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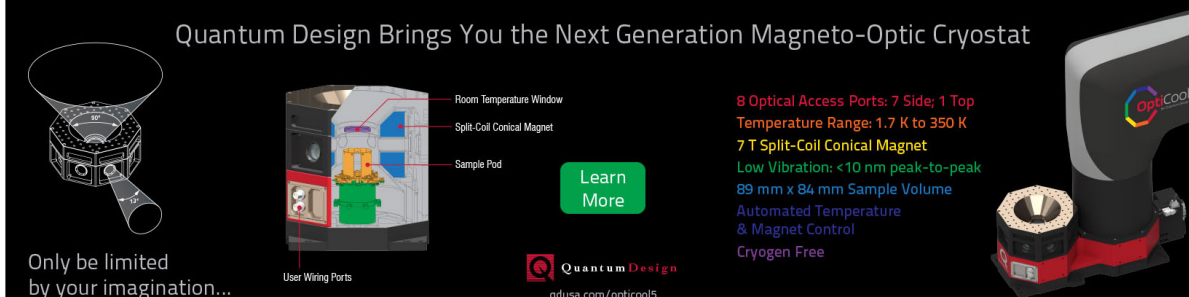
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High-quality epitaxial iron nitride films grown by gas-assisted molecular-beam epitaxy

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Thin films of γ' -Fe₄N were grown on polished (001) MgO substrates by molecular-beam epitaxy of iron in the presence of a gas flow from a rf atomic source. By means of x-ray diffraction, Mössbauer Spectroscopy, Rutherford backscattering/channeling, and scanning probe microscopy, it is shown that, with this method, single-phase, high-quality epitaxial thin films can be grown with a very smooth surface (root-mean-square roughness ~ 0.4 nm). Magnetic measurements reveal square hysteresis loops, moderate coercivities (45 Oe for a 33 nm thick film) and complete in-plane orientation of the magnetization. These properties make the films interesting candidates for device applications. © 2001 American Institute of Physics. [DOI: 10.1063/1.1392980]

During the past decades, iron nitride compounds were extensively investigated due to their excellent magnetic properties, which make them suitable for applications in high density magnetic recording heads and magnetic recording media. All iron nitrides are metallic conductors and metastable with respect to decomposition in Fe+N₂. The decomposition is limited by kinetic barriers. Among the ferromagnetic nitrides, γ' -Fe₄N phase is of special interest. This nitride has a cubic structure, contains 20 at. % N and is stable at temperatures below 400 °C. The saturation magnetization M_s is 205 emu/g. Up until now, polycrystalline thin films of γ' -Fe₄N were grown on (111) Si substrates by ion beam assisted evaporation¹ and reactive sputtering in a NH₃ atmosphere.² With N₂ as reactive gas in a dc magnetron sputtering facility, epitaxial γ' -Fe₄N films were grown on (001) Si substrates with a (002) Ag underlayer, as claimed by Brewer *et al.*³ Concerning purity, crystal quality, or roughness, no details were reported. Recent efforts were also concentrated on the growth and properties of multilayers containing iron nitrides.^{4,5} The small unit cell of the nitrides makes epitaxial growth on cubic substrates possible without domain formation as occurs, for instance, in the case of magnetite grown on such substrates.⁶ Moreover, the bonding between iron and nitrogen could prevent intermixing between adjacent layers in a multilayer system.

A different route can be explored for the growth of iron nitrides, molecular-beam epitaxy (MBE) of iron in the presence of nitrogen obtained from a rf atomic source.⁷ In this letter, we show that with this technique, high-quality epitaxial thin films of γ' -Fe₄N can be grown on (001) MgO substrates. The growth conditions as well as the structural and magnetic properties were investigated. Before growth, the MgO was annealed at 600 °C in 10⁻⁶ mbar O₂. The samples were grown with iron enriched to 99% in ⁵⁷Fe at deposition rates between 0.1 and 0.01 Å/s. During growth, the deposi-

tion temperature was 200 °C or 400 °C. The rf atomic source was used with pure nitrogen or a mixture of nitrogen and hydrogen in different ratios. The total gas pressure was 5 × 10⁻³ mbar and the applied rf power was 60 W. The thickness of the films was measured by Rutherford backscattering spectroscopy (RBS), whereas the nitrogen content was estimated from the amount of nitride phase as determined by conversion electron Mössbauer spectroscopy (CEMS).

To determine the optimum conditions for the growth of γ' -Fe₄N films on (001) MgO substrates, the deposition rate of iron, the gas composition in the rf atomic source, and the deposition temperature were varied. Two batches of samples were grown at a deposition temperature of 200 °C. For the first batch, the gas in the rf atomic source was only nitrogen, whereas for the second one, the gas consisted of a mixture of nitrogen and hydrogen, in different ratios. The results are summarized in Fig. 1. Surprisingly, the presence of hydrogen in the rf atomic source enhances the uptake of nitrogen in the nitride film and promotes the formation of a single phase.

This points to a more complex growth process in which the formation of N-H species plays a role. Possibly, the

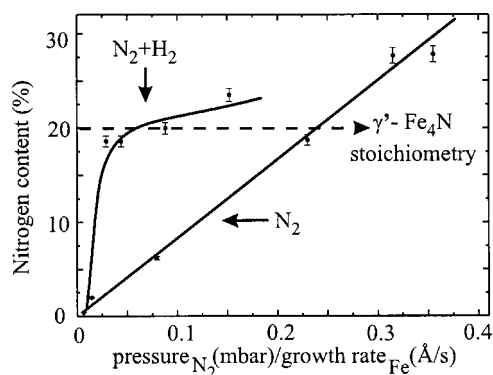


FIG. 1. Shown is the dependence of nitrogen uptake on the pressure of nitrogen in the atomic source divided by the growth rate of iron. The solid lines are guides for the eye.

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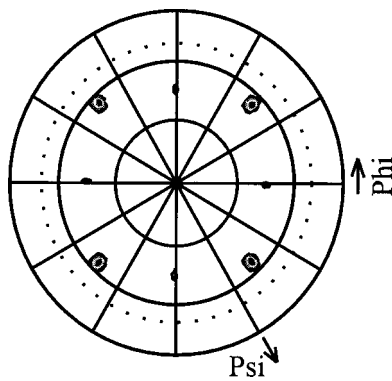


FIG. 2. X-ray ψ - ϕ pole scan with 2θ fixed for the (111) reflection of γ' -Fe₄N is shown.

excess nitrogen is carried away as NH₃. The optimum growth conditions for γ' -Fe₄N were found to be a deposition rate of iron in the range of 0.01–0.015 Å/s and a mixture of 20% N₂ and 80% H₂ in the rf atomic source. These conditions were used to grow a 15 nm thick sample. For structural characterization, we performed x-ray diffraction (XRD) measurements using CuK α radiation ($\lambda = 1.54$ nm) in a standard θ - 2θ geometry. Only the (002) reflections for both the MgO substrate (cubic; $a = 4.21$ Å) and the γ' -Fe₄N film (cubic; $a = 3.79$ Å) are present, showing a well-defined orientation of the nitride film with the c axis normal to the substrate. Additionally, texture measurements were performed in a Philips X'Pert MRD system. Figure 2 shows a ψ - ϕ pole scan with 2θ fixed for the (111) reflection of γ' -Fe₄N.

The appearance of only four sharp peaks corresponding to γ' -Fe₄N proves the epitaxial nature of the nitride film. The additional faint spots are due to the reflection of the x-ray with a different energy from the substrate. From the 2θ values corresponding to the (002) and (111) reflections, the in-plane (a) and out-of-plane (c) lattice constants were calculated. An a/c ratio of 3.76/3.80 was found.

Such a deviation corresponds to a tetragonal distortion, with an in-plane contraction and an out-of-plane expansion. This result, as well as the epitaxial nature of the nitride film, is rather peculiar since the substrate has a larger lattice constant, the mismatch being as high as 10%. Moreover, ψ - ω areal scans revealed a small tilt of around 0.2° for the (001) planes of γ' -Fe₄N with respect to the (001) planes of MgO. Despite the epitaxial nature, RBS/channeling experiments showed only weak channeling in the nitride film. To investigate a possible correlation between the crystallinity of the film and the deposition temperature, this was increased to 400 °C while the other growth parameters were kept the same as in the previous case. The thickness of the as grown sample was 33 nm.

Axial channeling measurements were performed by scanning the tilt angle θ from -4° to $+4^\circ$ with respect to the [001] and [011] directions of MgO. The results are shown in Fig. 3. Channeling dips were found in both axial directions. A shift of around 0.6° and 0.8° is present between the channel dips corresponding to the film and those of the substrate, for the [001] and [011] axial directions, respectively. No angular deviation between the MgO and the γ' -Fe₄N dips was found in the direction perpendicular to θ . Within experimental errors, these deviations can be explained by assuming

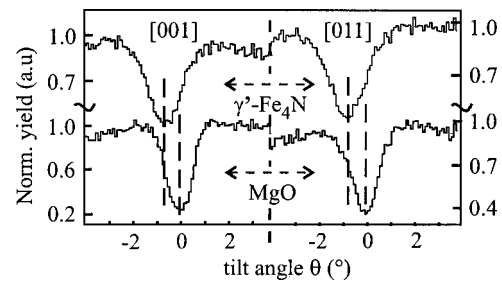


FIG. 3. Axial channel dip spectra measured around the [001] and [011] directions of the MgO substrate are shown.

a tilt of 0.6° between the crystal orientations of MgO and γ' -Fe₄N, and in addition, a tetragonal distortion of the nitride lattice, leading to an angular deviation of 0.3° between the [001] and [011] axial directions, in accordance with the XRD data. The minimum yields observed in the [001] direction for the MgO and γ' -Fe₄N were 22% and 45%, respectively. This points to some mozaicity in the MgO substrate, as was also observed with XRD. The higher minimum yield observed for γ' -Fe₄N can be explained by the presence of a noncrystalline ferrihydrite layer on top of the sample with a thickness ~ 50 Å. In the channeling measurements, the Fe in this layer was not separated from the Fe in the nitride layer.

Moreover, a small miscut from the (001) plane of about 0.4° was found for the substrate surface. The normal to the (001) planes of the substrate lies between the surface normal and the normal to the (001) planes of the nitride film. Apparently, these three normal vectors are in the same plane.

As previously reported,⁸ such a tilt is likely to be induced by a misorientation of the surface from the nominal (001) plane, although tilted growth has been reported also on nominally oriented substrates.⁹ Due to the large mismatch between the layer and the substrate, the observed tilt could be associated with a coherent relaxation of strain by misfit dislocations along the (111) planes which have a Burgers vector component perpendicular to the interface.

The surface morphology was studied in air using AFM. No cap layer was present for the samples used in the AFM study. Therefore, the surface layer was transformed into a ferrihydrite, which can alter the surface structure. Figures 4(a) and 4(b) show AFM images of a 33 nm thick γ' -Fe₄N film grown on a (001) MgO substrate heated to 400 °C during growth. The film exhibits a very uniform granular structure, with individual elongated flat islands and an average size $\sim 50 \times 200$ nm². These islands show weak signs of square symmetry along the [001] directions. The root-mean-

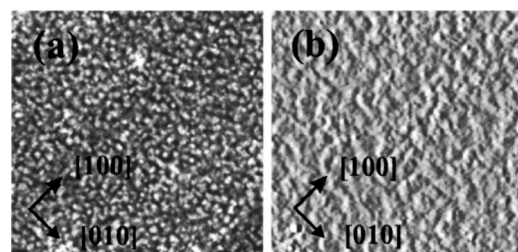


FIG. 4. AFM scans for a 33 nm thick γ' -Fe₄N film with no cap layer are shown. (a) shows the topographical image of a 2.1×2.1 μm^2 area (vertical range 3.1 nm). (b) shows the force image of a 1.1×1.1 μm^2 area. A smooth, regular surface with weak signs of square symmetry is observed.

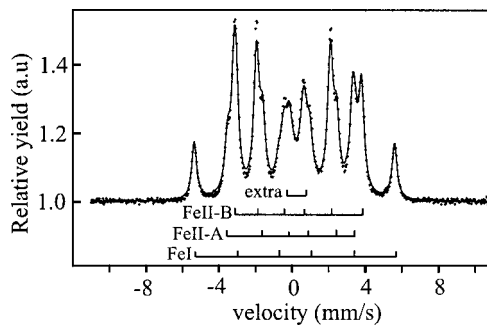


FIG. 5. Room temperature CEMS spectrum for a γ' - Fe_4N film with no cap layer present are shown. The contributions of the three components of the nitride phase and the extra phase are indicated. All subpectra are fitted with Lorentzian-shaped lines.

square (rms) roughness of the film, which is only 0.4 nm, corresponds to an average peak–valley height of approximately three atomic spacing (for a cleaned MgO substrate the rms roughness is 0.07 nm). For a 15 nm thick sample, also deposited at 400 °C, we measured a rms roughness of 0.2 nm. The observation of an island structure combined with a low roughness points to a layer-by-layer growth process, in which islands are formed, which coalesce in full layers. Additional AFM measurements on samples grown at a lower deposition temperature showed that the roughness decreases with increasing deposition temperature.

The magnetic properties of the nitride films were investigated by room temperature CEMS and vibrating sample magnetometry (VSM). Figure 5 shows the CEMS spectrum acquired for the 33 nm thick nitride film. No external field was applied. The spectrum of γ' - Fe_4N was deconvoluted in three magnetic components with a 3:4:1:1:4:3 intensity ratio of the lines in each component. Such a ratio indicates a complete in-plane orientation of the magnetization in the domains. With no cap layer present, an extra component accounting for $\sim 17\%$ of the total is found. When a cap layer is applied, this component is not present. The fit parameters corresponding to γ' - Fe_4N are in good agreement with previous reported data,^{10,11} whereas the ones corresponding to the extra phase resemble well those of ferrihydrite¹² (see Table I). Additional CEMS in an applied field and VSM confirmed an easy axis of magnetization along the [001] crystallographic direction.¹⁰ The VSM revealed square hysteresis loops and coercive fields in the easy axis direction of 45 Oe for a 33 nm thick sample and of 28 Oe for a 15 nm thick sample.

Concluding, high-quality epitaxial γ' - Fe_4N films were grown on (001) MgO substrates by MBE in the presence of a rf atomic source. The optimum growth conditions as well

TABLE I. Shown are fit parameters for the nitride and the ferrihydrite (extra): δ -isomer shift (all given with respect to Fe at room temperature), H -hyperfine field, ϵ -quadrupole splitting, Γ -linewidth, R.A.-relative area.

Component	δ (mm/s)	H (T)	ϵ (mm/s)	Γ (mm/s)	R.A. (%)
FeI	0.22	33.99	0	0.32	25
FeII-A	0.29	21.62	0.23	0.35	50
FeII-B	0.28	21.63	-0.44	0.35	25
extra	0.34	...	0.87	0.67	...

as the influence of particular experimental parameters on the formation of the nitride phase were established. The way nitrogen is taken up changes in the presence of H_2 in the atomic source, pointing to a more complex mechanism in the nitride phase formation, including a step which possibly involves formation of N–H species. When elevated temperatures are used for the substrate during the gas-assisted MBE growth, the present method enables the formation of smooth and epitaxial films.

The local properties of the surface point to a layer-by-layer growth mode for the nitride film. A peculiar tilt was found between the planes of the nitride film and the substrate. Magnetic measurements revealed square hysteresis loops and an easy axis of magnetization along the [001] crystallographic direction. The CEMS spectrum of γ' - Fe_4N is deconvoluted in three components, with parameters as expected for this structure. The magnetic domains have a complete in-plane magnetization. The sum of these properties makes γ' - Fe_4N layers interesting candidates for device applications.

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