Available online at www.sciencedirect.com
ScienceDirect
Journal of Magnetism and Magnetic Materials 320 (2008) 58–62
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Nanocomposite $Fe_{1-x}O/Fe_3O_4$, $Fe/Fe_{1-x}O$ thin films prepared by RF sputtering and revealed by magnetic coupling effects

B. Mauvernay, L. Presmanes*, C. Bonningue, Ph. Tailhades

CIRIMAT, UMR CNRS 5085, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex 9, France

Received 5 March 2007
Available online 22 June 2007

Abstract

Magnetic and semi-conducting nanocomposite iron oxide thin films have been prepared under bias polarization, by radio-frequency sputtering of a magnetite target. The nature of the phases obtained in the thin films depends on the bias power density. The increase in power density, from 0 to 110 mW/cm^2, allows the preparation of magnetite, magnetite/wustite and wustite/α-iron nanocomposites successively. Magnetic measurements at low temperature show exchange bias for two-phases films even though the minor phase is not detected by grazing angle X-ray diffraction. The exchange bias can reach very high values of about 4300 Oe. Electrical properties at room temperature are interpreted taking into account both the modifications of the film compactness, and the nature of the phases from which they are made.

Keywords: Iron oxides; Magnetic coupling; Exchange bias; Sputtering; Nanocomposite; Magnetite; Wustite

1. Introduction

The preparation of iron oxide thin films can lead to devices with attractive optical, magnetic, and semi-conducting properties, which can be tailored by altering the preparation parameters. Among all the vacuum processes used for producing films, the sputtering process is one of the most popular. It allows preparation of film at moderate temperatures, making deposition possible 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. But, the attractiveness of RF sputtering is also that it offers the possibility of preparing materials, especially oxides, which can be out-of-equilibrium or non-stoichiometric at room temperature (RT).

During sputtering of an oxide target, the layer grown on the substrate is submitted to continuous bombardment with high energy species from plasma and target, which can induce specific characteristics or properties [1–3]. In this study, we tuned bias sputtering conditions to obtain nanocomposite iron oxide from a magnetite target. With bias sputtering, the growing layer is submitted to a strong Ar^+ bombardment and leads to the formation of reduced thin films by impoverishment of the oxygen content in the growing layer.

Because of its great sensitivity, magnetic measurement, is particularly suited for determining the presence of phases with different magnetic properties. After field cooling and below the Néel temperature ($T_{Néel}$), the hysteresis loop of materials made of both antiferromagnetic (AFM) and ferromagnetic (FM) or antiferromagnetic and ferrimagnetic (FI) phases, is for instance shifted along the negative field axis. This loop shift is known as exchange bias (He) [4–8]. The measurement of the exchange bias parameter is particularly suitable to study nanocomposites made of AFM/FM or AFM/FI phases which are often difficult to reveal by X-ray or electron diffraction. In this report, magnetic measurements are used to study the influence of substrate polarization on phase formation and the occurrence of nanocomposites in thin films made of iron and oxygen. The resulting changes in the semi-conducting properties of such films are also studied.

*Corresponding author. Tel.: +33 5 61 55 81 03; fax: +33 5 61 55 61 63.
E-mail address: presmane@chimie.ups-tlse.fr (L. Presmanes).

0304-8853/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2007.05.042

2. Experimental

Iron oxide thin films were prepared by RF magnetron sputtering using a Fe_3O_4 ceramic target containing 5% of FeO. The apparatus is an Alcatel SCM-400 equipped with an RF-generator (13.56 MHz), and a pumping system composed of a mechanical pump coupled with a diffusion pump. A residual vacuum of 10^{-5} Pa was reached in the sputtering chamber before introducing the argon gas. The films were deposited on glass slides under pure argon gas flow and the working pressure was kept at a value of 0.5 Pa. The distance between the target and the substrates was 70 mm and the power density applied to the magnetite target was 860 mW/cm^2. Different RF bias power densities from 0 to 110 mW/cm^2 were also applied to the substrate. The conditions of deposition are summarized in Table 1.

Film thickness was measured using a Dektak 3030ST profilometer. Structural characterizations of the films were performed by grazing angle X-ray diffraction (XRD) ($\alpha = 1°$) on a Siemens D5000 diffractometer. The morphology and microstructure of the as-deposited samples were examined by scanning electron microscopy (SEM) performed on a JEOL JSM 6700F system. The resistivity was determined on the as-deposited samples with a QuadPro four-point probe device from Signatone, equipped with a Keithley SMU 237. Magnetic measurements were done at 5 K with a superconducting quantum interference device (SQUID) magnetometer MPMS quantum design 5.5, on samples deposited on both sides of a thin (0.1 mm) glass substrate.

3. Results and discussion

3.1. Preparation

Nanocomposite iron oxide thin films were deposited with variable bias applied during film growth. Fig. 1 shows that the deposition rate was affected by the substrate bias. When the RF bias applied to the substrate was changed from 0 to 110 W/cm^2, the deposition rate decreased linearly from 5.1 to 1.8 nm/mn. The deposition rate is due to sputtering from the accelerated Ar^+ ions at the surface of the growing film.

Fig. 2 shows XRD patterns of the biased and unbiased thin films. When no bias was applied to the growing film, the XRD pattern of the material obtained showed a pure Fe_3O_4 iron oxide with a well-defined spinel structure. The microstructure of such thin films is presented in Fig. 3a and shows a columnar structure. This type of structure is characteristic of sputtered thin films in diode configuration.

When the substrate was biased with 6 mW/cm^2, the XRD pattern of the thin film showed that all diffraction peaks of the spinel structure were shifted to lower angles. This shift signifies in-plane compression stress [9,10]. The shift and the broadening of diffraction patterns leading to a possible partial overlap of the spinel and wustite phase peaks made a clear identification of the crystalline phases impossible using only XRD.

For samples polarized with power densities lying between 16 and 63 mW/cm^2, XRD only revealed a NaCl-type diffraction pattern (Fig. 1) due to the $Fe_{1-x}O$ wustite phase. As the film grows, oxygen loss is caused by the strong bombardment by high-energy incident Ar^+ cations. Thus, the applied bias gradually led to the formation of a $Fe_{1-x}O$ phase. Fig. 3b shows a SEM image of a thin film prepared with a bias power density of 32 mW/cm^2. This image shows that bias sputtering tends to improve film densification and smoothness. As shown before [1,11], the average roughness R_a can be decreased by about 70–80% when the substrate is exposed to bias during the deposition process.

Finally, for the highest polarizations applied to the substrates (up to 80 mW/cm^2), α-Fe mixed with $Fe_{1-x}O$ iron oxide was formed. The SEM image (Fig. 3c) of thin film deposited with 80 mW/cm^2 again shows high densification of the thin film. We were unable to observe α-Fe nano-metallic particles by SEM.

According to the XRD patterns it is clear that the stoichiometry of the thin film can be controlled, simply by adjusting the bias power. The substrate bias acts as a key parameter to move through the Fe–O phase diagram from magnetite (Fe_3O_4) to reduced phases such as wustite ($Fe_{1-x}O$) and even metallic iron (α-Fe).

Table 1
Sputtering parameters

				Magnetron configuration			
Target (wt%)				95% Fe_3O_4–5% FeO			
Gas pressure (Pa)				0.5			
Target–substrate distance (mm)				70			
Film thickness (nm)				300			
RF power density (mW/cm^2)				860			
Bias power density (mW/cm^2)	0	16	32	48	63	80	110
Deposition rate (nm/mn)	5.2	4.2	4.0	3.5	3.0	2.8	1.8
Deposition temperature				Water cooling			
Substrate				Glass slide			