also rarely, although we found one case out of 32 where such an adatom did move. This would correspond to a dissociation energy $E_2=(0.99\pm0.05)$ eV if the role of second-closest neighbors is negligible. Adatoms with 1 closest neighbor are also better bound since only 5 adatoms have moved out of 89 observed. The resulting dissociation energy amounts to $E_1=(0.95\pm0.05)$ eV, again neglecting the influence of more distant neighbors.

### 6.4. Intermixing of Fe on Cu(100)

The structural and magnetic properties of ultrathin iron films grown on Cu(100) substrates have been extensively investigated during the last 15 years [7, 8]. This interest was triggered by the possibility to produce thin fcc Fe films by epitaxial growth at RT or lower temperatures [9]. The fcc $\gamma$-Fe phase exists in the bulk at temperatures above 1186 K. Ab initio calculations predicted that magnetic properties of the fcc Fe structure are strongly lattice-parameter dependent [10]. The Fe/Cu system is also interesting from the application point of view, for example, in building spin valves. It was soon realized that the Fe-on-Cu system is metastable, i.e. the surface free energy of Fe ($2.9$ J/m\(^2\)) is larger than the surface free energy of Cu ($1.9$ J/m\(^2\)), so Cu has a strong tendency to segregate to the surface [7]. For deposited films, the onset temperature for this process depends on the film thickness, and varies from room temperature for sub-monolayer films to 150 °C for thicker films (films fully covering the copper substrate) [11].

The mechanism of intermixing is still a point of discussion. For films deposited at RT it was believed that the intermixing is due to the exchange mechanism between arriving Fe atoms and Cu atoms of the substrate. More recent results point to the important role of steps. Either because the Fe atoms have exchanged place with the Cu atoms, or because the Fe atoms are incorporated into the vacancies present in the surface, the stress induced by the presence of the Fe inclusions could be responsible for the strong modification of the steps observed at RT [12]. These modified steps could serve as emitters of Cu atoms. The intermixing is a diffusion-driven process and at elevated temperatures the intermixing is more pronounced. In the case of Fe films deposited at RT and then annealed at high temperatures (490 K), Cu atoms from the substrate diffuse to the top surface through channels (pinholes) created in the Fe film [13].
Here we investigate the intermixing process, which occurs when Fe is deposited in the presence or absence of a flux of atomic nitrogen at the temperature of 400 °C. We monitored the composition of the surface with AES. The main result of this section is summarized in figure 6.5, which shows the Auger electron spectra taken after depositing of ~1.3 ML of Fe on Cu(100) under three different conditions: a) with the substrate held at room temperature; b) with the substrate at 400 °C; and c) with the substrate at 400 °C in the presence of a flux of atomic N. For this coverage, when iron is deposited at RT (case a), the Auger signals corresponding to the Fe MVV Auger transition (47 eV) and the Cu MVV transition (60 eV) have approximately the same intensity. At 400 °C (case b), as a consequence of the strong intermixing between the deposited Fe and the Cu substrate, the signal corresponding to Fe is barely discernible, indicating that all the material close to the surface is Cu, the deposited Fe being buried deep into the substrate. However, in the last case (case c), the intensities of the Auger signals are almost identical to those taken after deposition at RT, thus proving that the presence of N at the surface has suppressed the intermixing between the deposited Fe and the Cu substrate, or at least has reduced it to levels similar to those taking place at room temperature.

As a consequence of the different diffusion processes, the morphology of the surface presents very different aspects. After depositing 1.3 ML of Fe at RT the film has already started a stable layer-by-layer growth: the first level is almost completely filled and, except for some defects, there are at most three levels present on the surface (figure 6.6). As mentioned above, intermixing in this case seems to be limited to the first layer only. At 400 °C (figure 6.7), on the contrary, the film consists of circular islands, with a mean radius of 100 Å and a height ranging between 10 and 50 Å. Obviously this is the consequence of the strong intermixing of iron and copper. The STM images represent a screenshot of the segregation process of copper, which was interrupted by cooling the sample. As shown by AES, these islands are composed primarily of Cu. The LEED pattern reflects the same structure as of a Cu(100) substrate suggesting that round islands have a very flat and ordered surface. The density of islands amounts to ~50x10^{10}/cm^{2}. Some of the islands have a pinhole in the center with a radius of ~10-20 Å.
Figure 6.6. 1.3 ML of Fe was deposited onto a Cu(100) substrate at RT.

Figure 6.7. 1.3 ML of Fe was deposited onto a Cu(100) substrate at 400°C.

Figure 6.8. 1.3 ML of Fe plus N was deposited onto a Cu(100) substrate at 400°C.
When iron is deposited in the presence of an atomic flux of N plus H, the surface is again very flat (figure 6.8). A layer with the appearance of $\gamma'$-Fe$_4$N covers the surface completely, while new islands are starting to appear on the second level. A remarkable observation is that at very low coverages with Fe, “depressed” islands of Fe-N are observed. These islands are in, and not on top of, the surface Cu layer. A more detailed report on the growth of Fe$_4$N on Cu(100) will be presented in chapter 7.

Further on we will concentrate on the intermixing process occurring at 400 °C with no flux of N. We investigated the morphology of surfaces of the Cu(100) substrate after deposition of 0.3 and 1.3 ML of iron. The LEED pattern from these two samples was similar to the one of the clean Cu(100) surface, although for the lower coverage (0.3 ML) spots corresponding to a c(2x2) superstructure could be observed at low energies. This superstructure was also observed with STM (see figure 6.9). For the thicker sample (1.3 ML), no reconstruction was observed with LEED or STM. The Auger signal of iron in both cases is barely discernable. This indicates that the surface of these samples consists mostly of copper. This fact implies a strong intermixing between iron and copper resulting in segregation of copper to the surface.

Figure 6.9. 0.3 ML of Fe was deposited onto a Cu(100) substrate at 400°C.

For 0.3 ML of Fe (figure 6.9) the surface is covered by a number of islands of irregular shape. The average lateral size of the islands is 100 Å. There appear to be islands with three different heights – 1.9, 3.6 and 5.1 (±0.2) Å – which approximately correspond to 1, 2 and 3 MLs of copper or/and iron. The top of the islands is very flat, and a regular arrangement of atoms, with a 3.6x3.6Å$^2$ unit cell forming a c(2x2) superstructure with respect to the underlying Cu(100) substrate. This observation is in agreement with the observed LEED pattern. The density of islands in this case is 7x10$^{10}$/cm$^2$. The ratio of the deposited amount of iron to the density of islands is approximately the same after 1.3 ML Fe deposition, suggesting that the number of islands increases proportionally with the amount of deposited iron. This implies that the amount of iron per cluster is defined by the growth conditions.

The theoretical work of Spišák and Hafner [14] revealed a number of important points which are applicable to our research. They concluded that the large difference of the surface energies of Cu and Fe favours the incorporation of Fe atoms in and even below the top layer of the Cu substrate. The formation of compact buried Fe films is favored over interdiffusion and surface alloying in accordance with the demixing tendency of bulk Fe-Cu alloys [15]. The exchange of an Fe adatom with a Cu atom in the surface is an energetically favorable and thermally activated process with an activation energy of 1.45 eV. Although the authors
emphasize that this is the upper limit of the barrier, this energy is much higher than the activation energies for hopping diffusion of Fe or Cu adatoms on the Cu(100) surface (0.46 and 0.38 eV, respectively [7, 16]). Thus, the surfactant effect of Cu can be observed only at temperatures at least above RT. It was concluded that the exchange of Fe atoms at the perimeter of already existing Fe inclusions is energetically even more favorable. This implies that the formation of an Fe layer buried with one Cu layer is predicted. No energy is gained when the Fe island is buried with more than 1 ML of Cu. The interaction of a Cu adatom with an Fe impurity is repulsive if the impurity is in the subsurface layer. It was also found that it is energetically favorable to form buried Fe islands thicker than one ML, instead of a large island consisting of one ML.

Based on the results presented, and on the conclusions drawn by Spišák and Hafner, the intermixing process occurring at 400 °C can be described in more detail. Fe atoms deposited at a copper surface probably first form clusters (islands) because the mobility of Fe atoms is very high and the Fe-Fe interaction is stronger than the Fe-Cu interaction. Next, they are incorporated into the first layer by the exchange mechanism [17]. This leads to the formation of an Fe layer in the surface layer buried with one layer of Cu. A possible alternative way to form such a structure would be the coverage of Fe islands by Cu adatoms present at the surface [18]. This process leads to an Fe layer on top of the surface layer. However, this last mechanism is not likely to occur. The observation of “depressed” Fe-N islands in the case of co-deposition of Fe+N (see Chapter 7) would not be in line with this scenario. Also the trapping of deposited Fe atoms at Cu surface vacancies and their subsequent coverage with Cu adatoms is not a likely mechanism. The buried Fe islands may be thicker than 1 ML. The size of Fe clusters and the density of islands are determined by the growth conditions (temperature, deposition rate). The copper islands seen on a sample with 0.3 ML of iron deposited are kept in place by underlying iron clusters (otherwise they would diffuse away). Thin islands of copper covering iron clusters can form a c(2x2) superstructure corresponding to 0.5 ML of Cu. It cannot be excluded that in this case the Cu layer covering the Fe has a thickness of, for instance, 1.5 ML instead of 0.5 ML. This reconstructed surface is not predicted by theoretical calculations. It must be induced by the stress in the copper layer or iron layer beneath the half-monolayer island.

The surface of the substrate after deposition of 1.3 ML of iron consists of even thicker islands of copper with an increased density. The actual time of the deposition for this sample was increased in comparison with the thinner one from 30 s to 240 s. It seems that upon annealing the segregation of copper does not stop, and thicker islands develop. The formation of thicker Cu islands is not predicted by the theoretical work of Spišák and Hafner and cannot be explained by the energetics of the Fe-Cu system. On the contrary, the predicted energy gain is very small even when the thickness is increased from one to two MLs of copper. We suppose that the thickening of copper islands is a dynamical effect occurring while annealing. It is remarkable that a large fraction of Cu islands has a pinhole in the center. Typically, the width of the pinhole is 30-40 Å with a depth of 10 Å. It is not certain that the full depth can be probed with STM. The formation of Cu (or Ag) islands with a pinhole on top of an Fe layer was also observed after annealing a sample consisting of a Fe layer on top of a Cu or Ag substrate at temperature of 290 °C (for Cu [13]) and 320 °C (for Ag [19]). Up to now no satisfactory explanation of the segregation of Cu beyond 1 ML has been presented.

The formation of circular islands with a pinhole in the center suggests that the segregation of Cu to the surface takes place at pinholes. A wild guess is that the bottom of the pinhole is a monolayer of Cu covering Fe. The exchange of Fe/Cu may take place here if vacancies are present in the Fe/Cu bilayer.

Another process, that results in the formation of pinholes and can be responsible for the intermixing, is described by Gómez et al. [20]. The authors concluded from generic
computer simulations that 1 ML islands of Co, larger than a critical size, on Cu(111) are unstable and tend to “explode” upwards, dragging some copper atoms from the surface layer. The “explosion” can be accompanied by the formation of the pinholes. This mechanism is called a collective phenomenon requiring a certain amount of atoms in the islands and involving large displacements of the substrate atoms situated below the island.

6.5. Conclusions

The mechanism of growth of an iron nitride on a Cu(100) substrate in fluxes of iron and atomic nitrogen is a complex problem, which we approached in a preparatory study described in this chapter. The adsorption and diffusion of N and the behavior of Fe atoms at the copper surface were studied separately. The exposure of the copper surface to a flux of N atoms at a temperature of 400 °C resulted in adsorption of N at the copper surface. The observation of the diffusion of N adatoms at RT at the copper surface allowed us to determine the diffusion barriers for isolated atoms and for those in clusters. The diffusion barrier for isolated nitrogen adatoms amounts to \( E_{\text{barrier}} = (0.88 \pm 0.05) \) eV. This number implies a high mobility of N adatoms at our growth conditions, that is at 400 °C. The deposition of Fe atoms at an elevated temperature resulted in the segregation of copper atoms on top of iron clusters with formation of copper islands. The amount of islands increases nearly proportionally with the amount of deposited Fe. The Cu layer covering Fe clusters is thicker after deposition of 1.3 ML as compared to 0.3 ML of Fe. This may be an effect of the increased annealing time. It is proposed that the formation of 1 ML of Cu on top of an Fe island can be explained by the energetics of the Fe/Cu system. The formation of thicker islands must be a dynamical effect.

When Fe was deposited at RT, the intermixing was limited to 1 ML according to AES data. The surface of the sample after deposition of 1.3 ML of iron was flat and consisting of 2-3 atomic levels only.

The deposition of Fe at 400 °C in a flux of atomic nitrogen resulted in the formation of a flat surface with the appearance of Fe-N. AES spectra reflected the amounts of Fe and Cu similar to the case of deposition of Fe at RT. This is a proof of the suppression of intermixing between Fe and Cu. Probably, the formation of an Fe-N compound is the reason of the reduced intermixing. This study is the starting point for the investigation of the growth mechanism of Fe-N on Cu(100) to be described in the next chapter.

6.6. References
