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High perpendicular coercive field of $CoFe_2O_4$ thin films deposited by PLD

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Abstract

Thin films of $CoFe_2O_4$ were deposited on (1 0 0) Si and (1 0 0) MgO substrates by pulsed laser deposition (PLD).

The X-ray analysis shows the existence of single-phase spinel structure. Thin films deposited on (1 0 0) MgO substrates are epitaxial and completely oriented in-plane and out of plane due to the small lattice mismatch between Co ferrite and MgO. The surface microstructure was probed by atomic force microscopy and we can describe it like a tidy mosaic of monocrystals. Surprisingly, the films grew on (1 0 0) Si using 355 nm, reveal a complete (1 1 1) orientation in spite of the native oxide of the substrate when deposited. The films deposited with 266 nm also were textured in the (1 1 1) but with less particulate on the surface.

(1 0 0) films show at 35 K a perpendicular coercive field H_c as high as 12.9 kOe, meanwhile for the (1 1 1) films H_c was around 9 kOe. However, at room temperature, the (1 1 1) films deposited with 266 nm show a perpendicular coercive field of 5.1 kOe and a squareness of 0.86 which make them attractive for magneto-optic recording applications.

Keywords: Coercive fields; Pulsed laser deposition; Thin films; Cobalt ferrite

1. Introduction

Research on cobalt ferrite thin films has been very active because they are good candidates for magneto-optic devices. $CoFe_2O_4$, is one of the good candidates for high-density recording media because of its high coercivity, high magnetocrystalline anisotropy and moderate saturation magnetisation [1,2].

$CoFe_2O_4$ has the inverse spinel structure in which the octahedral B sites are occupied by eight Co^{2+} and eight Fe^{3+} cations, while the tetrahedral A sites are occupied by eight Fe^{3+}. In the case of thin films there is strong evidence for the dominant role of strain in its magnetic anisotropy [3]. By selecting substrates with different lattice parameters, it is possible to change the preferred orientation of the films, the amount of stress imposed and hence their magnetic properties [4].

In this work, epitaxial cobalt ferrite $CoFe_2O_4$ thin films were fabricated by pulsed laser deposition (PLD) on (1 0 0) Si and (1 0 0) MgO substrates. To our knowledge, this is the first time that highly (1 1 1) oriented cobalt ferrite thin films have been grown directly on Si substrates with suitable magnetic properties for applications.

2. Experimental

The Co-ferrite films were grown by pulsed laser deposition using a Nd:YAG laser, operating at 266 nm and 355 nm with a fluency of about 6 J/cm^2 and 10 J/cm^2 respectively. During deposition the substrate temperature was kept at 700 °C under 4 Pa oxygen pressure. The films were cooled down to room temperature in an O_2 atmosphere. The films were deposited onto (1 0 0) Si (CFO1, CFO2) and (1 0 0) MgO (CFO3) substrates and have a thickness of about 60 nm.

The $CoFe_2O_4$ target was prepared by sol–gel techniques. The required stoichiometric proportion of iron nitrate and cobalt acetate were weighed and diluted in water. A 3 M citric acid solution (50 ml) was added to each metal solution (50 ml) and heated at 40 °C for approximately 30 min with continuous stirring. The final mixture was slowly evaporated until a highly viscous gel was formed. The resulting gel was

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heated at ∼200 °C when it ignited in a self-propagated process. The final residue was calcined at 1000 °C for 2 h. Powders were pressed without binder into pellets at a pressure of 2 t and sintered in air at 1100 °C for 2 h, followed by a slow cooling in the furnace. The resulting target is homogeneous and single phase with a density greater than 92% with respect to the theoretical one.

The crystal quality and structures of the deposited films were characterised by X-ray diffraction (XRD) using Cu Kα radiation, atomic force microscopy (AFM) and magnetic force microscopy (MFM).

Magnetic measurements were carried out with a vibrating sample magnetometer (VSM) and by SQUID magnetometer with magnetic field applied parallel and perpendicular to the film surface.

3. Results and discussions

X-ray $\theta - 2\theta$ diffraction patterns of the films grown on Si are shown in Fig. 1a and b. The films deposited using 355 nm (CFO1) are highly (1 1 1) textured. The patterns corresponding to the ones grown with 266 nm (CFO2), although also (1 1 1) textured, show other reflections but with smaller intensities. A lattice constant of $a = 0.8310$ and 0.8308 nm were deduced by fitting the spectra for CFO1 and CFO2, respectively. These results are close to the target lattice parameter fitted, $a = 0.8303$ nm, and smaller than the one published by the JCPDS No. 22-1086 ($a = 0.8392$ nm).

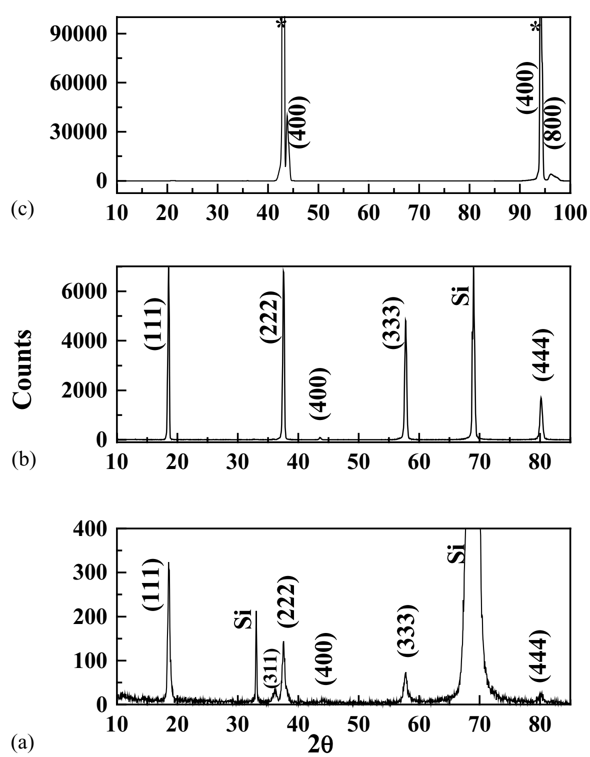

Fig. 1. X-ray $\theta - 2\theta$ patterns for (a) CFO2, (b) CFO1 and (c) CFO3 films. (∗) Substrate.

Optical inspection of the CFO1 and CFO2 shows that the latter film presents fewer droplets (produced by splashing) on the surface, and consequently a more adequate surface quality. The presence of droplets on the surface of the films deposited by PLD is one of the major drawbacks of the technique. However, the use of shorter wavelengths and low fluence reduces thermal effects on the target surface, leading to a decrease in the droplets ejected from it [5].

The surface microstructure was probed by an AFM observation and the image is shown on the left side of Fig. 2a, for the films deposited on Si with 355 nm. The values of the surface roughness were around 8 nm. The average crystalline size is about 70–100 nm which is close to the critical dimensions for single domains [6].

Due to the small lattice mismatch between the cobalt ferrite and the MgO substrate (about −0.37%) the growth is likely to occur in the Frank-van der Merwe mode. In fact, optical image of the (CFO3) film surface shows a tidy mosaic of square monocrystals. As a consequence, no grain boundaries are revealed. The film, that was deposited using 355 nm, resulted (1 0 0) epitaxial, as can be observed from Fig. 1c. The fitted value of the out-of-plane lattice parameter is $a = 0.8392$ nm. Assuming that the film is under tensile stress in the plane of the substrate, there was an increment in the ferrite volume. The extreme low roughness of the film surface prevents the resolution of features in the AFM image (Fig. 2b left side).

MFM images of the films are shown in the right sides of Fig. 2. For the films deposited on Si, the image shows magnetic contrast, which means magnetisation, is predominantly perpendicular to the plane of the films. Bubble domains are about 300 nm, much larger than thickness of the films and grain sizes. However, the MFM image of the CFO3 film presents a low signal-to-noise ratio. Domains cannot be clearly resolved which could mean that magnetisation perpendicular to the film surface is low. In-plane (IP) and out-of-plane (OOP) magnetisation loops were measured at 35 and 300 K. In Fig. 3 the IP and OOP magnetisation loops for the sample CFO3 are presented. These curves show broad hysteresis evidencing the existence of large magnetic anisotropies, other than the shape one. In spite of the fact that the coercivity, H_c, is rather large for both geometries we want to outline that H_{cper} is always larger than $H_{c//}$. These results indicate that the leading anisotropy term favours an OOP axis of magnetisation. As expected for magnetic materials, the coercivity increases with decreasing temperature reaching very large values at low temperature, i.e.: H_c increases around an order of magnitude between 300 and 35 K in all the samples and geometries.

Table 1 summarises the coercive fields and squareness of the loops at room temperature.

The high coercivity of the samples grown on silicon makes these films very attractive for technological applications.

$CoFe_2O_4$ is a compound known by its high intrinsic anisotropy. However, the origin of this property is still a matter of discussion. Moreover, surface anisotropy terms,

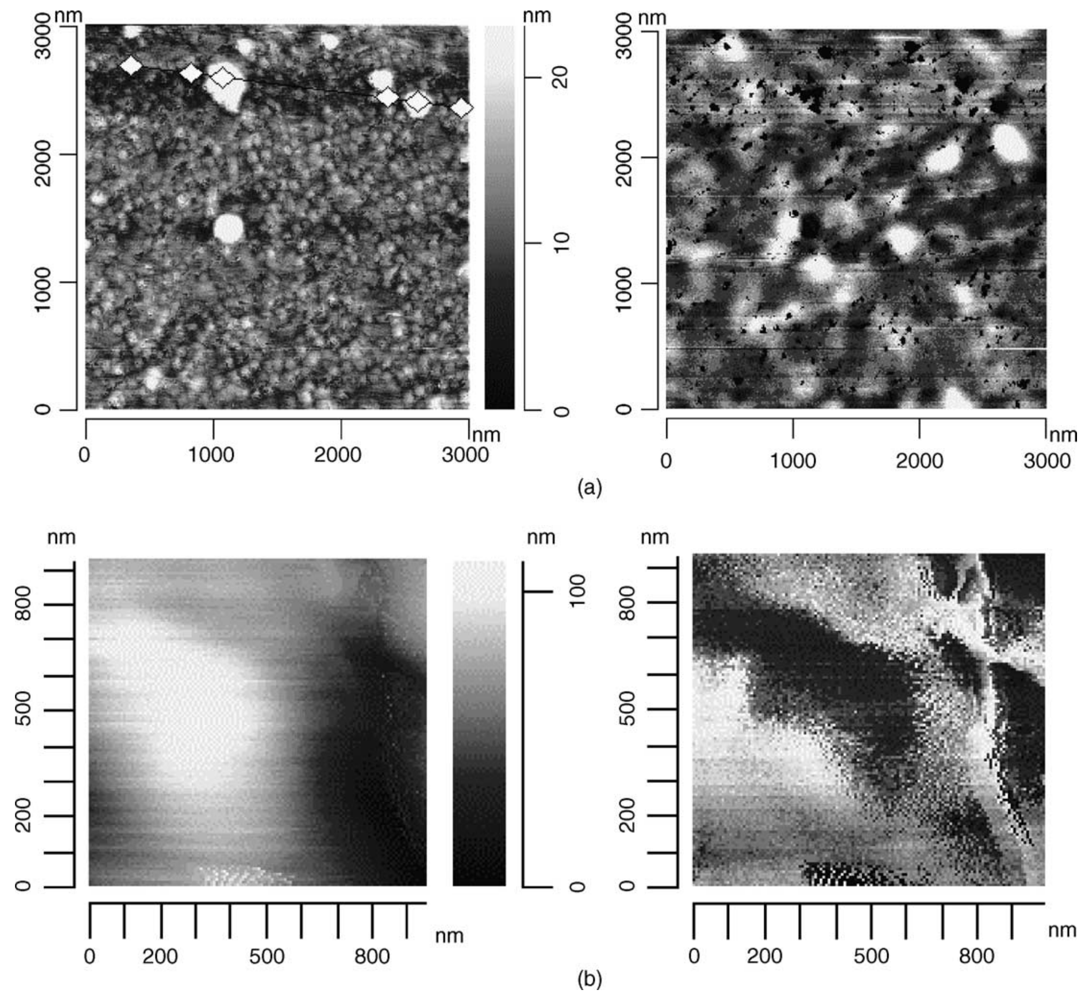

Fig. 2. Representative AFM (left side) and MFM (right side) images for $CoFe_2O_4$ thin films: (a) CFO1 and (b) CFO3.

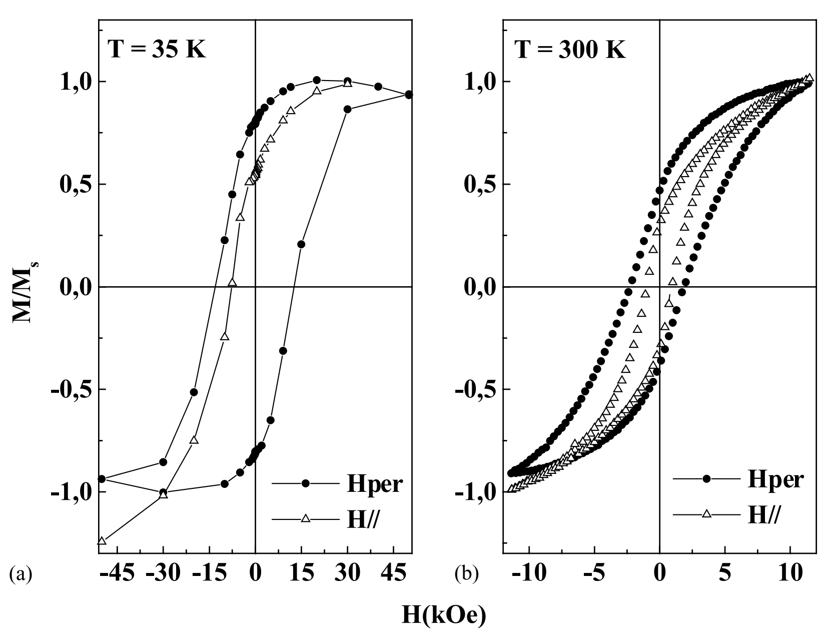

Fig. 3. IP and OOP magnetisation loops for CFO3: (a) 35 K and (b) 300 K.

Table 1
Coercive fields and squareness of the magnetisation loops at room temperature

Film	$T = 300$ K (VSM) (per $= \perp$)			
	$H_{c//}$ (kOe)	$S_{Q//}$	H_{cper} (kOe)	S_{qper}
CFO1	0.71	0.48	0.90	0.24
CFO2	2.90	0.88	5.10	0.86
CFO3	0.96	0.32	2.05	0.48

arisen from the film–substrate and film–vacuum interfaces, are expected to appear in thin films. To better understand the origin of these films hysteresis and to clarify its relation with the microstructure of the films more work is being carried out at present.

4. Conclusions

Highly oriented (1 1 1) and epitaxial (1 0 0) cobalt ferrite thin films has been grown with high perpendicular coercive fields, even at room temperature. The films deposited directly on Si substrates are (1 1 1) textured, in spite of the native oxides always present on the silicon surface. A strong dependence of the coercive field with temperature was found. The high perpendicular coercive fields at room temperature, especially for the films grown with 266 nm directly on Si, make them attractive for practical applications. However, more work is needed in order to understand the relationship between those high coercive fields and the microstructure.

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