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Nanocrystalline magnetite thin films grown by dual ion-beam sputtering

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ABSTRACT

We have explored the influence of an ion-assisted beam in the thermoelectric and magnetic properties of nanocrystalline magnetite thin films grown by ion-beam sputtering. The microstructure has been investigated by XRD. Tensile and compressive strained thin films have been obtained as a function of the parameters of the ion-assisted beam. The evolution of the in-plane magnetic anisotropy was attributed to crystalline grain size. In some films, magneto-optical Kerr effect measurements reveal the existence of uniaxial magnetic anisotropy induced by the deposition process related with a small grain size ($\leqslant$20 nm). Isotropic magnetic properties have observed in nanocrystalline magnetite thin film having larger grain sizes. The largest power factor of all the films prepared (0.47 $\mu W/K^2$ cm), obtained from a Seebeck coefficient of -80 $\mu V/K$ and an electrical resistivity of 13 mΩ cm, is obtained in a nanocrystalline magnetite thin film with an expanded out-of-plane lattice and with a grain size $\approx$30 nm.

1. Introduction

Magnetite (Fe_3O_4) is a well-known half-metallic material, whose electronic density of states should be 100% spin polarized at the Fermi level and which also shows a metal–insulator transition at about 125 K (Verwey transition). These properties together with its high Curie temperature (T_c = 859 K) make Fe_3O_4 a promising candidate for spintronic devices [1,2]. An important issue before implementation in new applications is to control the magnetic anisotropy when magnetite is in thin film form. Extensive work has been done to explore magnetic and electrical properties in thin magnetite films, however, its thermoelectric properties have not been widely studied [3,4].

Recently, a growing interest in thermoelectric devices is being developed as an alternative energy green source by harvesting wasted heat. The thermoelectric conversion efficiency is closely related to the figure of merit, ZT, that is determined by three main material properties: the thermopower, S, the electrical conductivity, σ, and the thermal conductivity, κ ($ZT = S^2\sigma T/\kappa$). When thermal conductivity is unknown, the thermoelectric power factor ($S^2\sigma$) is commonly used to determine the suitability of a thermoelectric material. Magnetite is a transition metal oxide composed of nontoxic elements with potential for mass production of thermoelectric devices. Recently Park et al. have demonstrated that magnetite could be a promising thermoelectric material for thermoelectric devices [3].

Fe_3O_4 crystallizes in an inverse spinel structure in which Fe^{3+} ions occupy the tetrahedral A-sites while the octahedral B-sites are occupied by both Fe^{2+} and Fe^{3+} ions. At room temperature, the electrical conduction results from charge transfer between the Fe^{2+} and Fe^{3+} ions in the octahedral layers. However, the situation is complicated when defects are present in the films since the existence of lattice disorder or vacancies may have an important effect on the conduction mechanism.

The thermoelectric properties of Fe_3O_4 films are characterized by an electrical resistivity of $\rho \approx 5$–10 mΩ cm and Seebeck coefficients between 40 and 80 $\mu V\,K^{-1}$ at room temperature [4–7] depending on the deposition conditions and the crystalline quality. Different solid solution systems based on magnetite or doped magnetite have been studied in order to improve the thermoelectrical properties as well as to control the conduction type [4–7]. In general, the presence of Zn impurities [4,5] produces films with higher negative Seebeck coefficient than magnetite, while it is possible to control the conduction type varying the Ti concentration impurities [5,6]. Mn and Ni impurities produce films with both a higher negative Seebeck coefficient and a higher resistivity with a low net effect in its power factor compared with that of pure magnetite [7].

Several PVD growth methods like pulsed laser deposition (PLD) [8–12], molecular beam epitaxy (MBE) [13–16] and magnetron sputtering [17,18] or rf-sputtering [19] have been used to grow

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magnetite thin films. However, other sputtering-based techniques such as ion-beam sputtering have been scarcely explored [20,21]. Ion beam assisted deposition, in an electron beam evaporation process, has been used very recently to obtain nanocrystalline magnetite [22]. To the best of our knowledge, there have been no studies combining ion beam sputtering with the use of a second ion beam to assist the deposition of magnetite thin films.

Many works have been focused on the investigation of the electrical transport and magnetic properties of epitaxial magnetite thin films grown on single crystal substrates [8,9,12–17], some on them focused on the in-plane magnetic anisotropy induced by the substrate [12–14,16] with the possible influence of interface bonding and strain effects. However the number of reports on magnetite thin films deposited in amorphous substrates is relatively small [8,19,21], in which no references to in-plane magnetic anisotropy are found.

We have demonstrated previously the capability of dual ion beam sputtering technique to obtain nanocrystalline iron nitride thin films in a wide range of phases and compositions [23]. The aim of this paper is to explore the capabilities of this technique to obtain nanocrystalline magnetite on amorphous substrates, in order to avoid misfit strain induced by the substrate, and to focus on the effects induced by the an ion-assisted beam. The use of a beam to assist the deposition has influence both in the surface mobility and the nuclei formation, which in turn influence the presence of anti-phase boundaries (APBs). APBs are common in magnetite thin films and are related to growth defects that significantly influences the electrical and magnetic properties of the films [14,15,18]. As the presence of APBs can be originated by a limited surface mobility, several attempts have been done to increase the surface mobility as, for example, through the use of an electric field during deposition [18].

2. Experimental

Iron oxide thin films were deposited on amorphous glass substrates using a dual ion beam sputtering system (DIBS) with a residual pressure of 2×10^{-5} Pa. A 3 cm Kaufmann-type ion source was used to sputter a 5 in. pure iron (99.99%) target with inert Ar^+ ions at an angle of 45°. The sputtering Ar^+ source was maintained at 600 eV and 1.4 mA/cm^2 for all the samples. Under these conditions the deposition rate in a non-assisted films, i.e. S1, is 0.4 Å/s. A controlled mixture of Ar and O_2 is introduced in a second ion source, en-Hall ion source, to assist the growing film. The O_2 relative flow rate is 13% to the total flow rate and the gas flow amount of Ar and O_2 gases are adjusted before introduction in the assisted ion source (with typical values of Φ_{Ar} = 1.7–2 sccm and Φ_{O2} = 0.25–0.3 sccm). In this kind of ion sources an independent control of the energy and fluxes is not possible and the energy and beam current density as well as the total gas flow was varied simultaneously. This reactive $O_2^+ + Ar^+$ assistance is made at 60° off normal of the substrates. During the deposition the pressure was maintained at 3×10^{-2} Pa.

The substrates were rotated at 2 rpm to increase the homogeneity of the deposit and were kept at ≈380 °C during the deposition. The thickness of the films, which ranged from 40 to 60 nm, was monitored with a quartz microbalance. The partial pressure of oxygen used during deposition was maintained during the cooling process, after deposition, until the temperature of the films was below 150 °C. The sputtering and assistance conditions are summarized in Table 1.

The analysis of the results have been made in terms of reduced energy that is the energy deposited, from the assisted beam, per Fe atom at the film, i.e. $E_{Fe} = E_a \times ARR$. E_a is the energy of assisted $O_2^+ + Ar^+$ ion beam and ARR is the ion-to-atom arrival ratio, i.e., the ion current density from the ion-assisted beam divide by the Fe atom current density at the substrate, J_{Fe}, calculated from the deposition rate of non-assisted film. We note in particular that in E_{Fe} we are not considering the energy deposited per atom due to the sputtering source.

The crystalline structure of the different films was analyzed by X-ray Diffraction (XRD) in $\theta/2\theta$ configuration. Integral Conversion Electron Mössbauer spectroscopy (ICEMS) measurements were performed using a ^{57}Co(Rh) source and a parallel plate avalanche counter (PPAC) [24]. The spectra were recorded at room temperature in the constant acceleration mode. All the spectra were computer fitted to determine the hyperfine parameters and the relative areas of the various components. All the isomer shifts were referred to the centroid of the spectrum of α-Fe at RT.

Electrical resistivity measurements were carried out at room temperature using a dc four-probe method. The conductivity type was determined through the measurement of the Seebeck coefficient at room temperature by a differential method. The Seebeck coefficient was obtained by establishing a temperature difference of 7–10 K between the ends of the sample by a heat source on one of the sides. Two point K-type thermocouples placed on the film surface measured the temperature difference, and two steel contacts, placed beside the thermocouples were used to measure the generated thermovoltage [25]. Seebeck coefficient is determined from the slope of ΔV vs. ΔT and Telkes criterion is used to elucidate the type of conductivity [26]. The magnetic anisotropy was investigated by using vectorial Kerr magnetometry in longitudinal configuration. The angular dependence of the hysteresis loops from 0° to 360° was measured every 9° at room temperature with a maximum applied field of 1 kOe.

Table 1
Main deposition parameters of magnetite thin films. Assistance parameters: energy (E_a) and current density (J_a) of assisted beam formed by a controlled mixture O_2^+ and Ar^+ ions. Sputtering parameters: Ar^+ current density (J_{sp}) and energy (E_{sp}). The table also includes the Fe atom current density at the substrate obtained by the deposition rate of non-assisted sample, the ion-to-atom arrival ratio ARR of $Ar^+ + O_2^+$ ions from the assisted beam to Fe atoms from sputter beam and the energy deposited per Fe atom $E_{Fe} = ARR \times E_a$.

Sample	E_a (eV)	J_a ($J_{Ar}^+ + J_{O2}^+$) (mA/cm^2)	E_{sp} (eV)	J_{sp} (mA/cm^2)	J_{Fe} (Fe atoms/cm^{2}s)	ARR	E_{Fe} (eV/atom)
S1	–	0	600	1.4	3.4×10^{14}	0	0
S2	42	0.038	600	1.4	3.4×10^{14}	0.70	30
S3	47	0.043	600	1.4	3.4×10^{14}	0.80	38
S4	53	0.046	600	1.4	3.4×10^{14}	0.85	43
S5	52	0.048	600	1.4	3.4×10^{14}	0.88	46
S6	54	0.052	600	1.4	3.4×10^{14}	0.96	52
S7	57	0.061	600	1.4	3.4×10^{14}	1.12	64
S8	62	0.060	600	1.4	3.4×10^{14}	1.11	69

3. Results and discussion

Fig. 1 shows the XRD patterns recorded from the different iron oxide thin films obtained under the deposition conditions shown in Table 1. For the sake of clarity, the corresponding lines for the (311), (222) and (400) diffraction planes of stoichiometric magnetite are indicated. The presence of a small and broad bump at $2\theta \approx 44.8°$ in sample S5 is probably related to the presence of α-Fe (110).

The dependence of the out-of-plane lattice constant, obtained from the (311) and (400) diffraction lines, as a function of the energy deposited per arriving Fe atom, i.e. E_{Fe}, is shown in Fig. 2a. The lattice parameter of bulk magnetite (a = 0.8395 nm according with JCPDS reference No. 04-015-3102) is also shown in Fig. 2a as a red[1] line. As E_{Fe} increases the out-of-plane lattice parameter decreases until it reaches a minimum value around 45 eV/atom and a change of behavior from higher to lower values than those of bulk magnetite is observed. For E_{Fe} > 55 eV/atom the lattice constant increases above the one of bulk magnetite.

The changes in lattice constant, observed in magnetite thin films deposited on crystalline substrates, are usually attributed to strain effects induced by the mismatch with the substrate. For example, in magnetite grown on MgO and STO single crystals, deviations of lattice parameters from bulk magnetite have been observed depending of the sign of mismatch with the substrate, and assigned to in-plane tensile or compressive strains [9]. However amorphous substrates, like glass, do not provide such kind of substrate induced strain. In this case, the behavior observed in lattice parameters should be attributed to the effects induced by the deposition conditions. An enlarged lattice parameter perpendicular to the film plane can be explained by an increase of the compressive stress component in the film plane. We have assigned to tensile-strained or compressive-strained magnetite to the films that show lower or higher values of the out-of-plane lattice parameter, as compared with bulk magnetite, respectively.

[1] For interpretation of color in Fig. 2, the reader is referred to the web version of this article.