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Influence of the oxygen pressure and annealing time in the magnetic and structural properties of Barium Ferrite thin films

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Our present work is focused in the influence of the oxygen pressure in the growth of Barium Hexaferrite (BaM) films deposited by Pulsed Laser Deposition on substrates of SiO2/(100)Si using a BaM stoichiometric target. Three deposits are presented to ambient temperature in atmosphere of oxygen of high purity, with 45, 100 and 850 mTorr respectively. Later on they were carried out a series of thermal treatments at 900°C in air during 2, 10, 60 and 180 minutes. It was found a strong dependence with the oxygen pressure in the magnetic and structural properties. It is puts on in evidence the importance of the oxygen pressure in the deposition even receiving the same thermal treatment later. Besides, tuning the magnetic and structural properties is possible by means of the control of the annealing time.

Keywords: Barium Hexaferrite; thin films; magnetic properties.

Se estudio la influencia del tiempo de recocido y de la presión de oxígeno durante el crecimiento de películas delgadas policristalinas de Hexaferrita de Bario (BaM) depositadas sobre SiO2/(100)Si usando blancos estequiométricos de BaM mediante Deposición por Láser Pulsado. Se presentan tres depósitos crecidos a temperatura ambiente en atmósfera de oxígeno de alta pureza, con 45, 100 y 850 mTorr respectivamente. Posteriormente se realizaron una serie de tratamientos térmicos a 900°C en aire durante 2, 10, 60 y 180 minutos. Se encontró una fuerte dependencia con la presión de oxígeno en las propiedades magnéticas y estructurales. Se pone en evidencia el rol que juega la presión de oxígeno durante el crecimiento aún recibiendo el mismo tratamiento térmico posterior a la deposición. Además, mediante el control del tiempo de recocido es posible “tunear” las propiedades magnéticas y estructurales de los films.

Descriptores: Hexaferrita de Bario; películas delgadas; propiedades magnéticas.

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1. Introduction

The characteristic of the low losses at microwave frequencies, high resistivity and strong magnetic coupling, obtained for Ferrite materials, making them irreplaceable constituents in microwave device technology. They can provide unique circuit functions that cannot be reproduced with any other materials. Moreover, the Ferrite is considered a material for the next generation magnetic microwave devices [1,2]. Ba-ferrites with magnetoplumbite structure, $BaFe_{12}O_{19}$ (BaM), have been intensively studied because of their high stability, excellent high frequency response, as well as their large magnetocrystalline anisotropy [3].

It is well known that the composition of BaM films strongly affects the magnetic properties and structure of the film [4]. Crystal size, shape, homogeneity, electric and magnetic property, they are strongly dependent of methods of preparation. Besides, is reported that crystal size is one of the most important factors influencing the microwave- absorbing property [5].

In the present work, we present the influence of oxygen pressure during the growth and post-annealing time in crystallographic characteristic and magnetic properties.

2. Experimental

By Pulsed Laser Deposition technique (PLD) [6], three deposits of BaM on SiO_2/(l00)Si were grown at room temperature, in those which, by means of a mass flow controller, the oxygen pressures of high purity were stabilized in 45, 100 and 850 mTorr, samples A45, B100, and C850 respectively. For the deposition we use a Nd- YAG laser and the same deposition parameters for each one of the films was maintained, 2.3 J/cm2 (p/pulse), 532 nm of wavelength, 6 ns pulse duration and 10 Hz repetition rate during 60 minutes. The films thickness was estimated in 350nm approximately (0.1Å/pulse,) [6].

The plasma emission was collected with the Ocean Optics HR400 spectrometers in the range of 200 nm - 600 nm (0.1 nm resolution) [7]. Later on deposited films received an ex-situ annealing in air to 900°C. The thermal treatment was carried out in four stages according to the annealing time, 2, 10, 60 and 180 minutes. In each one of these stages, it was measured of hysteresis loop by means of a Vibrant Sample Magnetometer (VSM) with the field applied in parallel and perpendicular direction to the surface of the film and the structural characterization it was achieved by X-ray Diffraction using Cu-K line.

3. Results and discussion

The as-prepared thin films are amorphous and nonmagnetic, only after annealing treatment barium ferrite crystallizes and magnetic behavior appears. Figure 1 shows the X-ray spectra obtain for the used target and for three samples after second and fourth annealing process. The diffraction peaks confirm the formation of a randomly oriented $BaFe_{12}O_{19}$ phase in the three samples, but the relating peaks to (00l) plane are not observed. For high growth oxygen pressure, the crystallographic structure of the film is deteriorated (see Fig. 1b, sample C850), and consequently the magnetic behavior is affected. In this sample it is observed secondary-phase peaks ($BaFe_2O_4$ maybe, in agreement with observed in the literature [8]) that it is notably reduced in later annealing.

The average crystal size was determined, in each one of the diffractograms, from the position of (205) diffraction peak by Scherrer's equation [9], D=K /($B_{1/2}$cos($\lambda\theta$)), where D is the average size of the crystals, K the Scherrer constant, the wavelength of radiation, $B_{1/2}$ the peak width at half height (corrected for the effect due to instrumental broadening), and θ corresponds to the peak position. We found, that the crystal size is increased with the increment of the annealing time (see Table I). A strong increase is obtain for sample B100 (∼93%) and A45 (∼42%), while for the C850 the increment was of the significantly smaller (∼19%). The oxygen pressure of growth is an important factor in the process of minimization of the energy during the annealing, facilitating this way tuning the crystal size by growth pressure.

To determine the influence of the oxygen pressure on the plume species that hit against on substrate surface, it was obtained the spectra of the plasma radiation during the deposition of each film. The plasma emission was collected with system Ocean Optics HR400, and the collector lens was positioned to 7 cm of plume and rotate 45° of the ablation plume direction (90° regarding to laser pulse) [7].

TABLE I. Crystal size (average), influence of the annealing time. In the right column, ratio Ba(II)/Fe(I) of plasma emission.

	Crystallite size (nm)		
	2^o annealing	4^o annealing	Ba(II)/Fe(I)
A45	53	75	0.770
B100	29	56	0.813
C850	21	25	0.855

The Fig. 2 show the emission plume spectrum for three oxygen pressure of growth normalized to Fe(I) peak (357,0097 nm, transition a^5F-z^3G^o).

Selecting the reference peak corresponding to Ba(II) (389.17790 nm, transition 2Po-2D), we found that rate of Ba/Fe increases with the increment of the oxygen pressure. As it is described below, this is in agreement with the magnetic behavior.

In order to determine the dependence of the magnetic properties, VSM measurements were realized to room temperature for parallel and perpendicular applied field. The Fig. 3 shows the hysteresis loops for the three samples in its respective firth and fourth annealing stages. It is observed that for successive annealing the differences between paral-

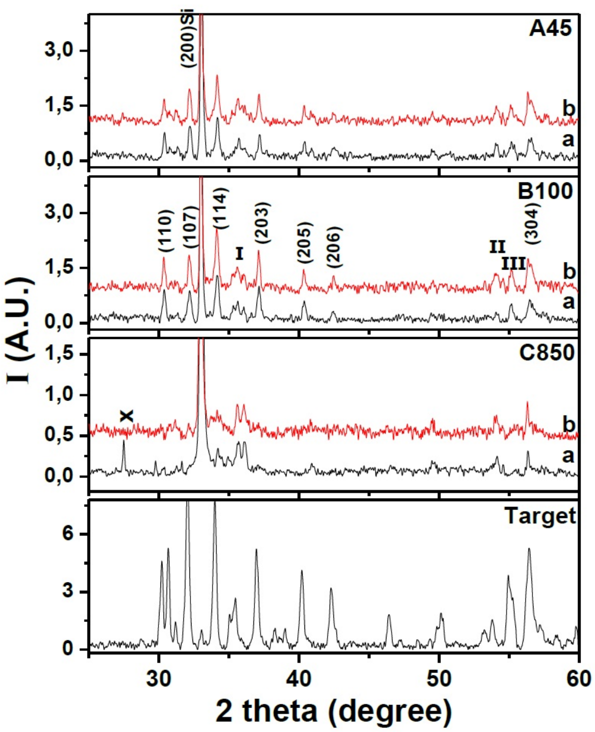

FIGURE 1. Diffraction pattern of samples A45, B100, and C850. The spectrum a and b correspond to second and fourth annealing respectively. (x represent secondary-phase peak, and BaM peaks of I is (201) (108), (202); II represent to (202) (301); and III is (217), (303), (0014) planes).

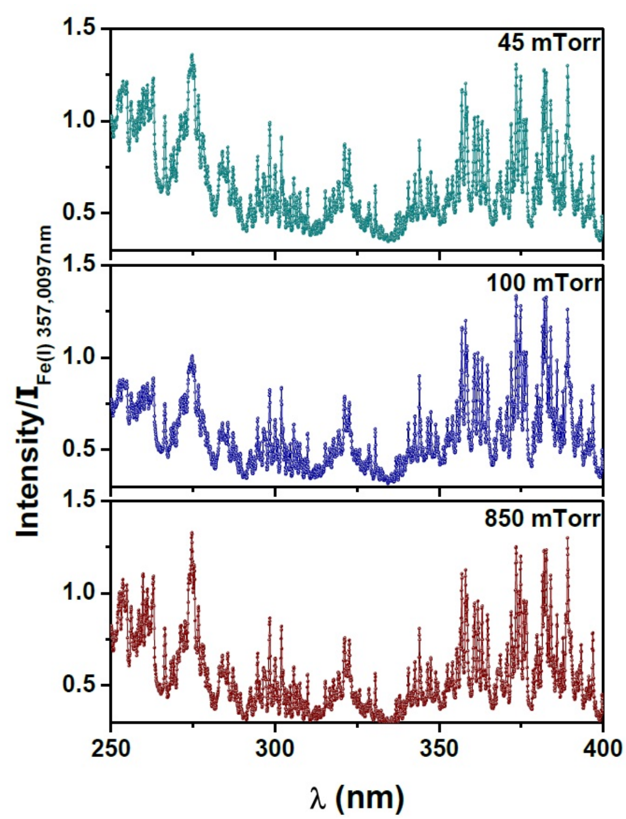

FIGURE 2. Spectra of emission of the plume for three oxygen pressure of the growth.

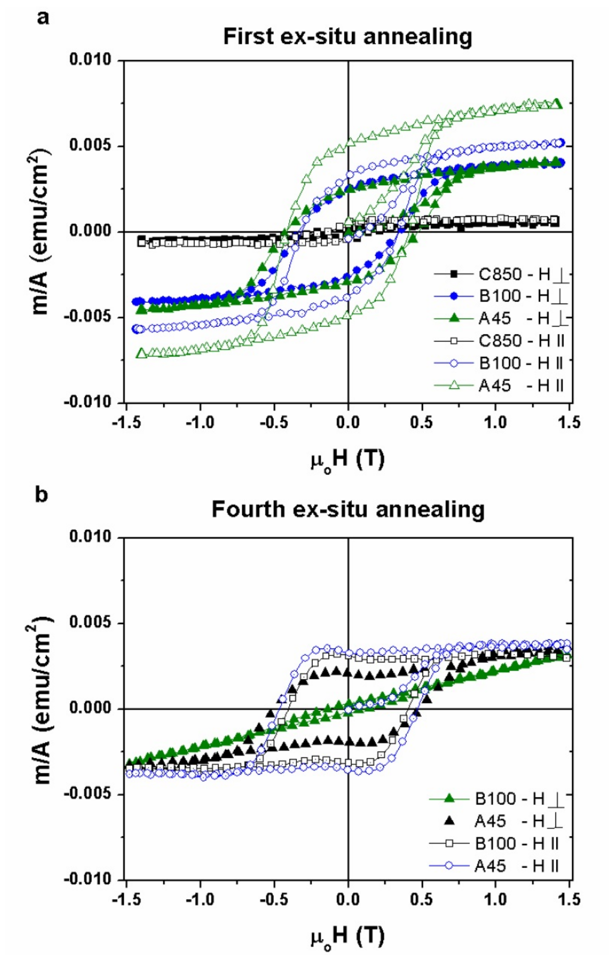

FIGURE 3. Spectra a) and b) hysteresis loop of the samples A45, B100 and C850 in the first and fourth annealing respectively.

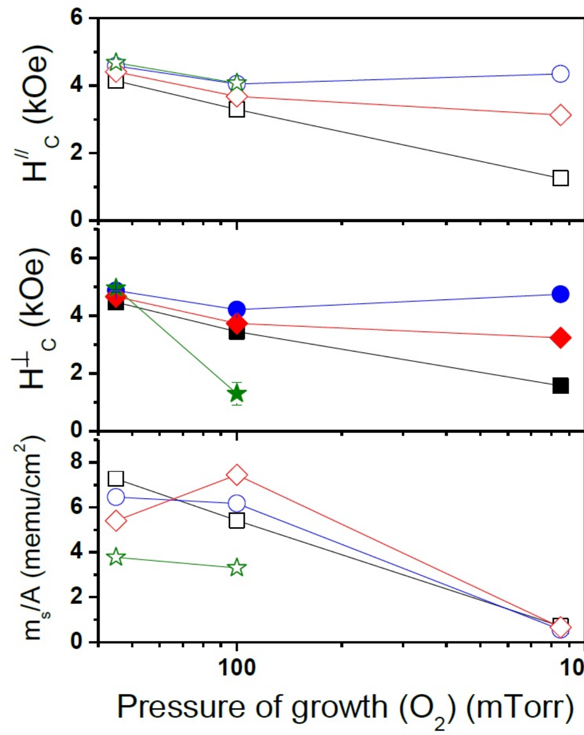

FIGURE 4. Coercive and moment/area dependence with growth pressure and annealing time. First annealing, (■,□), second annealing (○,●), third and fourth annealing, (◆,◇) and (☆,★) respectively. (H⊥ full Symbol, H// hole symbol).

lel (H_c //) and perpendicular (H_c ⊥) field applied disappear, except for sample B100, which is significantly different in fourth annealing.

In the Fig. 4, it is shows the dependence of magnetic moment and coercive field with oxygen pressure of growth. In agreement with structural properties, for sample with higher oxygen pressure deposition showed a poor magnetic behavior. The Fig. 4a shows a decrease of the coercive field with the increment of the pressure of growth, and with the increase of the annealing time, this falling tendency diminishes notably.

There are not significant differences regarding the direction of the applied field, except for the fourth annealing in the sample B100, which exhibits a remarkable reduction of HC for field applied in the perpendicular direction to the surface of the film (in this case, the determination of the demagnetizing factor causes a significant increment in the estimated error). But this preferential orientation is not reflected in the XRD pattern. The falling behavior of the moment/area ratio with respect to oxygen pressure is in agreement with that found for coercive field, and with the m/A magnitudes of the literature [8]. It is observed that m/A for sample B100 suffers an increment in the third annealing, but in the successive annealing, this is reduced.

In Fig. 5 it is shown the dependence with annealing time for all samples with parallel and perpendicular applied field. The effects of the annealing time are bigger for high pressures (see also Figs. 3), for the fourth annealing, since it degrades the magnetic properties. In this figure, are included datas published by A. Morisako *et al* [10]. They obtained BaM thin films deposited on SiO_2/Si wafer by Facing Target Sputtering system (FTS) at room temperature and with rapid post-annealing too. The sample B100 has a similar behavior of HC and m/A to that published by Morisako (MS of the authors in arbitrary units to compare the tendency), however for other two samples, the behavior is significantly different, indicating the influence of the oxygen pressure on the other species of the plume.

If the oxygen deficiency was the main cause of the differences between our films, it should be expected that the increment of the annealing time in the three deposits it equalize its physical properties, since all samples were post-annealed in air in the same conditions. This is not observed, but is well know the influence of Ba content in magnetic properties for the BaM phase [3,11], may be this is the reason for what the films present strong influence with the pressure of growth.

Two scenarios can be presented: a) the high oxygen pressure could cause the lost of stoichiometry in the species that

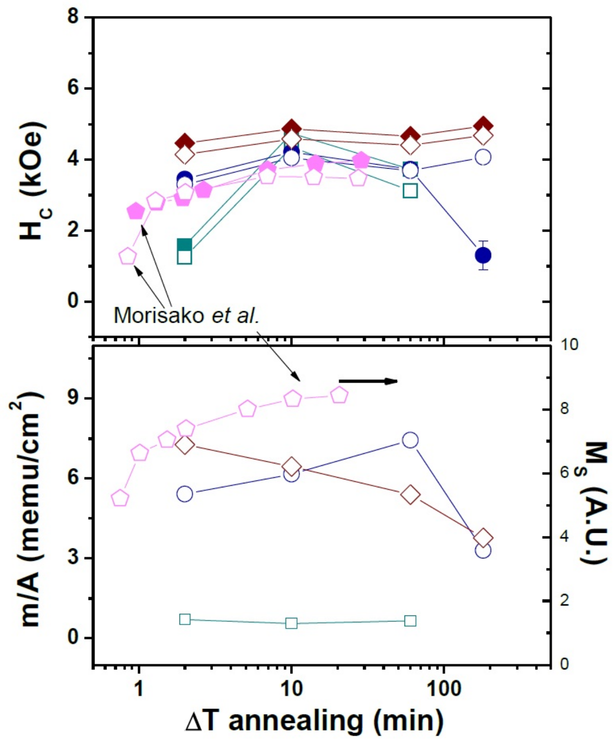

FIGURE 5. Coercive field and magnetic moment per area for three samples with respect to annealing time. The symbols (◆,◇), (●,○), (■,□) represent the sample A45, B100 and C850 respectively. (H full Symbol, H// hole symbol).

arrive to the substrate, that which ratio Ba/Fe of plasma emission (see Table I) it is increase with the pressure. b) Possible barium deficiency due to the inter- diffusion between films and substrate [12].

For short annealing times, the loss stoichiometric for diffusion of the Ba is not important, and the biggest influence comes from the decrease of Fe in the species that arrive to the substrate due to the high pressure, causing this way the proliferation of impurity phases (see Fig. 1). While for long times of ex-situ annealing, the diffusion of Ba on substrate is dominant and deteriorates the magnetic properties, that which leads to the deterioration found in the fourth annealing.

The perpendicular HC of sample B100 represents ∼30% of the value corresponding to parallel HC, this reduction may be caused by the incoherent rotation of magnetization, which is more pronounced in larger grains [13], this agrees with that found in the analysis of crystallites size, if the great increment is associated in this with the grain growth. Although this difference between $H_c \perp$ and H_c// would indicate the presence of preferential orientation of the film, this is not reflected in the XRD data.

For sample A45, HC shows a increase of ∼20% over the value reported by Morisako *et al.* it is of hoping that this sample has a reduced grain size, this gives a bigger energy cost in the motion of the domains walls.

4. Conclusions

The influence of oxygen pressure in the growth of the BaM films was corroborated in crystallographic structure and magnetic behavior. The growth in high pressure causes a reduced crystal size and this is not strongly influenced by the time of ex-situ annealing. While for low pressure, the crystallite size is bigger, the sample B100 is the one that receives the biggest influence in the crystallite size by ex- situ annealing (∼93%). The Fe content in the films could be related with the oxygen pressure, ratio Ba/Fe is increase with pressure of growth.

Mathematics We found that with this procedure is possible tuning crystal size, which is the most important factor of influence in the properties, of the BaM phase, of more interest at the present time (microwave-absorbing property).

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