Growth and characterization of epitaxial iron–nitride thin films

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ABSTRACT

Many of the Fe–nitride phases have been studied in much detail. Nevertheless there is still a debate on the most efficient, exact and controlled way of obtaining thin films of the desired iron nitrides phases. We present the recent state of our research focusing on the low and high nitrogen-iron phases and transformations between them due to irradiation, temperature and time exposure. Thin films of iron nitrides were deposited by Molecular Beam Epitaxy in Ultra High Vacuum conditions. We grew films of the FeN alpha (α''-$Fe_{16}N_2$), epsilon (ε-Fe_xN, $2 \leqslant x \leqslant 3$) and gamma ($FeN_y$, $y > 0.5$) phases. By changing the parameters of growth conditions we tried to obtain the α''-phase in its possible purest form. We grew the ε-phase mainly in a nonmagnetic form. We worked also on iron mononitride FeN, which is known to exist in different phases. There is a debate on the exact crystal structure and the coexistence of these phases. On the basis of room temperature Conversion Electron Mössbauer Spectroscopy analysis accompanied with Rutherford Backscatering Spectroscopy spectra we show our results on the growth and transformations of the samples under different conditions.

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1. Introduction

During the last decades iron nitride compounds have been intensively investigated because iron and nitrogen are among of the most abundant elements in nature, but also because these compounds are very interesting from a fundamental point of view and for industrial applications. The study of the iron nitrides phase diagram is a matter of interest in the field of basic research [1–4]. The most common compounds are the Fe_xN phases like α'-Fe_xN ($x > 8$), α''-$Fe_{16}N_2$ (bct), γ'-Fe_4N (fcc) and ε-Fe_xN ($x = 2$–3 (hcp)). All these phases contain less than 35 at.% N and have been well investigated. The α''-$Fe_{16}N_2$ phase with a composition up to about 11 at.% N, attracted considerable attention because of a possible very high saturation magnetization, reported to vary between 2.4 and 3.2 T [5]. The largest range of homogeneity in the Fe–N system (15–33 at.% N) is exhibited by the ε-phase with variable Fe-to-N ratio $Fe_{2-3}N$ [6]. At the N-rich side, three phases have been predicted theoretically: γ''-FeN (ZnS-type structure) and γ'''-FeN (NaCl type structure) for a nitrogen content of 50 at.% N [7–11], as well as Fe_3N_4 for higher nitrogen concentrations [12].

Thin layers of magnetic Fe–nitrides have a potential use in magnetic devices [13], other nitrides are used as coating materials. Other promising application make use of the recently observed catalytic properties of iron nitrides, which can be improved by increasing the nitrogen amount in the compounds [14]. There is

a strong interest in the field of spintronics to grow transition-metal nitride materials which are potentially ferromagnetic, on semiconductors [15,16]. A potential application of iron nitrides is the formation of an interlayer between the semiconductor and a ferromagnetic material as α-Fe.

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, since the growth of the α''-$Fe_{16}N_2$ phase in its pure form was rather unsuccessfully attempted by many experimental groups.

2. Experimental set-up

Thin films and multilayers of metal-nitrides were grown in UHV (Ultra High Vacuum) system with a base pressure of value lower than 10^{-10} mbar. The system was built as a series of three interconnected chambers for the different stages of preparation and growth. For the growth of iron nitride thin films, the main chamber (growth chamber) was equipped with evaporators (Knudsen-cells) for ^{57}Fe and Cu [8]. The deposition rate for each evaporator was calibrated by measuring the thickness of deposited layers by Rutherford Backscattering Spectroscopy (RBS). A typical deposition rate of ^{57}Fe was ~0.027 Å/s. Most of the samples were grown on polished or cleaved (001) MgO single-crystals. Prior to deposition, the MgO substrates were cleaned in situ by annealing at 600 °C in an oxygen atmosphere (10^{-6} mbar) for 2 h in a specially designed oxygen oven integrated with the UHV system. As a source of atomic nitrogen for the growth of nitrides, a home-made Radio Frequency (RF) atomic source was developed and mounted on the UHV system. A retractable tube was used to transfer and guide the gas from the plasma container to the surface of the sample during growth. The working pressure of the UHV system was about 10^{-6}–10^{-8} mbar during growth.

Samples were grown by N-assisted ^{57}Fe deposition or by postnitriding (with atomic N or a mixture of N + H) ^{57}Fe layers epitaxially grown on (001) MgO substrates. None of the Fe–N samples were mono-crystalline. After growth and cooling to RT all the films were capped in situ with 5 nm of copper in order to prevent oxidation.

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The Conversion Electron Mössbauer Spectroscopy (CEMS) measurements were performed in a home-made set-up with a ^{57}Co radioactive source. The conversion electrons were detected by means of a C_3H_6O gas-flow proportional counter. A pure Fe foil was used for calibration of the CEMS system. The isomer shift values are given with respect to α-Fe at room temperature. The CEMS spectra were fitted using a computer code called Modified Code Tracking Loop (MCTL) [17]. In this program, the spectra were analyzed by a least-square fitting routine by superimposing lines with a Voigt shape, optionally folded with a Gaussian, to derive the values of the hyperfine parameters and the relative area of each sub-spectrum.

Resonant RBS was used to determine precisely the N percentage in the layers, relative to the Fe content. These measurements were performed in a high vacuum chamber connected to the 5 MV tandem accelerator [18] at the Centro de Microanálisis de Materiales at the Universidad Autónoma de Madrid (CMAM/UAM). A He^{2+} beam was used for measuring the excitation curve of nitrogen. The energy of the emitted protons happens to be very close to that of the scattered α particles at the resonance energy, so the proton and α particle signals cannot be separated in our measurements. This effect has been carefully corrected [8].

The scattered ions were detected by standard Si-barrier detector located at a scattering angle of 165°. Two spectra were sequentially measured at the same spot and under the same conditions in order to check that there is no nitrogen loss during the measurements.

3. Results and discussion

Several samples were grown following a procedure leading to production of the α″-Fe$_{16}$N$_2$ which has nitrogen content of about 11 at.%. Also some studies have been done of the ε-Fe$_x$N ($x = 2$–3 (hcp)) phase which has a nitrogen composition ranging from 25 to 33 at.% N. Even though this phase is grown quite easily and is interesting, there is not much information in the literature [1,19]. Another studied phase was γ″-FeN, with a nitrogen content close to FeN with 1:1 Fe to N ratio.

After growth, structural and magnetic characterizations were performed in order to determine the properties of the thin iron nitride films. The stoichiometry was determined by resonant RBS. For magnetic characterization and phase identification CEMS was used.

3.1. α″-Fe$_{16}$N$_2$

Thin iron nitride films of 10–24 nm thicknesses were grown by MBE, the thickness was determined by RBS. In order to find the phase occurrence with high sensitivity, the samples were analyzed by CEMS. Some facts relevant for the growth of the α″-phase are the following: the α″-phase has a distorted bcc lattice configuration of the Fe sub-lattice; the best-quality α″-phase is formed at a temperature of 200 °C; in the Lehrer diagram the α″-phase appears at low temperature and at low nitriding potential of a NH$_3$/H$_2$ mixture [2,7,19]. Basing on these points we followed the mentioned route to grow the α″-phase: growing a bcc ^{57}Fe of 10–20 nm thick layer at 200–230 °C and applying a postnitriding procedure at 1×10^{-2} mbar for 2–4 h, at 100–200 °C. As a result we increased the highest fraction from 22% [7,19], obtained before, to 24 ± 2%. However there are several publications reporting higher values obtained by various methods [20–24]. We arrived at this result after several trials and applying small variations in the procedure. In addition to the α″-Fe$_{16}$N$_2$ phase in the sample there were present components from the ε-phase, which is the most easily formed phase during the deposition of iron with nitrogen. We assume that this phase is formed at the top of the sample. The additional component was pure iron, this could mean that the nitrogen was not diffusing deep enough. The α″-phase is probably formed between the two phases. The formation at $T < 200$ °C of a mixture of α″ + ε (without the γ′-phase) would be in accordance with the Lehrer diagram. Our highest α″-Fe$_{16}$N$_2$ phase content (24%) achieved up to now was obtained for the sample grown by postnitriding a ^{57}Fe film with a thickness of 20 nm at 200 °C with a working pressure in the chamber of 6.5×10^{-7} mbar and a nitrogen pressure in the source of 1.1×10^{-2} mbar. The nitrogen flow was

directed slightly out of the sample. The spectrum (Fig. 1) was fitted with two components corresponding to the phases: α″-Fe$_{16}$N$_2$ and γ″-phase. The α″-Fe$_{16}$N$_2$ phase was fitted with three components. The origin of the components in the α″-Fe$_{16}$N$_2$ phase is the cubic crystal structure of the cell, which contains two non-equivalent crystallographic iron sites. The corner iron atoms (FeI) have a local cubic symmetry and consequently a zero quadrupole splitting. On the other hand, the iron 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 magnetic field is perpendicular to the two axes going through the FeII-A sites and parallel to the axis going through the FeII-B sites [7]. 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 following parameters for FeI: $\delta = 0.001$ mm/s, $H = 33$ T, $\varepsilon = 0$ mm/s, R.A. = 9%, where: δ is the isomer shift given with respect to α-Fe at room temperature, H is the hyperfine magnetic field, ε is the quadrupole splitting and R.A. is the relative area. For FeII-A, we have: $\delta = 0.09$ mm/s, $H = 39$ T, $\varepsilon = 0.06$ mm/s, R.A. = 18% and for FeII-B: $\delta = 0.11$ mm/s, $H = 32$ T, $\varepsilon = -0.11$ mm/s, R.A. = 9%. The ratio of FeI:FeII-A:FeII-B is 1:2:1. On the other hand, 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 major contribution of 76%. The fit parameters for this phase 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 relativa area is the fraction of area under the curve of the corresponding subspectrum and is related with the actual phase concentration though the iron content of the FeN compound.

We also applied a low temperature treatment to avoid or suppress bcc to fcc/hexagonal transitions and we added H$_2$ to the gas in the RF source to lower the chemical potential at the sample surface, in analogy with the NH$_3$/H$_2$ mixture in the Lehrer diagram. This resulted in the formation of different phases but no α″-phase was grown.

For all the samples mentioned here the working pressure in the chamber during N exposure was about 1.2×10^{-6}–3.0×10^{-8} mbar.

We also studied the thermal stability of the α″-Fe$_{16}$N$_2$ phase. After growth, the sample was found to be a mixture of phases: α″, ε, and ^{57}Fe. After one year and a half the composition of the sample was checked out again by Mössbauer spectroscopy, but no significant changes were found. The sample was heated up in three steps to 150 °C for 30 min, to 150 °C for 1 h, and to 150 °C for 2 h, but again no changes were visible.
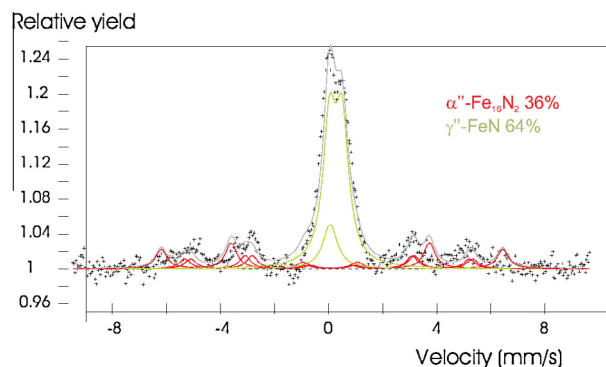
Fig. 1. Room temperature CEMS spectrum for the sample with the highest content in α″-Fe$_{16}$N$_2$ (24%) 24%. The given numbers are the relative areas measured under the subspectra. The y-axis represent the number of counts and is normalized to the background of the signal.