Fourfold in-plane magnetic anisotropy of magnetite thin films grown on TiN buffered Si(001) by ion-assisted sputtering

Pilar Prieto,*a Juan de la Figuera,b Laura Martin-García,b José Emilio Prieto,c,d and José F. Marcob

Highly oriented magnetite thin films showing well-defined fourfold in-plane magnetic anisotropy have been grown on TiN buffered Si(001) substrates by ion beam sputtering assisted by a second ion beam containing a controlled mixture of Ar+ and O2+ ions. The structure and composition of stoichiometric Fe3O4 and non-stoichiometric Fe2+Fe3+O4 magnetite thin films have been characterized by X-ray diffraction, Rutherford backscattering spectroscopy and Mössbauer spectroscopy. Magneto-optical Kerr effect measurements show that the maxima of the remanence and coercivity of all these films lie along the Si[010] and [100] directions. The introduction of Fe vacancies in magnetite does not alter the well-defined fourfold in-plane anisotropy but induces a decrease of the coercive field as the number of vacancies increases. Furthermore, the results indicate that a 5 nm TiN thick buffer layer is enough to maintain the Fe3O4[100]/TiN[100]/Si[100] epitaxial relationship.

1. Introduction

Magnetite, Fe3O4, has attracted great attention recently in spintronics due to its presumed full spin polarization of the charge carriers at the Fermi level, its relatively high electronic conductivity at room temperature and its high Curie temperature of 860 K. At room temperature, magnetite crystallizes in an inverse spinel structure with a formal chemical formula Fe3+Fe2+[Fe2+,Fe3+]BO4/C07.5%. However, the introduction of Fe vacancies in magnetite does not alter the well-defined fourfold in-plane magnetic anisotropy but induces a decrease of the coercive field as the number of vacancies increases. Furthermore, the results indicate that a 5 nm TiN thick buffer layer is enough to maintain the Fe3O4[100]/TiN[100]/Si[100] epitaxial relationship.

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studied the magnetic anisotropy of the system Fe₃O₄/TiN/Si(001), but they found an unexpected isotropic magnetic behaviour instead of the fourfold symmetry presumed for (001) epitaxial films.

The magnetic properties of Fe₃O₄ thin films are strongly affected by the presence of structural growth defects such as antiphase boundaries (APBs). APBs are common in magnetite thin films and are responsible for local anti-ferromagnetic ordering of the spins. The presence of APBs depends on the growth technique, the growth parameters (such as temperature or oxygen partial pressure), the nature of the substrate and the thickness of the films.13–15,24,34–37 PVD growth methods such as pulsed laser deposition (PLD),4,14,15,18–23,31 molecular beam epitaxy (MBE)4,7,9–13,16,27,34–36,38 and magnetron sputtering5,8,24,25,32,33 have been extensively used to grow magnetite thin films. However, other sputtering-based techniques such as ion-beam sputtering have been scarcely investigated.4,6,26,39 We have recently explored the capabilities of ion beam sputtering in combination with a second ion source (assisting beam) to obtain both nanocrystalline stoichiometric magnetite on amorphous glass substrates40 and epitaxial magnetite on single crystal substrates such as MgO and SrTiO₃.17 In this work we have extended the use of ion beam assisted deposition (IBAD) to grow magnetite thin films on TiN buffered Si(001) single crystals. We have characterized their magnetic properties by the magneto-optical Kerr effect (MOKE) and found fourfold magnetic anisotropy in the bilayer Fe₃O₄/TiN, a fact that has not been previously reported to our knowledge.

Since IBAD allows the independent control of both the number and energy of the Fe and O atoms impinging on the substrate, this technique is suitable for controlling the stoichiometry of the deposited film. Therefore, we have also investigated the effect induced by the presence of Fe vacancies on the magnetic behaviour of non-stoichiometric magnetite thin films.

2. Experimental

Magnetite thin films were deposited on Si(001) substrates using a dual ion beam sputtering system. Prior to deposition, the native SiO₂ was removed by dipping the substrate into a 5% HF solution for 2 min. TiN buffer layers were deposited on Si(001) by Ar⁺ ion sputtering from a 99.9% pure TiN target with a 3 cm Kaufmann-type ion source. Fe₂O₃ thin films were grown from a pure iron (99.99%) target under simultaneous bombardment of the deposition layer with a controlled mixture of low-energy oxygen and argon ions from an end-Hall ion source. The O₂ relative flow rate was adjusted to 13.3% of the total flow rate before introduction in the assisting ion source to obtain stoichiometric magnetite, and it was increased to obtain non-stoichiometric compounds. The total flow of Ar and O₂ at the assisting ion source was 1.5 sccm. The sputtering conditions were kept constant with the Fe atom current density at the substrate fixed at JFe = 1.4 mA cm⁻² and the energy of the sputtering Ar⁺ ions fixed at 600 eV. The energy and current density of the assisting ion beam show small variations due to the composition of the beam, as shown in Table 1, which also collects a summary of the deposition conditions. The assistance deposition conditions have been optimized previously on amorphous substrates,40 where the increase of O/Fe atoms as the current density increases competes with a preferential sputtering of oxygen atoms as the energy increases.

Both TiN buffer layers and magnetite layers were deposited at a constant substrate temperature of 350 °C.

The bilayer was deposited in a vacuum chamber with a base pressure of 2 × 10⁻⁵ Pa. During deposition the pressure was maintained at 3 × 10⁻² Pa and the substrates were rotated at 2 rpm to increase the homogeneity of the deposit. The oxygen partial pressure used during deposition was maintained constant during the cooling process, after deposition, until the temperature was below 150 °C.

The crystalline structure of the different films and the out-of-plane lattice parameters were analyzed by X-ray diffraction (XRD) using a Panalytical X’pert PRO in theta/2theta configuration using Cu Kα radiation (λ = 1.5418 Å). Low-energy electron diffraction (LEED) was performed after cleaning the surface by several cycles of sputtering with Ar⁺ ions at 1 keV. The LEED had a typical electron beam size of 1 mm² and was performed in a rear-view four grid optics diffractometer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E₀ (eV)</th>
<th>% O₂</th>
<th>JFe (mA cm⁻²)</th>
<th>Thickness (nm)</th>
<th>Fe₂O₃ dep. rate (nm s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>55</td>
<td>13.3</td>
<td>0.057</td>
<td>10.0</td>
<td>85.0 0.081</td>
</tr>
<tr>
<td>S2</td>
<td>56</td>
<td>17.0</td>
<td>0.058</td>
<td>10.0</td>
<td>76.0 0.061</td>
</tr>
<tr>
<td>S3</td>
<td>57</td>
<td>22.4</td>
<td>0.059</td>
<td>10.0</td>
<td>73.2 0.056</td>
</tr>
<tr>
<td>S4</td>
<td>58</td>
<td>25.6</td>
<td>0.060</td>
<td>10.0</td>
<td>65.3 0.049</td>
</tr>
<tr>
<td>S5</td>
<td>56</td>
<td>17.0</td>
<td>0.058</td>
<td>5.0</td>
<td>76.0 0.061</td>
</tr>
<tr>
<td>S6</td>
<td>56</td>
<td>17.0</td>
<td>0.058</td>
<td>17.0</td>
<td>76.0 0.061</td>
</tr>
</tbody>
</table>

Fe integral conversion electron Mössbauer spectroscopy (ICEMS) data were recorded at room temperature in constant acceleration mode using a ⁵⁷Co(Rh) source and a parallel plate avalanche counter. The spectra were computer-fitted and the isomer shifts were referred to the centroid of the spectrum of α-Fe at RT.

The in-depth composition and thickness of the different layers were determined by Rutherford backscattering spectroscopy (RBS) in a 5 MV tandem accelerator using two different ¹⁰⁰Ne⁺ energies, 2.0 and 3.045 MeV. The 3.045 MeV energy of the ¹⁰⁰Ne⁺ ions is selected to enhance resonantly the scattering cross section of oxygen atoms and, therefore, to enable a better quantification of oxygen. At this energy, the distribution and quantification of the elements were determined using the ¹⁴O(⁴He,⁴He)¹⁶O elastic-scattering cross sections reported by Cheng et al. and Feng et al.41,42 for the scattering angles of 165 and 170.5° used in the experiment and the SIMNRA simulation software package.42 RBS has also been used to estimate the thickness of the samples by considering a mass density of 5.15
and 5.22 g cm\(^{-3}\) for magnetite and titanium nitride, respectively. The thicknesses of the different layers and the deposition rates of the magnetite films have also been included in Table 1. The thickness estimated error, determined from the fit to two energies and two scattering angles and small density variation as composition changes, was of the order of 3.5%.

The angular dependence of the magnetization was investigated at room temperature by high-resolution vectorial-Kerr magneto-optical measurements in a longitudinal configuration. MOKE hysteresis loops were recorded by changing the in-plane angular rotation of the sample, \(2\theta\), keeping fixed the external magnetic field direction. The angular rotation, ranging from 0 to 360°, was probed at intervals of 4.5° with a maximum applied magnetic field of 110 mT.

### 3. Result and discussion

#### 3.1 Stoichiometric magnetite \(\text{Fe}_3\text{O}_4\)

Fig. 1 shows a \(\theta-2\theta\) scan of a 66 nm \(\text{Fe}_3\text{O}_4\) thin film grown on a 10 nm TiN buffer layer deposited on Si(001) at 350 °C (sample S1, Table 1). The diffraction pattern shows a main peak at 42.59°, which corresponds to the overlapping signals of the (004) diffraction plane of \(\text{Fe}_3\text{O}_4\) and the (002) diffraction plane of TiN (see the included respective reference lines taken from the JCPDS card No. 04-015-3102 and 00-038-1420). A very narrow, additional peak at 32.99° corresponds to the TiN(002) diffraction plane of the substrate. This forbidden Si(200) reflection is generally caused by multiple diffractions in theta/2theta scans.\(^{43}\) Since the orientation of the substrate, the result suggests that the \(\text{Fe}_3\text{O}_4\)/TiN bilayer has grown epitaxially on the Si substrate with a strong degree of orientation. This is confirmed by the LEED patterns taken at 86 eV and 136 eV (Fig. 1, inset), which show the single epitaxial relationship cube-on-cube of the bilayer \(\text{Fe}_3\text{O}_4[100]/\text{TiN}[100]/\text{Si}[100]\).

The small difference between the lattice parameter of \(\text{Fe}_3\text{O}_4\) (\(a = 0.839\) nm) and twice the lattice parameter of TiN (\(a = 0.424\) nm) is the cause of the overlap observed between the TiN(002) and \(\text{Fe}_3\text{O}_4\)(004) peaks in the diffractogram. In fact, the expected lattice mismatch determined by their bulk lattice spacings (\(d_{\text{Fe}_3\text{O}_4} - 2d_{\text{TiN}}/2d_{\text{TiN}}\), is only \(-1\%\). The lattice parameter obtained in this work for the bilayer \(\text{Fe}_3\text{O}_4/\text{TiN} (0.849\) nm) is larger than that of bulk magnetite and also slightly larger than twice that of bulk TiN. The larger out-of-plane lattice parameter relative to magnetite suggests an in-plane compressive strain in the \(\text{Fe}_3\text{O}_4\) films.

It is difficult to distinguish magnetite and maghemite on the basis of XRD. Mössbauer spectroscopy is the most appropriate technique to identify both phases since it is crystal site and valence state sensitive and can distinguish between Fe\(^{3+}\) and Fe\(^{3+}\) cations occupying octahedral and octahedral/tetrahedral sites, respectively.

The Mössbauer spectrum of bulk stoichiometric magnetite shows two distinct sextets, one associated with the tetrahedral A site that contains only Fe\(^{3+}\) ions, and the second one associated with the octahedral B site that contains an equal number of Fe\(^{3+}\) and Fe\(^{2+}\) ions. The hyperfine parameters of the B sextet, labelled as Fe\(^{2.5+}\)\(_B\), are intermediate between those of Fe\(^{3+}\) and Fe\(^{3+}\). In fact, Fe\(^{2.5+}\)\(_B\) corresponds to the average signal from the cations at the octahedral sites that participate in the fast electron hopping process between Fe\(^{2+}\) and Fe\(^{3+}\) ions.

The ICEMS spectrum of a stoichiometric \(\text{Fe}_3\text{O}_4\) thin film grown on 10 nm TiN buffered Si(001) (sample S1) is shown in the inset of Fig. 1. The spectrum has been fitted in terms of two sextets components, as in bulk magnetite. The obtained Mössbauer parameters are included in Table 2. The hyperfine magnetic field, \(H_{hyp}\), and isomer shift, \(\delta\), for the Fe\(^{3+}\) A-site are 48.4 T and 0.26 mm s\(^{-1}\), respectively, whereas for the Fe\(^{2.5+}\) B-site are 45.0 T and 0.63 mm s\(^{-1}\), respectively. These values are close to those reported for bulk magnetite\(^{5,44}\) as well as for stoichiometric magnetite thin films.\(^{5,7,19}\) In addition, the area ratio of the two sextets, 1.9, is the expected for stoichiometric magnetite.\(^{44}\)

In Fig. 2, the Rutherford backscattering spectra of sample S1 recorded at a scattering angle of 170.5° and 2.0 and 3.045 MeV \(^4\text{He}^+\) energies are shown (Fig. 2a and b, respectively). The spectra

### Table 2 Mössbauer parameters obtained from the fit of the Mössbauer spectra recorded from stoichiometric \(\text{Fe}_3\text{O}_4\) and nonstoichiometric \(\text{Fe}_{x-y}\text{O}_y\) thin films grown on TiN buffered Si(100) substrates. The numbers in parentheses indicate the errors of the fits.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe(^{3+}) A/B</th>
<th>Fe(^{2.5+}) A/B</th>
<th>Fe(^{3+}) A/B</th>
<th>Fe(^{2.5+}) A/B</th>
<th>Fe(^{3+}) A/B</th>
<th>Fe(^{2.5+}) A/B</th>
<th>Fe(^{3+}) A/B</th>
<th>Fe(^{2.5+}) A/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>(0.26(1))</td>
<td>(-0.02(2))</td>
<td>(48.4(1))</td>
<td>(0.40(4))</td>
<td>(34(3))</td>
<td>(2.2)</td>
<td>(0.63(1))</td>
<td>(-0.03(3))</td>
</tr>
<tr>
<td>S2</td>
<td>(0.27(2))</td>
<td>(-0.01(3))</td>
<td>(48.6(1))</td>
<td>(0.48(6))</td>
<td>(36(5))</td>
<td>(2.4)</td>
<td>(0.61(2))</td>
<td>(-0.00(4))</td>
</tr>
<tr>
<td></td>
<td>Doublet 0.34(7)</td>
<td>1.54(15)</td>
<td>0.44(20)</td>
<td>4(1)</td>
<td></td>
<td></td>
<td>Doublet 0.65(10)</td>
<td>1.72(24)</td>
</tr>
<tr>
<td>S3</td>
<td>(0.26(2))</td>
<td>(0.01(3))</td>
<td>(48.4(1))</td>
<td>(0.48(6))</td>
<td>(45(5))</td>
<td>(2.7)</td>
<td>(0.62(2))</td>
<td>(0.05(4))</td>
</tr>
<tr>
<td></td>
<td>Doublet 0.65(10)</td>
<td>1.72(24)</td>
<td>0.48(30)</td>
<td>3(1)</td>
<td></td>
<td></td>
<td>Doublet 0.44(14)</td>
<td>1.68(27)</td>
</tr>
</tbody>
</table>

X-ray diffraction pattern of a \(\text{Fe}_3\text{O}_4/\text{TiN}[100]\) bilayer in \(\theta-2\theta\) configuration. The insets show the low-energy electron diffraction pattern at 86 (right) and 136 eV (left), respectively, as well as the ICEMS Mossbauer spectrum with the corresponding fitted lines (see Table 2).
show the expected Fe, Ti, Si and O channels. The presence of a low amount of Ar (<1%) indicates that this element has also been incorporated during the sputtering process. Additionally, a small bump corresponding to a nitrogen signal can also be observed in the 2 MeV spectrum. The simulation at both energies can be well-fitted with a 10 nm TiN$_{0.9}$ layer and a 85 nm Fe$_3$O$_4$ layer without the presence of any intermixing at the TiN/Fe$_3$O$_4$ interface. The estimated error in the composition was determined from the fit to two energies and two scattering angles.

The magnetic anisotropy of the Fe$_3$O$_4$ films grown on TiN buffered Si(001) substrates and the angular dependence of the magnetization reversal were investigated at RT by high-resolution vectorial-Kerr magneto-optical measurements in a longitudinal configuration. Three representative hysteresis loops at $H = 0^\circ$, $H = 22.5^\circ$ and $H = 45^\circ$ are shown in Fig. 3a for the bilayer stack Fe$_3$O$_4$/TiN. $H = 0^\circ$ was set parallel to the in-plane Si[110] crystallographic orientation. These hysteresis loops show different remanence and coercivity values depending on the in-plane orientation of the magnetic field. At $H = 45^\circ$, parallel to the Si[100] orientation, the in-plane hysteresis curve displays an almost rectangular shape. This has the highest remanence and coercivity of all the orientations considered indicating that this is the magnetization easy axis of the films. The coercive field at the easy axis (57 mT) is somewhat higher than those obtained on Fe$_3$O$_4$ films grown using the same deposition method both on single crystal oxides and amorphous substrates whose values range from 22 to 45 mT depending on the substrate. However it is in good agreement with the 57 mT value found by Xiang et al. for a 90 nm magnetite thick film grown on TiN/Si(001). These values are an order of magnitude larger than the values shown for bulk magnetite. The discrepancy is usually attributed to defects in the thin films, such as antiphase boundaries, well documented in Fe$_3$O$_4$ films grown on MgO substrates. In fact, Xiang et al. have observed the presence of intrinsic APBs in Fe$_3$O$_4$/TiN bilayers. These structural defects can act as pinning centers for the magnetic domain wall motion and thus control the magnetic domain structure, as previously observed by Wei et al. and by TEM by Kasama et al.

The polar plots of remanence and coercivity are shown in Fig. 3b and c respectively. In Fig. 3b the $|\cos 2\alpha|/|\sin 2\alpha|$ dependence expected for biaxial anisotropy systems, rotated 45° and normalized to our $M_r/M_s$ values, has been also included. It is clear that the Fe$_3$O$_4$/TiN/Si(001) bilayer presents a very-well defined in-plane fourfold symmetry in which the maxima of both coercivity and remanence, which correspond to the magnetization easy axis of the films, appear at $2\alpha = 45^\circ$, 135°, 225° and 315°. These angles correspond to the [010], [001], [010] and [100]Si directions, respectively. This observed fourfold symmetry, expected for a cubic system, is in marked contrast to the isotropic behavior reported by Xiang et al. in Fe$_3$O$_4$ films grown on TiN buffered Si(001), and attests the high quality of these films.

It is puzzling that the in-plane easy-axis directions are the in-plane [100] ones. On bulk magnetite at room temperature the [111] and [100] directions are the easy axes and hard axes of the magnetization, respectively, while the [110] direction is the intermediate one. In the (001) surface the magnetization would be expected to lie along the projection of the bulk [111] axis, i.e., the in-plane [110] directions. Such easy axes have been observed on the (001) surface of bulk magnetite crystals. However, this is not always the case for thin films. In (001)-oriented films, on one hand there are reports of in-plane [110] easy axes by Torque, FMR and MOKE magnetic measurements. But, on the other hand, there are also reports of [100] in-plane easy axes. In addition, there are also reports of in-plane magnetic isotropic (001) films. In fact, Schemme et al. reported that they could switch the easy axis by changing the preparation procedure. We have reported previously single-crystal Fe$_3$O$_4$ thin films where the magnetization easy axes lie along the in-plane [100] directions. This holds for different deposition methods (PLD or ion beam assisted sputtering) and (001)-oriented substrates (MgO, SrTiO$_3$ or LaAlO$_3$). In the present work, we find again the same in-plane [100] easy axes, which are parallel to the Si[100] ones.

At this point, we suspect that the density, distribution and orientation of APBs, clearly dependent on the deposition process,
as well as on the strains induced by the substrate, are the origin of the different magnetic easy axes found on (001) oriented Fe3O4 thin films. Further experiments will be needed to explain this behavior in detail. However, it is clear that we observe a well-defined fourfold anisotropy, as good as any obtained for films grown on single-crystal oxide substrates.

3.2 Non-stoichiometric magnetite Fe3−xO4

In non-stoichiometric magnetite, Fe3−xO4, the Fe vacancies are expected to be distributed randomly over the octahedral B sites. The vacancies screen the charge transfer and freeze the hopping process.9 For each vacancy, five Fe3+ ions in octahedral sites become trapped and the rest of cations at the octahedral sites are responsible for the hopping process. Therefore, non-stoichiometric magnetite can be formulated as (Fe3+)A(Fe2+0.635Fe3+0.365)B6O42−. The vacancy parameter, δ, can vary continuously from 0 to 1/3 yielding all the stoichiometries between Fe3O4 to γ-Fe2O3, where maghemite, γ-Fe2O3, corresponds to (Fe3+)A(Fe5/3+0.33Fe2+0.66)B6O42−. Thus, it has been reported44 that the Mössbauer spectrum of non-stoichiometric magnetite can be fitted using three different sextets: one corresponding to Fe3+ (A), the second corresponding to Fe3.5+ (B) and the third corresponding to Fe2.5+ (B). Often, though, the two Fe3+ sextets strongly overlap and, thus, a fit model considering only two sextets (one accounting for Fe3+ and the other accounting for Fe2.5+) is used.

Nonstoichiometric magnetite can be grown by controlling the oxygen partial pressure during the deposition process9 or during further annealing of stoichiometric magnetite in oxygen or air atmospheres.37 In our system, we have tuned the oxygen content by changing the content of O2+ ions at the assisting ion beam keeping constant the other deposition parameters (see Table 1) to obtain non-stoichiometric films. We have denoted those samples S2, S3 and S4. Their respective ICEMS spectra, together with that recorded from sample S1 for comparison purposes, are presented in Fig. 4.

Fig. 4 Room temperature ICEMS Mossbauer spectra recorded from samples S1, S2, S3 and S4. The corresponding fits, whose parameters are shown in Table 2, are also included.

The Mössbauer spectra of samples S2–S4 have been analyzed in terms of two sextet components as mentioned above. In addition, a paramagnetic doublet has been included to fit more accurately the central part of the spectra. The fitting parameters are collected in Table 2. The hyperfine parameters of both sextets are compatible with the presence of magnetite, however, the sextet ratio departs from the 1.9 ratio shown by stoichiometric magnetite indicating the non-stoichiometric character of the films. The sextets of the non-stoichiometric films show broader linewidths than those of S1, which could indicate a certain loss of degree of crystallinity.

The fitting parameters of the doublet used for samples S2, S3 and S4 are also included in Table 2. The area of this doublet accounts only for 3–5% of the total area and the determination of its hyperfine parameters is affected by a large error due to the strong overlap with the other components. The isomer shifts show considerable variation from sample to sample ranging from pure Fe3+ in sample S2 to a value which can be considered intermediate between Fe3+ and Fe2+ in the rest of the samples, particularly in S3. The corresponding quadrupole splittings are also unprecedentedly large for Fe3+ species. Therefore the data do not allow an unambiguous identification of the doublet. It is known that FeO can be formed at the interface between the substrate and the Fe3O4 film and that strongly oxidized wüstite can be fitted to several contributions, comprising both Fe2+ and Fe3+.48 However, given the small intensity of the doublet, we have not considered the possibility of a more elaborated fitting including various paramagnetic contributions.

From the area ratio of the two sextets [Fe3+]A,B and (Fe2.5+)B it is possible to obtain the vacancy parameter δ:

$$\beta = \frac{1(f_A/f_B) + 5\delta}{2 - 6\delta}$$

where $f_A$ and $f_B$ are the recoil fraction of each cation site. The recoil free fraction of the two sites is very close but not identical and we assume a value of $f_A/f_B$ of 0.94.49 The evolution of the vacancy parameter with assisting ion beam oxygen content is presented in Fig. 5a. Starting from sample S1, which corresponds to stoichiometric magnetite, sample S2 shows a low vacancy parameter $\delta \approx 0.01$ which increases significantly to $\delta \approx 0.06$ and 0.05 for samples S3 and S4, respectively, which are clearly more oxidized. Since the spectrum of maghemite can overlap
with that of the tetrahedral Fe$^{3+}$ component of magnetite, the presence of a small amount of maghemite cannot be discarded.

Important information about the magnetic structure of the magnetite thin films can be derived from the analysis of the relative areas of the lines of the Zeeman sextets. The relative line area of a magnetically split sextet is $3 : x : 1 : 1 : x : 3$. The $x$ value depends on the angle between the incident $\gamma$-rays and the hyperfine field ($\theta$) through the formula $4 \sin^2 \theta / (1 + \cos^2 \theta)$. When the $\gamma$-rays impinge perpendicularly on the sample surface (as in the present case), the $x$ values may change from 0 (magnetization perpendicular to the film surface) to 4 (magnetization in-plane). A $x$ value larger than 2 indicates a tendency to in-plane magnetization, which is precisely what is observed in all the present samples. This tendency seems to increase as the oxygen content at the assisting beam increases, since $x$ reaches 2.2, 2.4, 2.7 and 2.5 for samples S1, S2, S3 and S4, respectively. In all the cases, however, out-plane components still remain.

Fig. 5b shows the dependence of the growth rate of the iron oxide thin films as the oxygen content flow increases at the assisting ion source. The observed decrease as the oxygen content increases is the expected behavior as it was also found in other sputtering deposition processes of iron oxides and other oxides. During sputtering the target atoms collide with atoms and molecules in the chamber before reaching the substrate. This results in a partial loss of energy and direction on their way to the substrate. As oxygen is a bi-atomic molecule its radius is larger than that of Ar and the sputtered Fe atoms suffer more collisions as the oxygen partial pressure is increased producing a decrease of the deposition rate. In addition, the presence of reactive oxygen could result in the formation of an oxide layer on the target surface and this also reduces the deposition rate.

Fig. 5e shows the evolution of the lattice parameter with the oxygen content at the assisting ion beam. We have plotted the values obtained from the peaks corresponding to (004) and (008) diffraction planes of Fe$_3$O$_4$. The observed decrease of the lattice parameter value can be an indication of a compressive strain reduction. However, since the lattice parameter of bulk maghemite, 8.351 Å, is slightly smaller than that of bulk magnetite, 8.391 Å, this would be also expected if a small amount of maghemite was present in the samples.

Finally, the oxygen concentration of the films, obtained by RBS, is shown in Fig. 5d. In this figure, for a better visualization of the results, the limits of the O/Fe ratio scale were set at 1.33 and 1.5 which are the values that correspond to magnetite and maghemite, respectively.

As expected, the O/Fe ratio increases as the oxygen flow at the assisting beam is increased.

The magnetic anisotropy of the nonstoichiometric Fe$_{3-x}$O$_4$ thin films grown on TiN buffered Si(001) substrates has been also studied by the vectorial-Kerr magneto-optical effect in a longitudinal configuration and the results are summarized in Fig. 6. Two hysteresis loops recorded at $\theta_{H} = 0^\circ$ and $\theta_{H} = 45^\circ$ for sample S4 (Fig. 6a) indicate that even under more oxidized conditions the strong fourfold anisotropy is preserved. $\theta_{H} = 45^\circ$ is parallel to the Si[100] orientation and the in-plane hysteresis curve displays an almost rectangular shape with high remanence and coercivity indicating that the magnetization easy axis of the sample lies in this crystallographic direction as it has been previously observed for the stoichiometric magnetite film (sample S1). In order to compare the in-plane magnetic anisotropy of the films during oxidation, we have studied the dependence of coercivity on $\theta_{H}$ for samples S1, S2, S3 and S4 (Fig. 6b). In all the samples a very-well defined in-plane fourfold symmetry is observed indicating the presence of cubic magnetocrystalline anisotropy with maxima of coercivity and remanence at $\theta_{H} = 45^\circ$, 135$^\circ$, 225$^\circ$ and 315$^\circ$. It can be also observed that the coercive field decreases at both the easy and hard axes as the oxygen content in the assisting beam is increased (Fig. 6c). This evolution of the coercivity values seems to be related to the Fe vacancy concentration obtained by ICEMS, the O/Fe ratio obtained by RBS and the relaxation of the lattice observed by XRD. These results are in
agreement with those found by Wei et al.,37 who reported that the partial oxidation of magnetite induces faster saturation and softer films due to a partial deactivation of the APBs.

The well-defined four-fold in-plane magnetic anisotropy found in all the samples seems to disagree with the x value found by ICEMS. In such a case, the x value should be close to 4 since values close to 2 indicate either a random direction of magnetization or a magnetization parallel to the [111] direction.9 Voogt et al.,9 Margulies et al.8 and Wei et al.37 have also found similar x values in stoichiometric magnetite thin films. However, the origin of the anomalous out-of-plane component of the magnetization determined by ICEMS is not well understood yet. The increase of the anomalous out-of-plane component of the magnetization determined by ICEMS is not well understood yet. The increase of x with oxidation, also observed by Voogt et al.,9 suggests a decrease of the density of active APBs. Again, regardless of the particular mechanism involved, it is clear that the oxidized films maintain a high quality that provides well-defined magnetocrystalline anisotropy on Si(001) thanks to the TiN buffer layer.

3.3 Effect of TiN thickness

The TiN thickness dependence on the magnetic properties has been investigated by comparing the 5, 10 and 17 nm TiN buffered Si(001) substrates (see Table 1). In Fig. 7a the dependence of coercivity on the in-plane magnetic field angle for samples S2, S5 and S6 is shown. A well-defined fourfold anisotropy for the three TiN thicknesses studied in this work is observed. In order to compare the strength of the fourfold in-plane magnetic anisotropy, we have represented in Fig. 7b the ratio between the coercive fields at the easy and hard axes as a function of TiN thickness. High values of this ratio of 1.48 have been obtained for samples grown on 5 and 10 nm thick TiN buffer layers indicating that a TiN thickness as low as 5 nm is enough to obtain an epitaxial growth of the bilayer stack on Si(001). However, the ratio is slightly reduced to 1.43 for the sample grown on the 17 nm thick TiN layer, indicating a possible reduction of the film quality upon increase in TiN thickness.

4. Conclusions

We have integrated Fe3O4 thin films onto (001) silicon single crystals by using a TiN buffer layer. We reported a compositional study and the structural and magnetic characterization of Fe3O4/TiN/Si(001) bilayers grown by ion beam sputtering. Crucial for possible applications, no detectable interdiffusion at the Fe3O4/TiN interface was observed by RBS. A very well

defined fourfold magnetic anisotropy, with easy axes along Si[100] and [010] directions, combined with the XRD and LEED results, indicate the high quality of the Fe3O4 films. These results are also extended to nonstoichiometric magnetite Fe3-δO4 thin films where Fe vacancies are introduced by increasing the oxygen content in the assisting beam. A reduction of the coercivity at both the easy and hard axes as the Fe vacancy concentration is increased has been detected.

These results demonstrate the successful epitaxial growth of high quality stoichiometric Fe3O4 and nonstoichiometric Fe3-δO4 thin films on Si(001) substrates through a TiN buffer layer, a procedure that might be relevant to incorporate magnetite in spintronic devices.

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References
