Chapter 8. Low energy ion scattering study of Fe₄N on Cu(100)

8.1. Introduction

For a better understanding of the reconstructed Fe₄N surfaces one would like to know the position of atoms at the surface in both c(2x2) as well as p4g(2x2) configurations. A precise knowledge of the atomic positions is needed for calculations of the electronic structure of the surface. The outcome of such calculations can be used in the determination of the forces driving surface processes and in depicting the mechanism of phase nucleation and growth. Low-energy ion scattering (LEIS) is a very useful technique to determine the atom positions in surface layers [1]. Scattered ions of an energy in the range of 1-10 keV probe the structure of up to 6 topmost layers of atoms depending on the geometry. Details of this technique are described in Chapter 2. The inter-atomic potentials governing the scattering processes in LEIS are well known. This gives us a possibility to simulate scattering events accurately and to fit the calculated angular distributions of scattered and recoiled atoms to experimental data by adjusting the position of atoms. Here, we employ this technique to the surface of thin Fe₄N films.

There are two principal planes of atoms of the Fe₄N(100) crystal, which can represent the bulk-terminated surface as was discussed in the previous chapter: the plane containing nitrogen (N-terminated) or the plane containing Fe atoms only (Fe-terminated). The N-terminated surface has a c(2x2) symmetry with respect to a Cu(100) substrate (as well as to MgO(100)). Fe atoms in the Fe-terminated surface are not all equivalent since the N atom underneath every fourth Fe atom of the surface distinguishes this Fe atom from others (see figure 8.3). Thus the Fe-terminated surface would also give a c(2x2) LEED pattern.

In Chapter 7 the morphology of the surface of Fe₄N was studied with STM. We concluded there that the Fe₄N surface does not have two types of termination. On the contrary, the surface has the same appearance everywhere, and a mono-atomic step does not change the apparent termination. However, flat terraces of Fe₄N show two regions (white and gray) with height difference in the range of 0.2-0.5 Å depending on the applied voltage. Nearly atomic resolution STM images allowed us to conclude that both patches are at the same actual height and only the presence or absence of N atoms at the iron grid makes them appear differently. This implies that N adsorbs at both planes regardless the composition of the underlying layer. This conclusion will be verified with LEIS scans in this chapter. The experimental data as well as simulated scans will be presented here. The comparison of simulated angular scans for scattered and recoiled atoms calculated with different trial positions of the surface atoms leads to a precise determination of atom positions of the surface of Fe₄N phase. In this way we are able to uncover the difference between the c(2x2) and p4g(2x2) surface phases.
particles. With this data a LEIS TOF-spectrum summed over a range of azimuthal angles could be reconstructed and compared with the experiment. The program MATCH was meant to also reproduce the intensity ratios between scattered and recoiled atoms. However, this feature of the program was not tested until present. The error in the determination of the position of atoms was estimated by simulating scans with different displacements.

<table>
<thead>
<tr>
<th></th>
<th>LEED</th>
<th>Scattering angle</th>
<th>Incoming angle</th>
<th>Thickness, Å</th>
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<tbody>
<tr>
<td>1.</td>
<td>Fe₄N / MgO(100)</td>
<td>c(2x2)</td>
<td>52°</td>
<td>15°</td>
</tr>
<tr>
<td>2.</td>
<td>Fe₄N / Cu(100)</td>
<td>c(2x2)</td>
<td>54°</td>
<td>12°</td>
</tr>
<tr>
<td>3.</td>
<td>Fe₄N / Cu(100)</td>
<td>p4g(2x2)</td>
<td>51°</td>
<td>11°</td>
</tr>
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Table 8.1. The list of samples measured with LEIS.

The samples, which will be discussed in this chapter are listed in table 1. They were grown on MgO(100) and Cu(100) substrates at 400 °C. The surface structure of these substrates is, of course, different. However, the surface unit cell is a square in both cases (see figure 8.1) and the LEED pattern of both substrates has the same appearance (except the absolute distance between spots). A schematic arrangement of atoms in the reconstructed surfaces was shown in figure 7.14.

Figure 8.1. The unit cells at surfaces of a Cu(100) (left) and MgO(100) (right) substrates.

The LEIS scans taken from sample 2 along with the simulated curves are shown in figure 8.2a. The reconstructed TOF-spectrum summed over 180° is compared with the experimental sum in figure 8.2b. The simulations were carried out with a N-terminated surface of Fe₄N where N atoms are shifted outwards by (0.19±0.05) Å with respect to the crystallographic plane. This shift would not change the appearance of the LEED pattern. The calculated contribution of iron recoils seemed to be much higher than that in the experimental TOF-spectrum. This is, at least partly, due to a lower efficiency of the channel-plate detector for Fe atoms than for Ar atoms.

Simulations with the Fe-terminated surface of Fe₄N were also performed. Since the experimental conditions we have chosen were such that the major contribution to the yield was coming from the first layer, we would see practically no nitrogen yield from an Fe-terminated surface. This statement was confirmed by the simulations. Surprisingly, the scans of Fe-recoiled and Ar-scattered particles are very similar for the two terminations (figure 8.2). Still, a rather peculiar feature was observed in the simulated Ar-spectrum, which we also see in the experimental scan, namely, a small peak at 0° (marked with an arrow in figure 8.2a). This peak comes from the second iron layer. Ar ions channel in between two rows of Fe atoms at the topmost layer (see figure 8.3), get scattered by atoms in the second layer and then leave the sample again passing in between the rows of the surface layer. This process is possible only when no N is present in the topmost layer. The peak corresponding to the scattering from the Fe-terminated surface is present in the experimental spectrum, suggesting that the surface has both patches of N-terminated and of Fe-terminated surfaces.
Figure 8.2. LEIS scans taken from sample 2 and fitted with a) the N-terminated surface of Fe₄N with N atoms sticking outward from the crystallographic plane by 0.19 Å and c) with the Fe-terminated surface. The grey curve is the simulation; the experimental (continuous curve) TOF-spectrum summed over 180° and the reconstruction from simulated scans for b) the N-terminated surface and d) for the Fe-terminated surface. The azimuthal angle of 0° corresponds to the Fe₄N <110> crystallographic direction.

Figure 8.3. The Fe-terminated surface of Fe₄N watched along a <110> direction corresponding to 0° in the scans.
Figure 8.4. a) LEIS scans taken from sample 1 and fitted with the same N-terminated surface of Fe$_4$N as sample 2. The grey curve is the simulation. b) The experimental (continuous curve) TOF-spectrum summed over 180° and the reconstruction from simulated scans for the N-terminated surface. The azimuthal angle of 0° corresponds to the Fe$_4$N <110> crystallographic direction.

Experimental spectra taken from sample 1 (with MgO as a substrate) were fitted with exactly the same arrangement of atoms in the N-terminated slab as in the case of sample 2 (figure 8.4). This fact suggests that Fe$_4$N phase relaxes at a given thickness and then the influence of the substrate to the surface structure is negligible. In this case the features of the scans did not allow us to conclude if there are Fe-terminated patches present at the surface.

Figure 8.5. The movement of surface atoms when transformed from c(2x2) (left) to the p4g(2x2) (right) reconstruction of the surface. Here small bright balls represent N atoms, gray balls, which actually are shifted, are Fe surface atoms, black balls are Fe atoms in the sub-surface layer.
Experimental scans taken from a p4g(2x2) reconstructed surface (sample 3) were simulated with the “clock” reconstructed surface. On such a surface Fe atoms are shifted along the <100> directions as schematically shown in figure 8.5. This picture very much resembles the structure observed at the surface of the sample with the p4g(2x2) reconstructed surface with STM (figure 8.6). The best fit of LEIS scans shown in figure 8.7 was obtained with Fe atoms shifted by (0.27±0.05) Å and N atoms shifted outwards by (0.34±0.05) Å. Scans simulated with a N-free surface with shifted Fe atoms have much broader features and do not represent the features of experimental scans. We conclude that the surface of the produced sample is fully covered with N. Thus, we cannot confirm that the p4g(2x2) reconstructed surface of this particular sample has a mixed termination as we observed with STM (see figure 7.6f). However, we can argue that the concentration of N at the surface is higher than in case of the sample with a c(2x2) reconstruction of the surface since no indication of the presence of an N-free surface was found. On the contrary, broad features present at simulated scans for the N-free surface would blur the sharp peaks observed in the experimental scans of Ar-scattered and Fe-recoiled atoms. This is in agreement with the conclusion of the study with AES and LEED described in Chapter 7 that the concentration of N at the p4g(2x2) reconstructed surface is higher.

The problem, which is still to be solved, is the total area of the peak of N-recoils in TOF-spectra taken from samples with these two reconstructions, which must be proportional to the concentration of N atoms at the surface. Calculations show that the experimental ratio of N-peak area to the Ar-peak area normalized on calculated yields is larger by 30% in the case of c(2x2) than in the case of the p4g(2x2) surface structure. This is in contradiction with both results of the fitting of LEIS scans and the results of AES and STM experiments. It can be that the absolute yields reproduced by the program are not correct.
8.3. Conclusions

LEIS scans were taken from both c(2x2) and p4g(2x2) reconstructed surfaces of Fe₄N. LEIS azimuthal scans from these surfaces were simulated with model structures and TOF-spectra were reconstructed. The simulations confirm that the c(2x2) reconstructed surface consists of both N-terminated and Fe-terminated surfaces of Fe₄N. The c(2x2) surfaces of the samples grown on MgO(100) and on Cu(100) substrates were modelled with the same arrangement of the atoms at the N-terminated surface, which implies that the layer is fully relaxed at this thickness (180 Å). The scans from a p4g(2x2) reconstructed surface have very sharp features, which can be explained by a very well ordered surface with the complete occupation of every other hollow site with N. The model structure of the surface (figure 8.5) is to be compared with the high-resolution STM image obtained from a sample with the same reconstruction of the surface as seen with LEED (figure 8.6). The weaving structure observed in the STM image can be recognized in the model image. Thus, our findings confirm the conclusions of the AES, LEED and STM studies and add the precise positions of atoms at the surfaces with both superstructures. However, the presence of N-free p4g(2x2) reconstructed areas at the surface is not confirmed. This may point to the presence of a range in the possible concentrations of N at the surface when the p4g(2x2) reconstruction occurs. It is noteworthy that in this study we determined the relative positions of the atoms in the first layer. The positions of these atoms with respect to atoms in the second layer was not determined. Such a determination is possible with LEIS, when steeper angles of the incoming ions are used, so that atoms in the second layer can be hit.
8.2. The c(2x2) and p4g(2x2) reconstructed surfaces of Fe$_4$N

The LEIS scans were taken in the setup in Groningen. Samples produced in Groningen normally gave a c(2x2) LEED diffraction pattern. In order to obtain a surface with the alternative p4g(2x2) reconstruction we had to change the growth parameters. Trying to approach the growth parameters used in Madrid, we applied a somewhat slower growth rate of iron. Thus, we were able to produce both samples with c(2x2) and with p4g(2x2) reconstruction of the surface and we measured LEIS azimuthal scans from these surfaces.

The basics of the LEIS technique were already described in Chapter 2. We used a collimated beam of Ar$^+$ ions with an energy of 5 keV. The time resolution in a time-of-flight (TOF) measurement is defined by the width of the beam pulses, which was 200 ns. The dose of Ar$^+$ ions per scan amounted to $\sim 10^{12}$ cm$^{-2}$. With this low dose no surface damage is introduced during the measurements, as was verified in our experiments. TOF-spectra were acquired with a channel-plate detector, which had an opening of 1°x1°. We used a 52° or 54° scattering angle and varied the angle of incidence in the range of 12-15°. TOF-spectra were taken for a range of azimuthal angles (normally 180°) with a constant time per step. The contributions of scattered Ar and recoiled Fe and N atoms were obtained by fitting corresponding peaks in every spectrum of the sequence with a Gaussian plus an exponentially decaying tail. The Fe peak was fitted taking into account a background with an exponential shape. This background is due to scattered Ar atoms.

The simulations were performed with the computer code MATCH. A detailed description of this unique fast code can be found elsewhere [2]. In the past this type of measurements and simulations were successfully done for a number of structures [3]. The idea of this code is to simulate trajectories of incoming and (reversed-time) outgoing particles separately. The detection probability of the main scattering event from a certain atom is taken as the product of the close-encounter probabilities of the incoming and the outgoing particles. In addition, the energy difference between projectile and scattered or recoiled particle has to correspond to the kinematics of the collision. Thus, not only trajectories should cross within a short distance but also the energies should match. In the matching process it is assumed that an atom is at the right position for the collision to happen. Later the event is weighed with the probability (given by the thermal vibration amplitudes) that the atom is at this position. The interactions between a projectile and a target atom are calculated within the binary-collision approximation (BCA) using the Universal potential [4, 5] with an adjusted screening length. In the program a slab of arbitrary size and thickness consisting of a surface layer of atoms and a number of underlying layers can be defined. Periodic boundary conditions are assumed in lateral directions. Thermal vibrations are included by assuming displacements of the atoms in three directions. In this way frozen lattices can be obtained by either choosing displacements at random, assuming non-correlated Gaussian thermal displacements or by taking snapshots from molecular dynamics calculations. In our simulations the amplitudes of thermal vibrations in the surface-plane were 0.12 Å for N and 0.07 Å for Fe atoms and in the direction perpendicular to the surface we used 0.15 Å for N and 0.09 Å for Fe atoms. Normally, we simulated 200 particles scattered on 200 frozen lattices. This procedure produces 200x200 incoming and the same amount of outgoing particles. The amount of particles scattered from deeper layers depends on the geometry of the experiment and can be appreciable from up to 6 layers. However, in the geometry we used more than 95% of the yield comes from the first layer, and only at certain azimuthal angles the contribution of the second layer can be recognized due to a surface channeling effect. We used a slab containing 5 layers. Adjusting the position of atoms, we were able to simulate spectra which fit well to the experimental data. The program’s output includes angular distribution scans of scattered projectiles and of recoiled N and Fe atoms. These scans were calculated for different energy bins of outgoing
8.4. References