Magnetic Study of α'' and γ''-Phases of Iron Nitride Thin Films

E.Z. Frątczak[a,b,*], J.E. Prieto[a], M.E. Moneta[b]

[a]Centro de Microanálisis de Materiales, Universidad Autónoma de Madrid E-28049 Madrid, Spain

[b]University of Łódź, Department of Solid State Physics PL 90-236 Łódź, Poland

Most of the Fe–nitride phases have been studied in much detail. Nevertheless, there is still a debate about the most efficient, exact and controlled way of obtaining thin films of the desired iron nitride phases. Thin films of iron nitrides were deposited by Molecular Beam Epitaxy in Ultra High Vacuum. By changing the growth parameters we tried to obtain the α''-phase in its purest form. We worked also on iron mononitride, FeN (γ''-FeN) which is known to exist in different phases. The stoichiometry of the samples was determined by means of resonant Rutherford Backscattering Spectroscopy. The samples were studied by room temperature Conversion Electron Mössbauer Spectroscopy. We achieved as much as 24% of pure α''-phase and provide evidence of the existence of γ''-FeN with vacancies and of the transformation of nonmagnetic γ''-phase into magnetic ε-phase after time exposure.

1. Introduction

The study of the Fe-N phase diagram is a matter of interest in the field of basic research [1, 2] and for applications, particularly as magnetic materials in the field of spintronics [3]. In this work we present new methods of growing of α''-Fe$_{16}$N$_2$, FeN$_y$ ($y > 0.5$) and we focus on the identification of their phases and their transformation to ε-phase.

2. Experimental set-up

Thin films of Fe-N were grown in a Ultra High Vacuum (UHV) system with a base pressure of better than 10^{-10} mbar. As a source of atomic N for the growth of nitrides, a home-made Radio Frequency (RF) atomic source was developed and mounted on the UHV system. The pressure in the UHV system was about 10^{-6}–10^{-8} mbar during growth. Samples were grown by N-assisted ^{57}Fe deposition or by postnitriding ^{57}Fe layers epitaxially grown on polished or cleaved (001) MgO single-crystal substrates. After growth and cooling to room temperature (RT), all the films were capped in situ with 5 nm of Cu in order to prevent oxidation [4].

The Conversion Electron Mössbauer Spectroscopy (CEMS) measurements were performed in a home-made set-up with a ^{57}Co radioactive source. The CEMS spectra were fitted using the computer code MCTL [5].

Resonant Rutheford Backscattering Spectroscopy (RBS) was used to determine precisely the N percentage in the layers, relative to the Fe content.

3. Results and discussion

Thin α''-Fe$_{16}$N$_2$ films were grown by Molecular Beam Epitaxy (MBE) of ^{57}Fe layers. As a result we have increased the highest fraction from 22.1%, obtained before [6], to 24±2%. We achieved this result after several trials and applying small variations in the procedure.

Our highest α''-Fe$_{16}$N$_2$ phase content (24%) achieved up to now was obtained by postnitriding a ^{57}Fe film with a thickness of 20 nm at 200°C with a pressure of 6.5×10^{-7} mbar and a N pressure of 1.1×10^{-2} mbar. The spectrum (Fig. 1) was fitted using two components for the α''-Fe$_{16}$N$_2$ and γ''-phases. The α''-Fe$_{16}$N$_2$ phase was fitted using three components. The origin of the components in the α''-Fe$_{16}$N$_2$ comes from the cubic crystal structure of the unit cell. The corner atoms (FeI) have a local cubic symmetry and a zero quadrupole splitting, while the atoms at the face-centered position (FeII) have an axial symmetry and are distinguished as FeII-A and FeII-B sites. For the unit cell the Electric Field Gradient (EFG) tensor for the hyperfine field is perpendicular to the two axes passing through the FeII-A sites and parallel to the axis passing through the FeII-B sites [6]. The three magnetic components (sextets) corresponding to the FeI, FeII-A and FeII-B sites of the α''-Fe$_{16}$N$_2$ phase point to a pure phase with parameters FeI: $\delta = 0.001$ mm/s, $H = 33$ T, $\varepsilon = 0$ mm/s, $R.A. = 9\%$; FeII-A: $\delta = 0.09$ mm/s, $H = 39$ T, $\varepsilon = 0.06$ mm/s, $R.A. = 18\%$; FeII-B: $\delta = 0.11$ mm/s, $H = 32$ T, $\varepsilon = -0.11$ mm/s, $R.A. = 9\%$, where: δ is the isomer shift given with respect to α-Fe at RT, H the hyperfine field, ε the quadrupole splitting and $R.A.$ the relative area. The values we measured are somewhat higher but consistent with those given in [7]. The FeI:FeII-A:FeII-B ratio is 1:2:1. However in the spectrum shown in Fig. 1, besides the contribution of 24% α''-Fe$_{16}$N$_2$, an additional phase γ''-FeN is present with a contribution of 76%. The fit parameters are a singlet ($\delta = 0.06$ mm/s, $R.A. = 10\%$) and a doublet ($\delta = 0.26$ mm/s, $\varepsilon = 0.46$ mm/s, $R.A. = 54\%$). The $R.A.$ is the fraction of area under the curve of the corresponding subspectrum and is related with the actual phase concentration, rather than the Fe content of the FeN compound.

The γ''/γ'''-FeN N-rich phases are theoretically predicted to coexist. According to the calculations, as stoichiometric phases, both should have a N content of

*corresponding author; e-mail: ewelinazofia@gmail.com

50 at.% N but with different configurations inside the fcc Fe cage. The two structures correspond to the ZnS-type for γ''-FeN phase and a NCl-type for the γ'''-FeN [2, 4].
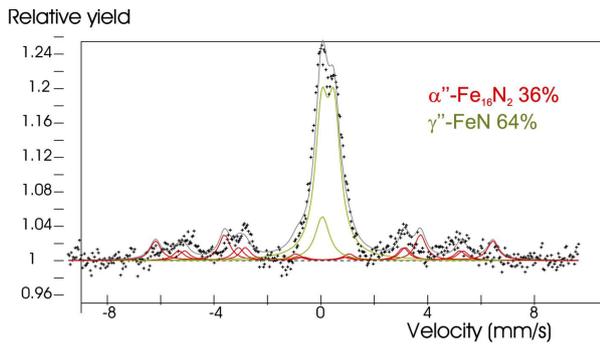
Fig. 1. RT CEMS spectrum for α''-Fe$_{16}$N$_2$ sample with the highest content of this phase 24%. The given numbers are the $R.A.$ measured under the subspectra.

An 18 nm sample was grown by simultaneous ^{57}Fe evaporation and nitriding at a temperature of 150 °C and N pressure 1×10^{-1} mbar for 1 h. The working pressure was 6.8×10^{-6} mbar. The CEMS result is shown in Fig. 2 and it contains 100% of γ''-FeN$_y$($y > 0.5$) phase. In our work this nonmagnetic phase was fitted with a singlet and a doublet. The singlet corresponds to a pure γ''-FeN$_y$ phase and the doublet to the same phase with vacancies. The high doublet-to-singlet ratio means that the content of the phase with vacancies is significant, so the real N-to-Fe ratio deviates from the 1:1 assumption. RBS results (not shown) confirm the N-to-Fe ratio obtained from CEMS spectra of this sample. The CEMS fit parameters for the singlet are: $\delta = 0.006$ mm/s, $R.A. = 24\%$ and for the doublet: $\delta = 0.26$ mm/s, $\varepsilon = 0.46$ mm/s, $R.A. = 76\%$.
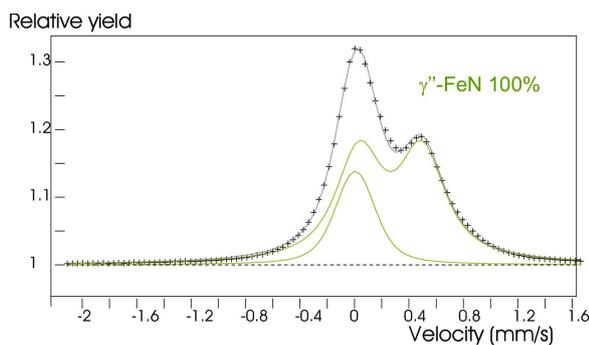
Fig. 2. RT CEMS spectrum for γ''-FeN sample. The given numbers are the R.A. measured under the subspectra.

The influence of time exposure was also studied. Analysis of the sample by CEMS made immediately after growth and after two years proved that the time exposure produced a transition of a part of the phase containing vacancies to a nonmagnetic ε-phase, which has

2.1:1 of Fe:N fraction [6]. After two years the fraction of phase containing vacancies decreased by 13±3%. After this time the spectrum (Fig. 3) shows the previously detected γ''-FeN phase (Fig. 2) and the appearance of another ε-Fe$_{2.1}$N paramagnetic phase. The fit components for ε-Fe$_{2.1}$N doublet are: $\delta = 0.3$ mm/s, $\varepsilon = 0.2$ mm/s, $R.A. = 1\%$. Here the phase content is 99.5% for the γ''-FeN phase and 0.5% for the ε-Fe$_{2,1}$N phase.
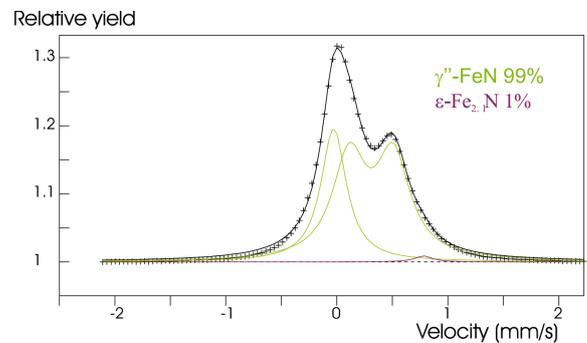
Fig. 3. RT CEMS spectrum for γ''-FeN sample after time exposure. The given numbers are the R.A. measured under the subspectra.

4. Conclusions

The synthesis of thin films of Fe-N: α''- and γ''-phases and transformation into ε-phase were described. Depending on growth parameters such as deposition temperature, pressure of N and H in the RF source, different phases were grown. The highest fraction (24%) of α''-Fe$_{16}$N$_2$ was obtained by postnitriding an epitaxial Fe layer at 200°C. We also show evidence that γ''-FeN$_y$ ($y > 0.5$) is formed. Although the CEMS fits show the existence of two phases, a singlet and a doublet, we attribute the singlet to the pure γ''-FeN phase and the doublet to the γ''-FeN phase containing vacancies.

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