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Elaboration and characterization of $Fe_{1-x}O$ thin films sputter deposited from magnetite target

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Abstract

Majority of the authors report elaboration of iron oxide thin films by reactive magnetron sputtering from an iron target with $Ar–O_2$ gas mixture. Instead of using the reactive sputtering of a metallic target we report here the preparation of $Fe_{1-x}O$ thin films, directly sputtered from a magnetite target in a pure argon gas flow with a bias power applied. This oxide is generally obtained at very low partial oxygen pressure and high temperature. We showed that bias sputtering which can be controlled very easily can lead to reducing conditions during deposition of oxide thin film on simple glass substrates. The proportion of wustite was directly adjusted by modifying the power of the substrate polarization. Atomic force microscopy was used to observe these nanostructured layers. Mössbauer measurements and electrical properties versus bias polarization and annealing temperature are also reported.

Keywords: Iron oxide; Sputtering; Electrical properties and measurements; Mössbauer spectroscopy

1. Introduction

The preparation of iron oxide thin films can lead to devices with attractive optical, magnetic, and semiconducting properties, which can be tailored by the parameters of preparation. Among all the processes for producing films, the sputtering process is one of the most popular. This method allows film preparation at moderate temperatures, making it possible to deposit on various substrates with high homogeneity and good uniformity. As a consequence, the sputtering technique is widely used in research laboratories as well as in industrial production units.

The majority of authors active in the field of iron oxide thin films, reports the elaboration of such films by reactive magnetron sputtering from a Fe target applying an $Ar–O_2$ gas mixture [1–3]. The proportion of oxygen present in the plasma then determines the stoichiometry of the oxide. However the control of this chemical reaction is quite difficult. A convenient method to obtain substituted-ferrite thin films is by radio frequency (RF) sputtering of a mixed ferrite target [4–6]. Physical and chemical properties of as-such grown films are highly dependent on the sputtering conditions (argon pressure, RF power, target/substrate distance, magnetron…). These sputtering conditions act on the energy and on the angle of incidence of the particles that are ejected from the target [7,8] and consequently act on the film growth and microstructure.

During sputtering, the layer growing on the substrate is subjected to continuous bombardment by energetic species emitted from the target or retro-diffused. In the case of oxide deposition, oxygen atoms can even be ejected from the film when the bombardment becomes stronger [9,10]. These extreme conditions of preparation lead to interesting reducing preparation conditions from which non-stoichiometric or out-of-equilibrium oxides can result [11,12].

As for the sputter deposition of wustite thin films, most authors [3,13–15] attempted to use reactive magnetron sputtering from a Fe target. However, upon increasing oxygen content, different phases ranging from α-Fe to $Fe_{1-x}O$, Fe_3O_4, and α-Fe_2O_3, were obtained. Only Peng et al. [16] mentioned the possibility of obtaining wustite thin film directly from an oxide target and without bias for the high RF power applied to the target. They also succeeded in changing the Fe_2O_3/Fe_3O_4 ratio by using bias polarization.

Instead of using reactive sputtering from a metallic target, the present authors produced $Fe_{1-x}O$ containing thin films by direct sputtering from a magnetite target in a pure argon gas flow with

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Table 1
Sputtering parameters

Target: Fe_3O_4	Without magnetron configuration			
Gas pressure (Pa)		0.5		
Target–substrate distance (mm)		55		
RF power density (W/cm^2)		2.8		
Bias power density (W/cm^2)	0	0.03	0.06	0.12
Film thickness (nm)	500	480	460	430
Deposition rate (nm/min)	16.6	16	15.3	14.3
Substrate		Glass slide		

applied bias power. In this report, they present and discuss the influence of substrate polarization on the proportion of wustite in the as-such obtained films and the consequences of this proportion on the electrical properties of the films.

2. Experimental details

Iron oxide thin films were prepared by RF-sputtering method using a pure Fe_3O_4 ceramic target. The apparatus is an Alcatel SCR650 equipped with an RF generator (13.56 MHz), and a pumping system composed of a mechanical pump coupled with a turbo molecular pump. A residual vacuum of 5×10^{-5} Pa was reached in the sputtering chamber before introducing the deposition gas. The films were deposited on glass slides for all studies. The distance between the target and the substrates was 55 mm and the power density applied to the magnetite target was 2.8 W/cm^2. Different RF bias power densities from 0 to 0.12 W/cm^2 were also applied to the substrate. The gas used in this study was argon and the working pressure was kept at a value of 0.5 Pa. The conditions of deposition are summarized in Table 1.

Film thicknesses were measured using a Dektak 3030ST profilometer. Structural characterizations of the films were performed by glancing incidence X-ray diffraction (XRD) on a Siemens D5000 diffractometer. Morphology and microstructure of the as-deposited samples were examined by atomic force microscopy (AFM), performed on a Veeco D3000 system. The resistivity was determined on the as-deposited and annealed samples with a QuadPro four-point probe device from Signatone equipped with a Keithley SMU 237. A selected thin-film sample was also examined by ^{57}Fe Mössbauer spectroscopy at room temperature (RT). Mössbauer spectra (MS) in transmission geometry and with two different velocity increments per channel, i.e., ~0.045 mm/s and ~0.015 mm/s, respectively, were recorded with a ^{57}Co (Rh) source using a conventional time-mode spectrometer with a constant-acceleration drive and a triangular-reference signal. Accumulation of the data was performed in 1024 channels until a background of at least 10^6 counts per channel was reached. The spectrometer was calibrated by collecting at RT the MS of a standard α-Fe foil and the isomer-shift values quoted hereafter are with reference to this standard. The absorbers consisted of a stack of four thin glass substrates (0.1 mm), with on each side a film of thickness 300 nm. The spectra were analysed assuming symmetrical components with Lorentzian line shapes.

3. Results and discussion

Iron oxide thin films were deposited with variable bias polarization applied during film growth. The conditions of preparation are reported in the Table 1. The thickness of the coating was not drastically affected by the substrate polarization. When the RF polarization applied to the substrate varied from 0 to 0.12 W/cm^2, the thickness decreased from 500 nm to 430 nm. Fig. 1 shows X-ray diffraction patterns of the biased and nonbiased thin films. When no bias was applied to the growing film, the XRD pattern of the obtained product showed a pure Fe_3O_4 iron oxide with a well-defined spinel structure (Fig. 1a). When the substrate was polarized, a loss of oxygen in the growing film might be induced by the strong bombardment by high-energy incident Ar^+ cations. Fig. 1 reveals that the applied bias polarization gradually leads to the formation of a reduced phase $Fe_{1-x}O$. A mixture of Fe_3O_4 with $Fe_{1-x}O$ was deposited when the substrate was polarized with 0.03 W/cm^2, while a pure wustite phase according to XRD was obtained by increasing the bias power density up to 0.06 W/cm^2. Finally, for the highest polarization that we applied to the substrate (0.12 W/cm^2), α-Fe mixed with $Fe_{1-x}O$ iron oxide was formed. Temperature during the deposition process was not probed in situ, but the glass substrate did not melt which proves that temperature did not exceed 500 °C. Normally wustite is not formed at such low temperature. The oxygen stoichiometry of the iron oxide depends on temperature and on oxygen partial pressure. For example in the literature it is claimed that bulk FeO can be prepared from a hematite and iron mixture in evacuated and sealed vitreous silica tubes at 1273 K [17,18].

According to the XRD patterns it is clear that the stoichiometry of the thin film can be controlled by simply adjusting the bias power. The polarization of the substrate acts as a key parameter to move into the phase diagram of Fe–O.

Fig. 2 shows the electrical resistivity of "as-deposited" thin films versus the applied RF bias power density. The evolution of the resistivity proceeds along three tendencies. First, the resistivity decreases from 0.045 Ωcm to 0.035 Ωcm when bias power density increases from zero to 0.03 W/cm^2. XRD has shown that for 0.03 W/cm^2 bias power density a significant

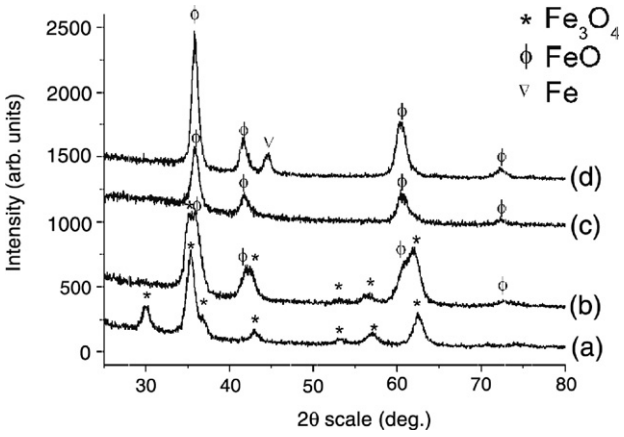

Fig. 1. X-ray diffraction patterns for thin films deposited with different bias power density, (a) 0 W/cm^2, (b) 0.03 W/cm^2, (c) 0.06 W/cm^2, and (d) 0.12 W/cm^2.