Applied Surface Science 359 (2015) 742–748

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Role of the substrate on the magnetic anisotropy of magnetite thin films grown by ion-assisted deposition

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ARTICLE INFO

Article history:
Received 15 July 2015
Received in revised form
29 September 2015
Accepted 24 October 2015
Available online 11 November 2015

Keywords:
Magnetite thin films
Magnetic anisotropy

ABSTRACT

Magnetite (Fe_3O_4) thin films were deposited on MgO (0 0 1), $SrTiO_3$ (0 0 1), $LaAlO_3$ (0 0 1) single crystal substrates as well on as silicon and amorphous glass in order to study the effect of the substrate on their magnetic properties, mainly the magnetic anisotropy. We have performed a structural, morphological and compositional characterization by X-ray diffraction, atomic force microscopy and Rutherford backscattering ion channeling in oxygen resonance mode. The magnetic anisotropy has been investigated by vectorial magneto-optical Kerr effect. The results indicate that the magnetic anisotropy is especially influenced by the substrate-induced microstructure. In-plane isotropy and uniaxial anisotropy behavior have been observed on silicon and glass substrates, respectively. The transition between both behaviors depends on grain size. For $LaAlO_3$ substrates, in which the lattice mismatch between the Fe_3O_4 films and the substrate is significant, a weak in-plane fourfold magnetic anisotropy is induced. However when magnetite is deposited on MgO (0 0 1) and $SrTiO_3$ (0 0 1) substrates, a well-defined fourfold in-plane magnetic anisotropy is observed with easy axes along [1 0 0] and [0 1 0] directions. The magnetic properties on these two latter substrates are similar in terms of magnetic anisotropy and coercive fields.

1. Introduction

Magnetite, Fe_3O_4, has attracted great attention for spintronic applications due to its presumed full spin-polarization of the charge carriers at the Fermi level [1], its relative high electronic conductivity at room temperature and its high Curie temperature of 860 K [2,3]. At room temperature, magnetite crystallizes in the inverse spinel structure with a formal chemical formula $Fe_A^{3+}[Fe^{2+}Fe^{3+}]_BO_4^{2-}$. One third of the Fe cations occupy the tetrahedral A-sites as Fe^{3+} whereas the rest of Fe^{2+} and Fe^{3+} occupy octahedral B-sites. An important issue for application in new devices is to control the magnetic anisotropy when the thickness of the magnetite films is reduced to the nanometer scale. Overall, the magnetic properties of magnetite thin films are influenced by the interfacial strain induced by the substrate and by the film growth microstructure.

Many works have focused on the study of in-plane magnetic anisotropies induced by the substrate [4–16]. The MgO substrates have been widely explored [4–10] due to its low lattice mismatch with Fe_3O_4 (0.3%). In general, in-plane magnetic anisotropies have been reported for magnetite grown on MgO (1 0 0) and MgO (1 1 0) substrates [4–8]. However, depending on the defects induced by the deposition process, it is also possible to find an in-plane isotropic behavior as reported by Cheng et al. [9]. Recently, some works reported perpendicular magnetic anisotropy in Fe_3O_4 films deposited on MgO (1 1 1) substrates [7]. Despite of the high lattice mismatch between Fe_3O_4 and $SrTiO_3$, magnetic anisotropy of Fe_3O_4 grown on $SrTiO_3$ substrates has been reported [8–11]. As in the case of MgO substrates, depending on the deposition process, both in-plane magnetic anisotropy [8,10,11] and in-plane magnetic isotropy [9] have been found. In addition, in-plane magnetic anisotropies have been also reported on Fe_3O_4 films grown epitaxially on silicon substrates using buffer layers [12,13]. Semiconductor single crystals substrates such as GaAs (1 0 0) [14] and InAs (1 0 0) [15], as well as metallic substrates [16], have been used to induce in-plane anisotropies. Moreover, other mechanisms capable of inducing magnetic anisotropies, in addition to the choice of the substrate, have been investigated such as the use of flexible substrates to control the strain [17].

Several PVD deposition techniques have been used to deposit Fe_3O_4 thin films. These included pulsed-laser deposition (PLD) [7,8,10,11,18], molecular beam epitaxy (MBE) [4–6,9,12,14,15,19] and magnetron sputtering [13,19–21]. However, other

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http://dx.doi.org/10.1016/j.apsusc.2015.10.180
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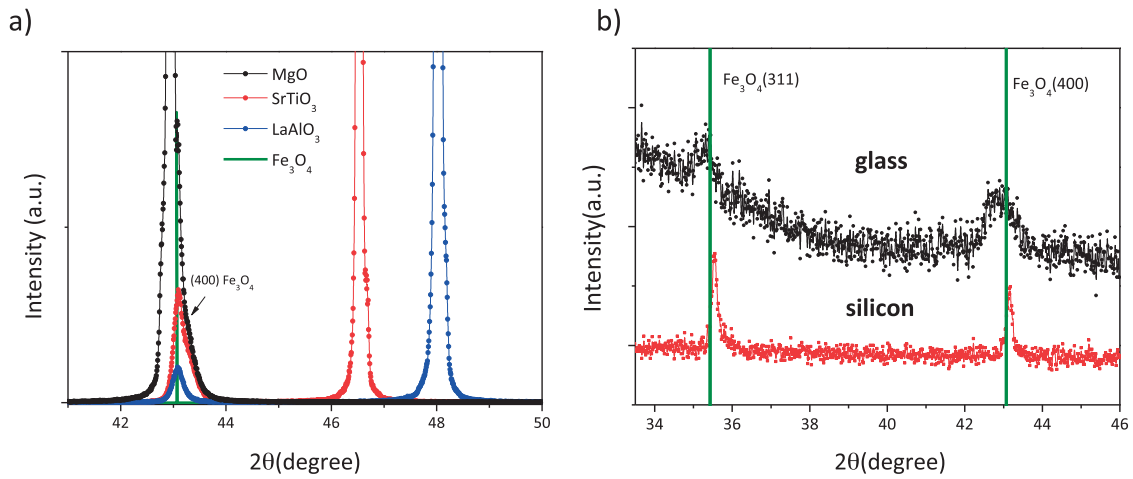

Fig. 1. XRD diffraction patterns of magnetite thin films grown on (a) oxide single crystal substrates of MgO, $SrTiO_3$ and $LaAlO_3$ and (b) Si with native SiO_2 and glass substrates.

Table 1
Lattice parameter, XRD and AFM mean grain sizes and AFM surface roughness of polycrystalline Fe_3O_4 thin films grown on glass and silicon substrates.

Substrate	XRD		AFM	
	Lattice parameter(nm)	Size (nm)	Size (nm)	RMS roughness (nm)
Glass	0.843	14	29	2.5
Silicon	0.837	45	51	5.2

sputtering-based techniques such as ion-beam sputtering have been scarcely explored [22,23]. In a previous work, we have demonstrated the capability of dual ion beam sputtering to obtain nanocrystalline magnetite on amorphous glass substrates [24]. In this technique a second ion beam is used to control the composition and to increase the surface mobility that may affect the number of antiphase boundaries (APBs) nucleated in the films. APBs are common in magnetite thin films and are growth defects responsible for local anti-ferromagnetic ordering of the spins [25].

In this work we have extended the use of dual-ion-beam sputtering to grow magnetite on oxide single crystals as well as on other substrates such as silicon with a native oxide layer, which provides an amorphous-like substrate. Since the magnetic properties of magnetite are strongly influenced by the deposition conditions, in this study we have kept constant the deposition parameters (the sputter and assisted ion energies and current densities) as well as the substrate temperature. Thus, only the substrates were changed to reveal the role of the substrate in the microstructure and magnetic properties of the films. In the particular case of single crystal substrates of MgO and $SrTiO_3$, which show a well-defined four-fold magnetic anisotropy, a supplementary study involving small changes in the deposition rate has been also carried out.

2. Experimental

Iron oxide thin films were deposited by dual ion beam sputtering on MgO, $SrTiO_3$ and $LaAlO_3$ single crystals, silicon with a native SiO_2 layer and glass substrates. The films were grown by Ar^+ sputtering with a 3 cm Kaufmann-type ion source of a pure iron (99.99%) target and simultaneous bombardment with a controlled mixture of low-energy oxygen and argon ions from an end-Hall ion source. The O_2 relative flow rate was adjusted to 13.3% of the total flow rate before introduction in the assisted ion source. The energy and current density of the assisted beam were 57 eV and 0.061 mA/cm^2, respectively. The energy of the sputter beam was 600 eV and the current density was 1.4 mA/cm^2. Under these experimental conditions the deposition rate was 0.052 nm/s.

The films were deposited in a vacuum chamber with a residual 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 temperature of the substrates was kept constant at around 400 °C. After deposition, the partial oxygen pressure was maintained constant during the cooling process until the temperature was below 150 °C.

The single crystal substrates used in this work have been chosen in terms of their lattice compatibility with Fe_3O_4. The mismatch between Fe_3O_4 and MgO is −0.3%. $SrTiO_3$ and $LaAlO_3$ have been used to investigate the effect of lattice mismatch in the magnetic anisotropy. These substrates show large mismatch, 7.0% and 9.7% for $SrTiO_3$ and $LaAlO_3$, respectively.

The crystalline structure of the different films was analyzed by X-ray Diffraction (XRD) in the θ/2θ configuration. Rutherford backscattering spectroscopy (RBS) ion-channeling was performed with $^4He^+$ ions of 3.045 MeV at a scattering angle of 170.5° to analyze the crystalline quality, composition and thickness of the films. The 3.045 MeV energy of the $^4He^+$ ions was selected to resonantly enhance the scattering cross section of oxygen atoms and, therefore, to enable a better quantification of the oxygen content in the films. At this energy the distribution and quantification of the elements were determined using the $^{16}O(\alpha,\alpha)^{16}O$ elastic-scattering cross sections, as reported by Cheng et al. [26]. The distribution and quantification of the elements were determined by simulation with the SIMNRA software package [27]. Atomic force microscopy (AFM) was used to characterize the morphology of the film surfaces. AFM measurements were performed in standard tapping mode with an Agilent Technologies 5100 scanning probe microscope using Si tips. Scans of 5×5 and 2×2 μm^2 were performed for the evaluation of the average surface roughness and for the analysis of the grain size and shape.

The angular dependence of the magnetization of the Fe_3O_4 films grown on the different substrates was investigated at RT 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 (α_H) and keeping fixed the external magnetic field direction. The angular rotation, ranging from 0 to 360° was probed at intervals of 4.5°. The maximum magnetic field applied was 110 mT.

3. Results and discussion

Fig. 1a shows the XRD diffraction patterns of the Fe_3O_4 thin films grown, under the conditions described in the previous section, with a deposition rate of 0.052 nm/s on MgO (0 0 1), $SrTiO_3$ (0 0 1)