Manipulation and control of the growth of magnetic iron nitride films
Grachev, Sergey Yu.

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2003

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Citation for published version (APA):

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Chapter 2. Experimental techniques and setups

2.1. Introduction

From an experimental point of view, the study of a growth mechanism is complex and requires special equipment and experimental methods to be applied. The first necessary requirement is to supply extremely clean conditions and provide fluxes of very pure substances. For this purpose ultra-high vacuum (UHV) conditions are used, which reduce the flux of the residual gas at the surface of the sample down to \(~10^{-9}\) Langmuir per second (L/s) [1]. This is sufficient for keeping a sample or a substrate clean for 10-50 hours depending on the reactivity of the sample material with residual gases. Molecular beam epitaxy (MBE) is one of the few methods for production of a very pure flux of metal atoms [2]. In our version of gas-flow assisted MBE, we heated a small amount of an ultra pure metal in a cell (called Knudsen-cell or K-cell) to a temperature at which sublimation of the metal occurs. To obtain a clean flux of N atoms or other reactive N-containing species we used several methods. We tried to use pure ammonia as a background gas during growth. This supplied a flux of ammonia at the surface of the growing sample which adsorbs and decomposes into N and H adatoms. We also used a hot nozzle made of iron to direct a gas flux to the surface. When \(\text{N}_2\) or \(\text{NH}_3\) are led through such a hot nozzle, these gases decompose at the iron surface, and a flux containing atomic nitrogen is produced. Another method we applied is to produce N atoms in a plasma discharge and to guide the output of the discharge to the surface of the sample [3]. The discharge was ignited and maintained by a radio-frequency electromagnetic field. The source was designed in our group. Two similar sources were made and used to produce samples in UHV systems, which were provided with different on-line characterization instruments. One system, in our research group in Groningen, was equipped with low-energy electron diffraction (LEED) optics, and ion beams for low-energy ion scattering (LEIS) and for Rutherford backscattering spectroscopy (RBS). The second source was used in a similar MBE system in Madrid, provided with LEED optics, used also for Auger electron spectroscopy (AES), and with a scanning tunneling microscope (STM). In this way the samples could be studied with complementary \textit{in-situ} techniques. In addition, we also used a number of \textit{ex-situ} techniques for the characterization of the samples. The two setups and experimental methods we used will be described in this chapter.

2.2. The setups

2.2.1. The setup at the Groningen University

The setup at the Groningen University was exploited already for many years and has been described in detail in several papers and theses [4]. It is a state-of-the-art instrument, which was meant to produce thin metal films by MBE and then to apply ion beam analysis.
techniques to investigate the composition and structure of films grown. We could take full advantage of the instruments present in the set-up, but we also adapted it to our purposes by adding new equipment. It consists of two chambers for the preparatory treatment of a substrate and for the post-treatment of a sample, and a main chamber. In the preparatory chambers a substrate or a sample could be annealed, sputtered with $\text{Ar}^+$ ions, or annealed in $\text{O}_2$. The main chamber was supplied with several K-cells for evaporation of metals ($^{57}\text{Fe}$, natural Fe, Cu, Ag, Cr), with low-energy electron diffraction (LEED) optics, and with several detectors for ion beam analysis. The beam line was attached to the main chamber through a valve. Two types of beams could be used: a high-energy ion beam from a Van der Graaff accelerator for Rutherford back-scattering spectroscopy (RBS), and a low-energy ion beam for low-energy ion scattering spectroscopy (LEIS). A substrate in a sample-holder could be inserted into the head of a three-axes goniometer (angular precision of 0.1°). In this position the temperature of the sample could be controlled in the temperature range of 100 – 750 K. The base pressure in the chambers was $10^{-10}$ mbar maintained by turbo-pumps, ion-pumps and two Ti-sublimation pumps.

2.2.2. The setup at the Universidad Autonoma de Madrid

A stainless-steel ultra high vacuum (UHV) chamber was equipped with a home made scanning tunneling microscopy (STM) unit of the inertial approach type described elsewhere [5] and commercial rear-view four-grid low-energy electron diffraction (LEED) optics (OMICRON Vakumphysik, GmbH), which was also used to acquire Auger electron (AES) spectra. The sample holder allowed in situ transfer of a sample from the LEED optics to the STM head. Deposition of Fe was carried out by evaporation from an Fe rod heated by electron bombardment. For low coverages, the deposition rate was calibrated by measuring the fraction of covered surface in the STM images. Larger coverages were deduced from the evaporation time and cross-checked by the ratios of the low and high energy Auger peaks of Fe with respect to those of the substrate. Considering the uncertainties involved, the error in the amount of deposited iron has been estimated to be around ~50%. A radio-frequency (RF) plasma source was attached to the chamber via a valve and was stationed on a separate table. After a sample was grown, the valve had to be closed and the RF source had to be detached from the chamber in order to isolate the STM from vibrations.

2.3. Substrate and sample preparation

In order to produce a sample of a desired composition and crystal quality one must take special care of the substrate cleaning procedure and of the sample preparation itself. The main goal of a cleaning procedure is to remove contaminations from the surface (and sometimes from the bulk of the crystal too) and to prepare a defect-free, atomically flat substrate surface. The principle of a cleaning process depends on the chemical and physical nature of the material of the substrate. We used various crystals as substrates: insulating MgO(100), conductive SrTiO$_3$(100) doped with Nb (mixed termination) and metallic Cu(100) and Ag(100). Each of these substrates requires a particular cleaning recipe. The cleaning procedure usually consists of a cleaning step in air followed by a treatment in vacuum.

MgO(100) crystals are widely used as a substrate because of their inert chemical properties, low price and the relatively simple cleaning procedure required. Mono-crystalline slabs of MgO, cut and polished along many directions and miscut angles, are available on the market. Also thick cubic mono-crystals of MgO can be bought. They can be cleaved in vacuum or in air to obtain slabs. The surface topography of different types of MgO(100) substrates was investigated with atomic-force microscopy (AFM) by F.C. Voogt [6]. The
Experimental techniques and setups

The surface of an as-received polished MgO(100) substrate is still rough and needs further treatment. A surface of a cleaved MgO(100) substrate exhibits large macro-steps with a height of ~150 nm. The terraces contain smaller steps (~2 nm high), which run in a <100> direction. In order to get rid of surface contaminants and at the same time to prepare an ordered surface, a recipe was proposed and tested for both polished and cleaved samples: annealing in an oxygen atmosphere at a pressure of 10^{-6} mbar for 4-6 hours. With this treatment the impurities (C and O-containing absorbents) were oxidized and removed. Also, the microsteps were removed from cleaved sample surfaces. Cleaved MgO(100) substrates still have macrosteps running in a <110> direction (the usual direction of cleavage).

SrTiO\textsubscript{3} is an insulator that becomes conductive when doped with Nb. It has a perovskite crystal structure where planes of Sr monoxide and Ti dioxide parallel to the <100> plane of the crystal alternate. By special chemical and vacuum treatments a surface terminated by one of these oxides can be obtained [7]. The terminated versions of the SrTiO\textsubscript{3}(100) monocrystals became available on the market recently, although the price is still quite high. Normally, doped crystals do not have one single termination. A well-ordered surface with a mixed termination can be obtained by annealing at 550-700°C in O\textsubscript{2}. We checked our substrates with LEED. The pattern contained sharp spots of the expected cubic symmetry with a low background.

Ag(100) and Cu(100) single crystals are also easily accessible on the market. The cleaning procedures are well known and are similar for these two metal substrates. Annealing at elevated temperatures (~400-500°C) for a few hours is needed for as received crystals in order to get rid of bulk contaminants (H, B, C, S, O), which are practically always present. Then several cycles of sputtering (RT, Ar\textsuperscript{+} ions 500-1000 eV, 15 min, ~5µA) and annealing (400°C for silver, 600°C for copper, for 5-10 min) normally result in a contamination-free well-ordered surface as we checked with Auger electron spectroscopy and with LEED. Substrates which were used for the growth of a thin film could be regenerated by sputtering at RT for a sufficient time to get rid of the grown film followed by the normal cleaning procedure.

2.4. Auger electron spectroscopy

Auger electron spectroscopy was already mentioned above as a tool to control the level of contaminations at the surface. Nowadays, this is one of the main applications of this technique. It is also used to monitor the composition of a growing film because quantitative analysis of intensities of the lines is possible [8].

Figure 2.1. The spectrum of electrons emitted from a sample bombarded by electrons.
Chapter 2

If we bombard a sample with electrons of an energy of a few keV, electrons will be emitted. They will have an energy spectrum, shown schematically in figure 2.1. The Auger process results in secondary electrons with a relatively sharply defined energy. The principle of the Auger process is described in figure 2.2. The primary electron produces an initial hole by ionization of a core level (K or L shell). Both primary and core electrons leave the atom with a not sharply defined energy. The initial hole in the core level tends to be filled by an electron originating from an energetically higher level. This transition may be accompanied by the emission of a characteristic X-ray photon, or alternatively the energy gained by the electron that “falls” into the deeper atomic level is transferred to another electron of the same or a different shell. This latter electron is then emitted with a characteristic Auger energy, thereby leaving the atom in a double-ionized state (two holes in different levels or in the same level). Since the emitted Auger electron carries a well-defined kinetic energy that is directly related to differences in core-level energies, measurement of this energy can be used to identify the particular atom species. This makes AES suitable for chemical analysis. Since the escape depth of electrons is restricted to a few monolayers (the typical probing depth in AES is in the range 10-30Å), AES is more sensitive to the surface of the sample than, for example, X-ray spectroscopy techniques.

We used AES in the setup in Madrid for both the contamination check and the analysis of the surface composition of grown films. On the basis of chemical analysis with AES we arrived at important conclusions concerning the intermixing and determination of the growing phase as described in chapters 6 and 7.

Figure 2.2. The scheme of the Auger process. A primary electron produces an initial hole in a core level. The escaping electron is indicated by a broken arrow. Another electron from a higher shell (core levels in a, b, c and the valence band of a solid in d) fills up the initial hole. The energy released by the deexcitation process is then transferred to a third electron, which leaves the system as an Auger electron with a characteristic energy.
2.5. X-ray diffraction

The X-ray diffraction method is sensitive to the long-range order in solids. It became a standard tool for the examination of structure of materials. In an x-ray diffraction (XRD) experiment, a collimated beam of x-rays is scattered from a sample. The x-rays are reflected from planes of atoms. The condition for constructive interference, in which the waves reflected from a certain family of planes \( hkl \) must be in phase, leads to Bragg’s law:

\[
n\lambda = 2d_{hkl} \sin \theta,
\]

where \( n \) indicates the order of diffraction, \( \lambda \) is the wavelength of the x-rays, \( d_{hkl} \) is the interplanar distance and \( \theta \) is half of the scattering angle [9]. The intensity of the scattered beam has a sharp maximum when the waves are specularly reflected from a family of planes at the Bragg angle. The intensity of reflections is given by the structure and composition of the material. The measurement of the 2\( \theta \) value of the peaks gives the interplanar distances, from which the phase present in the sample can be identified and the macrostrain in the sample can be deduced. Tilting the sample while keeping the scattering angle constant allows to determine the orientation distribution of crystallites in the material. The width of a reflection on the 2\( \theta \) axis is determined by the microstrain in the sample and by the size of the crystallites. Information on these quantities can be extracted from XRD spectra.

We used XRD to determine phases, the strain and the orientation of the crystallites in our samples. CuK\( \alpha \) radiation with a wave length of \( \lambda = 1.542 \) Å was used. For identification of compounds we used a conventional x-ray diffractometer in a specular 0-20 geometry and in an offset mode. In a specular geometry, the incident and outgoing beams make an angle \( \theta \) with the surface of the sample. In an offset mode with an offset of \( \omega \), the sample is tilted such that the incoming angle is always equal to \( \theta - \omega \) and the outgoing angle is \( \theta + \omega \) while \( \theta \) is the scanning angle as in the specular case. The offset angle \( \omega \) could be set in the range of \(-6\) to \(6^\circ\) in the 0-20 scanning XRD scanning system we used. The diffraction pattern taken in the specular 0-20 mode yields information about interplanar spacing for planes parallel to the surface. In an \( \omega \)-offset mode, diffraction occurs on planes tilted by \( \omega \) with respect to the surface.

In some cases, the distribution of orientations of crystallographic planes in a large solid angle should be found. For this purpose, the scattering angle 20 is fixed to probe a certain interplanar spacing and the sample is rotated about all three axis. From the position of maxima in the intensity, the distribution in orientation of crystallites with respect to the surface and with respect to the orientation of the substrate can be found. This type of measurements were performed in a Philips X’Pert MRD system, in which the orientation of the sample is implemented by a 3-axes goniometer. We used a linearly focused x-ray beam with germanium monochromator in the primary optics, and an anti-scatter slit, Soller slit and programmable receiving slit in the secondary optics.

2.6. Low-energy electron diffraction

Low-energy electron diffraction or LEED has become the main and the most widely used technique for obtaining geometrical information about ordered surfaces. The reasons why LEED is considered to be an appropriate probe of surface structure are a limited penetration depth of low energy electrons and a suitable wavelength. A monochromatic beam of electrons of energies in the range of 20-300eV is commonly used to get a diffraction pattern from the surface of the sample. The electron wavelength in this case is equal to 2.6-0.7Å, which is in the range of interatomic distances and of the period of surface structures. Electrons which are scattered elastically are filtered by grids from electrons with lower
energy. The diffraction pattern is primarily due to the first layer of atoms, but there are weaker contributions of the second and even the third layers. The intensities of diffraction spots depend on the chemical composition and on the positions of atoms at the surface.

The symmetry of the LEED pattern reflects the symmetry of the surface itself [10]. The quantitative analysis of intensities of diffraction spots as a function of the wavelength can give the precise positions of atoms at the surface. LEED is sensitive to any disorder at the surface, which destroys the surface symmetry, particularly due to contaminations at the surface and to high densities of steps. This fact makes it a very easy and effective technique for checking the crystalline order of a substrate and of a grown film as well.

In the present work LEED was used in both setups, in one case with an incidence angle of the electrons of 45° (in Groningen) and with an angle of 90° (in Madrid). LEED pictures were recorded with a CCD camera. We used it both for the routine substrate check and for the characterization of grown films. In Madrid the voltage on the retarding grids was varied in such a way that different ranges of energies of emitted electrons could be observed (retarding grid Auger spectroscopy). From these data Auger data can be constructed.

2.7. Rutherford back-scattering spectroscopy and channeling

Rutherford back-scattering spectroscopy (RBS) is an excellent tool for the analysis of the composition and for profiling the depth distribution of elements in thin films. RBS measurements are carried out with H\(^+\) or He\(^+\) ions in the 0.5-4 MeV energy range [11]. To a good approximation, particles with this energy scatter in binary Coulomb collisions from atomic nuclei unscreened by the surrounding electron clouds. Accordingly, the collision probabilities are given by the Rutherford cross-section. The energy transfers in the elastic collisions are easily calculated from the conservation laws of energy and momentum. The ratio between the energy of the particles before and after collision is determined by the mass ratio of the particles and by the geometry of the collision. Thus, the mass of atoms can be determined from the energy of scattered projectiles.

A particle entering the sample experiences an energy loss. Particles of the energy range mentioned loose their energy mainly due to inelastic collisions with electrons. In the interaction with electrons the direction of the ions propagating in the solid is hardly affected. This means that RBS spectra can be interpreted using single-scattering theory, in which it is assumed that the trajectory of an ion in the solid is straight before and after one major scattering event. In this theory the occurrence of multiple-scattering is neglected. The energy loss is proportional to the path length over which a particle has traveled through the sample. It results in a stopping power of a material, which defines the energy loss per distance covered. Knowing the stopping power of the material of the sample, the energy scale can be translated into the depth scale for each element. Thus, the elemental composition as a function of depth can be measured for a depth range up to 1-2 µm. The depth resolution for thin films is determined by the energy resolution of the detector. We used a silicon detector, which has a resolution of 14 keV. This yields a depth resolution of the order of 50 Å in the optimized geometry. For larger depths (> 1000 Å) the resolution is affected by the straggling in the energy loss. This spread increases with depth.

If the incoming beam is directed along a major crystal axis, the particles of the collimated beam are steered in the channels formed by rows of atoms. The density of atoms which are “seen” by a beam particle is largely reduced because surface atoms shadow deeper atoms. This effect, called channeling, results in a dramatic decrease of the backscattering yield. For some perfect crystals the remaining yield is as low as 2% of the yield obtained for incidence along a “random” direction. The channeling effect is very sensitive to defects and
Experimental techniques and setups

interstitial impurities in the film. Channeling along a major axis can be considered as a sensitive measure of the perfection of a crystal.

In the present study most of the RBS measurements were done in-situ in an UHV chamber with a base pressure of $10^{-10}$ mbar. A 1 MeV He$^+$ beam was used. The scattering angle at which a silicon surface barrier detector was placed was equal to 150°. The sample to be investigated was mounted on the head of a three-axes goniometer, allowing an orientation of the sample with an accuracy of better than 0.1°. A detailed analysis and fitting of RBS spectra was obtained using the program RUMP [12].

![Channeling along a [100] string](image)

**Figure 2.3.** Random and [100]-string RBS spectra from an Fe$_4$N sample grown on a MgO(100) monocrystal.

Figure 2.3 shows spectra taken from a Fe$_4$N film grown on a MgO(100) substrate. The two spectra correspond to different incidence directions: “random” and along a <100> string direction. The yield along the string amounts to 11% of that for the “random” direction showing the epitaxial nature of the film and a low density of defects.

Elastic recoil detection (ERD) is a technique similar to RBS. In ERD experiments the depth profile of light elements in a heavier matrix is determined from the energy spectrum of recoiled particles measured at forward angles [13]. A beam of ions with a mass heavier than the mass of the recoiled ions, and with an energy in the MeV region, is used. We applied ERD for precise determination of the amount of light elements in selected samples.
2.8. Low-energy ion scattering spectroscopy

This method is an excellent tool for quantitative structural analysis of surfaces. This is because the penetration depth of a low energy beam used is restricted to a few atomic layers. Also the scattering processes are well understood and can be simulated by recently developed computer codes. In a low-energy ion scattering (LEIS) experiment a surface is bombarded with a beam of noble gas ions with the energy in the 0.5-10 keV range and elastically scattered or recoiled particles are detected [14, 15]. The major part of the outgoing particles are neutrals, only a few percent of them are ionized. Depending on the energy and the mass, outgoing particles cover the distance from the sample to the detector in a different time. When the beam is chopped into sharp (width of 200 ns) time pulses, the time-of-flight (TOF) can be measured by determining electronically the time difference between the beam pulse and the arrival time of the emitted particle in the (micro-channel plate) detector. In this way a TOF-spectrum can be obtained. A typical spectrum in the geometry we normally used is shown in figure 2.4. In the spectrum, obtained during bombardment of an Fe$_4$N layer grown on a Cu(100) substrate, peaks with different flight times show up. These peaks can be identified as being due to particles as indicated in the figure.

![Figure 2.4](image)

**Figure 2.4.** A typical LEIS spectrum taken with a 5 keV Ar$^+$ beam from a Fe$_4$N sample grown on a Cu(100) substrate. This spectrum is the sum of 180 spectra taken at different azimuthal angles with a step of 1°.

The probability to detect a scattered or recoiled particle can be largely affected by shadowing and blocking effects. A flux of primary ions, described by a beam of parallel trajectories, can be deflected by a scattering target atom in such a way that a shadow cone is formed behind the scatterer (see figure 2.5). At the same time, the flux density is enhanced at the envelope of the shadow cones. Obviously, scattering from an atom located inside a shadow cone is not possible. In contrast with this, the scattering probability at atoms situated in the envelope of a shadow cone is enhanced (focusing effect). A similar cone can be formed when a target atom blocks the yield of scattered or recoiled particles leaving the sample. The combination of shadowing and blocking effects gives rise to an angular distribution of scattered and recoiled atoms that depends on the atomic arrangement and, to a smaller extent, on the thermal vibrations. The surface structure of the sample can thus be determined by
measuring angular distributions of the flux of scattered and recoiled particles in different geometries. By comparing this angular distribution with the angular distribution obtained by computer simulations of the whole scattering process for all angles and geometries calculated for trial structures, the “true” structure can be determined. Of course, in the simulations the influence of thermal vibrations must be included. Thermal vibrations make the features in the angular distribution less sharp.

The measurements were carried out in the UHV system in Groningen [4]. A pulsed beam of Ar\(^+\) ions with an energy of 5 keV was used. In order to analyse the energy distribution of scattered and recoiled particles the TOF method was employed. The particles were detected with a channel plate detector. Azimuthal scans were taken by measuring the TOF spectra every 1 or 2° with the same amount of beam charge. In order to determine the atomic structure of investigated layers, the simulation of trajectories of a number (10000 or more) of particles scattered from, and recoiled out of, the first few (3-6) atomic layers and ending in the detector were carried out for several trial structures. Satisfactory fits of experimental data were obtained. The calculations were done using the program MATCH [16].

![Figure 2.5. The formation of a shadow cone.](image)

### 2.9. Conversion electron Mössbauer spectroscopy

Mössbauer spectroscopy (MS) is used to get information on the local electron environment of nuclei [17]. In contrast to XRD, MS is sensitive to the close surrounding of nuclei, and amorphous and nanocrystalline materials can be studied as well as poly- and mono-crystals.

A nucleus placed in a solid has a certain probability to resonantly absorb or to emit (if excited) a recoilless \(\gamma\) quantum, i.e. without absorption or emission of a phonon. This process is called the Mössbauer effect. In the present work we used the transition from the first excited state of the isotope \(^{57}\)Fe at 14.4 keV into the ground state. The excited isotope \(^{57}\)Fe was obtained from the decay of its parent \(^{57}\)Co. The fraction of recoilless absorption/emission in iron at RT is about 0.80.

An electric field gradient at a nuclear site can be caused by the atomic electrons, by ligands, or by the charge distribution in the lattice. The interaction between the quadrupole moment of a nucleus and the electric field gradient results in the splitting of the excited state of the \(^{57}\)Fe nucleus. Consequently, the transition energy also splits. Similar to the electric
quadrupole interaction, the magnetic hyperfine interaction results in the splitting of energy levels. It is caused by the interaction of the magnetic dipole moment of the nucleus with the magnetic field at the nucleus. The electron density at the nucleus can cause a change of the nucleus radius between an excited state and the ground state. This effect results in the so-called isomer shift, which is the shift of the transition energies. The hyperfine parameters, namely, isomer shift (IS), hyperfine field (HF), and quadrupole splitting (QS) can be extracted from the Mössbauer spectrum. These parameters are tabulated for many compounds, which can be identified by comparison of experimental with published data.

The splitting and shifts of transition energies induced by the described effects is of the order of $10^{-9} - 10^{-7}$ eV. These shifts are sufficient to prevent resonant absorption of $\gamma$ rays. However, they can be compensated for by moving the emitter with respect to the absorber utilizing the Doppler effect. An excited nucleus can transfer its energy to a $\gamma$ quantum or to an electron. In Conversion Electron Mössbauer Spectroscopy (CEMS), which was used in this work, the conversion electrons due to the decay of resonantly excited nuclei are detected.

We used CEMS to identify Fe-N phases in produced films. The use of iron enriched in the isotope $^{57}$Fe for production of our samples made the acquisition of CEMS spectra more efficient. Each phase has its iron atoms in a set of specific electron environments, which results in a particular Mössbauer pattern with a certain set of hyperfine parameters. This makes it easy to recognize a phase by its Mössbauer spectrum. Changes in crystal structure, stoichiometry, or a high density of defects or impurities will result in the change of hyperfine parameters and will be immediately observed with CEMS.

Three compounds were observed in our samples most frequently, namely $\alpha$-Fe, $\gamma'$-Fe$_4$N, and $\epsilon$-Fe$_2$N. Their hyperfine parameters taken from literature are listed in Table 2.1. However, the hyperfine parameters of $\epsilon$-Fe$_2$N strongly depend on the content of N.

<table>
<thead>
<tr>
<th></th>
<th>IS, mm/s</th>
<th>HF, Tesla</th>
<th>QS, mm/s</th>
<th>Content, %</th>
</tr>
</thead>
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<tr>
<td>$\alpha$-Fe</td>
<td>0</td>
<td>33.0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>$\gamma'$-Fe$_4$N [18]</td>
<td>0.24</td>
<td>34.06</td>
<td>0.22</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>21.55</td>
<td>-0.43</td>
<td>25</td>
</tr>
<tr>
<td>$\epsilon$-Fe$_{2.58}$N [18]</td>
<td>0.39</td>
<td>10.2</td>
<td>0.01</td>
<td>31.6</td>
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<tr>
<td></td>
<td>0.33</td>
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<td>53.7</td>
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<td></td>
<td>0.26</td>
<td>27.1</td>
<td>0.02</td>
<td>14.7</td>
</tr>
</tbody>
</table>

Table 2.1. The hyperfine parameters of $\alpha$-Fe, $\gamma'$-Fe$_4$N and $\epsilon$-Fe$_{2.58}$N.

All the CEMS measurements were done at RT after exposure to air. The fitting procedure was done with the computer code MCTL developed in our group. Spectra were fitted with Voigt-type peaks [19] and then the hyperfine parameters were compared with the literature data.

### 2.10. Atomic force microscopy

This relatively recent technique is used in surface science for obtaining two-dimensional profiles of the surface morphology by sensing the force (commonly, perpendicular to the surface) exerted to a sharp tip. AFM has the great advantage that it can be used on insulators as well as conductors in contrast with STM (see the next paragraph). A key element here is a sensitive cantilever arm, which deflection is typically monitored by a He-Ne laser beam reflected from the cantilever onto a position sensitive diode array detector [20].
The sharp tip is attached to the end of the cantilever. If AFM works in contact mode, then the tip actually scratches the surface, gently touching it. The interatomic force between atoms of the surface and atoms of the tip causes the cantilever to deflect. The scanning of the surface along a certain direction gives the height profile or the force profile. AFM has a height sensitivity of ~0.1 nm and the lateral resolution is good enough to resolve individual atoms under optimal conditions. The cantilever arm has a high characteristic resonance frequency, which allows, in addition to steady-state measurements, many phase sensitive schemes.

We used AFM in contact mode in air in order to determine the morphology of selected samples (see chapter 5). A commercial microscope (Dimension 3001) was used.

2.11. Scanning tunneling microscopy

The scanning tunneling microscope (STM) 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. A finely sharpened conducting tip is positioned within 1 nm from the specimen and operated by a piezoelectric transducer. The piezo-element allows to control the tip position with subnanometer precision in three dimensions. When a voltage (of the order of 1 V) is applied between the tip and the surface, electrons tunnel through the gap. The resulting tunneling current varies with the tip-to-sample spacing and the voltage applied. This current is used to produce STM images by scanning the tip over the surface. Unlike AFM, STM cannot image insulating surfaces.

STM can be designed to scan a sample in constant-height, spectroscopic or constant-current mode. In the constant-height mode, the tip is moved in a horizontal plane over the sample and the tunneling current varies depending on the topography and electronic properties of the surface. In the spectroscopic mode (see below) the height is kept constant and the voltage is varied. In the constant-current mode, STM uses a feedback system to keep the tunneling current constant by adjusting the height at each point of the surface being measured. This is the mode usually applied to produce STM images of the topography. In this case, the heights of the tip are recorded during scanning. The current depends exponentially on the gap length. So if the system keeps the tunneling current constant to within a few percent, the tip-to-sample distance will be constant to within a few hundredths of an Angstrom. This makes the STM sufficiently sensitive to image individual atoms of the surface.

Rather than measuring physical topography, STM measures a surface of constant tunneling probability. If an area of the sample has oxidized, the tunneling current will drop abruptly when the tip encounters that area. In constant-current mode, the STM will move the tip closer to maintain the set tunneling current. This area then will appear depressed on the scan image. Chemical contrast provided by this effect can be of great advantage as will be demonstrated in chapter 6 for N atoms adsorbed on a copper surface.

STM can also be used in the spectroscopic mode. Then I-V curves are measured at constant height. Thereby the density of states (DOS) above and below the Fermi level can be probed. Other spectroscopic techniques detect and average the data originating from a relatively large area. The big advantage of scanning tunneling spectroscopy (STS) is that it can probe the electronic structure of the sample surface with atomic resolution.

We used a home-made STM to examine freshly grown samples in-situ. All the measurements were done at room temperature. The STM tip was a chemically etched, polycrystalline tungsten wire. The piezo-drives were calibrated vertically by measuring the step height in a clean Cu(100) surface, and laterally by measuring the nearest neighbors.
distance in images with atomic resolution. STM images were recorded in the constant current mode with bias voltages of up to 2 V and typical currents of 1 nA. A detailed description of this microscope was published elsewhere [5].

2.12. References