Stoichiometric Magnetite Grown by Infrared Nanosecond Pulsed Laser Deposition

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Abstract

Pulsed laser deposition (PLD) is a versatile technique for the fabrication of nanostructures due to the possibilities it offers to control size and shape of nanostructured deposits by varying the laser

parameters. Magnetite nanostructures are currently promising materials to be used in computing, electronic devices and spintronic applications. For all these uses the fabrication of uniform nanostructured pure magnetite thin films is highly advantageous. In PLD of magnetite the laser irradiation wavelength and substrate temperature crucially affect the composition, crystallinity, surface structure and the magnetic properties of the grown samples. This work shows that the use of nanosecond IR laser at 1064 nm enhances the quality of the resulting magnetite thin films, compared to the extensively used UV wavelengths. Deposition at 1064 nm upon heating the substrate at 750 K produces thin films constituted by stoichiometric magnetite nanoparticles with sharp edges and sizes ranging from 80 to 150 nm, with a Verwey transition at 119 K and a coercivity of 232 Oe at room temperature, close to those of pure bulk magnetite. Thus, IR PLD together with the use of self-prepared hematite sintered targets allows preparing low-cost pure magnetite nanostructured thin films.

Keywords

Pulsed laser deposition, Nanocrystalline Magnetite fabrication, Magnetic properties

1. Introduction

Pulsed laser deposition (PLD) has been widespread used for the fabrication of metal, oxides and semiconductor nanostructured thin films due to the possibilities it offers to control the size, shape and crystalline phase of the nano deposits by varying the laser and other growth parameters.[1-3] In particular, the wavelength effect on the formation of nanostructured films produced by PLD has been studied in a very diverse range of materials[1-7] and an increase of the nanoparticle mean diameter with wavelength has been reported. An important drawback of the laser deposition method is, however, the presence in the film of micrometer sized particulates. These particulates are generally attributed to ablation of loosely connected target flakes, splashing of molten target material and deep target heating for irradiation with a poorly absorbed wavelength that lead to explosion of bubbles and condensation in the high density plume.[4] Typically it has been shown that the use of UV laser wavelengths in PLD yields smoother films, with fewer and smaller particulates than those obtained when visible or IR lasers are used.[5-7]

Half-metallic ferromagnetic materials, characterized by 100% spin polarization and having only one spin-subband at the Fermi level, are being actively investigated.[8] One example is magnetite (Fe_3O_4), the oldest known magnetic material that has attracted enormous attention due to its high Curie temperature (858 K),[9] and a metal–insulator transition (Verwey transition) at 120 K.[10-12] Magnetite nanostructures are thus promising materials for computing and electronic devices, spintronic applications and biomedicine.[13-19] Their performance will be dependent on the chemical and physical characteristics of the nanoparticles and their surfaces. Thus, the control of the particle size, shape, distribution and crystallinity is of crucial importance for the development of applications. The fabrication method should allow for tailoring the size and surface chemistry of the magnetic nanoparticles to meet the specific application demands.

Recent PLD investigations of magnetite thin films are routinely performed with UV lasers, generally in an attempt to minimize the presence of particulates on the resulting films, therefore disregarding the use of IR irradiation and its optimization for the production of quality magnetite films. Magnetite thin films have been grown by PLD using magnetite as target material on different substrates.[20-28] Other works have shown the possibility of low-cost fabrication of magnetite thin films by PLD using hematite ($\alpha\text{-Fe}_2\text{O}_3$) targets.[29-40] The influence of the nature[24, 25, 34, 36] and temperature[26, 39] of the substrates, ambient pressure,[27, 28] or film thickness[31, 37] on the magnetic properties of the deposits has been studied.

In this work, we report on the growth of magnetite nanostructured films by PLD using nanosecond pulses at wavelengths of 213, 532, and 1064 nm on Si (100) substrates from self-prepared sintered hematite targets. The deposits were characterized by atomic force microscopy (AFM) to determine the surface morphology, by X-ray diffraction (XRD) to examine their crystallinity, and by micro-Raman and Mössbauer spectroscopies to determine their composition and stoichiometry. Magnetic characterization was carried out by superconducting quantum interference device magnetometry (SQUID) and magneto-optical Kerr effect (MOKE). The results extend previous knowledge on the modulation of the size, shape and polycrystallinity of the nanostructured films that can be achieved under different experimental conditions, namely laser wavelength and substrate temperature. The use of IR PLD as an alternative to more conventional UV PLD has shown to enhance the quality of the prepared magnetite thin films. This, in combination with the use of self-prepared hematite sintered targets, yields a low-cost procedure to prepare pure magnetite nanostructured thin films for different applications.

2. Experimental section

The experimental PLD system consists of a stainless-steel vacuum deposition chamber pumped down to 2×10^{-4} Pa by a turbo-molecular pump.[41] Hematite targets were prepared from a > 99% iron (III) oxide powder (Sigma Aldrich, particle size < 5 μm) that was pelletized into disks of 10 mm diameter and about 2 mm thickness using a hydrostatic press at 8 Ton cm^{-2} followed by sintering at 1173 K in air for 8 hours. Targets were placed on a rotating sample holder and ablated with a Q-switched Nd:YAG laser (FWHM 15 ns, 10 Hz) at the excitation wavelengths of 213, 532, and 1064 nm. The laser beam was focused onto the target at 45° to a spot area of 0.14 mm^2 with a typical fluence (laser energy per unit area) of 8 times the ablation threshold fluence for each irradiation wavelength. The corresponding ablation threshold fluences were determined by measuring the minimum single pulse energy necessary to yield a luminous plume as detected by eye and the diameter of the irradiated region by the print left on an unplasticized polyvinyl chloride sheet. Based on the obtained ablation thresholds the used irradiation fluences were 0.8, 2.4 and 4 J cm^{-2} for 213, 532 and 1064 nm, respectively. The Si (100) substrates were ultrasonically degreased in acetone and methanol for 10 minutes and mounted on a heating element that allows operation in a temperature range between 300 and 773 K, as measured by a thermocouple. The substrates were placed in front of the target at a distance of 40 mm. Deposits were grown by delivering 144000 pulses to the target (resulting in a deposition time of around 4 hours).

The morphology of the deposits was examined by AFM (Multimode 8, Bruker) in tapping mode, and the images were analyzed with the Nanoscope Analysis 1.40 software. The mean roughness (R_a), determined from AFM analysis, is the arithmetic average of the deviations in height from the center plane of the sample and corresponds to the average of 5 independent

measurements in different locations of the sample. The thickness values result also from the average of 5 different measurements in different positions. The size distribution and average diameter of the deposited nanoparticles were obtained by determining the nanoparticle diameters from the profiles of the height in the AFM images. For each image, 10 parallel profiles were acquired at ca. 200 nm intervals and the results of three different images were readily averaged. The crystalline quality and composition of the deposits were studied by XRD (Philips XPert) using Cu K α (0.154184 nm) radiation in the $\theta/2\theta$ configuration. Micro-Raman spectra were obtained with a confocal Renishaw Raman microscope, RM-2000, equipped with a Leica microscope, and an electrically refrigerated CCD camera. A Helium-Neon laser at 632.8 nm was used as excitation source (20 mW laser, 50x objective). Ten scans were collected and summed up over the 100–2000 cm $^{-1}$ Raman shift range to provide good signal-noise ratios. The wavenumber resolution and acquisition time were 5 cm $^{-1}$ and 10 s, respectively. The analysis was performed at room temperature (RT) using the focused beam on a randomly oriented sample.

Integral Conversion Electron Mössbauer Spectroscopy (ICEMS) data were recorded at RT in a conventional constant acceleration spectrometer using a $^{57}\text{Co(Rh)}$ source and a parallel plate avalanche counter. All the isomer shifts were referred to the centroid of the spectrum of $\alpha\text{-Fe}$ at RT.

The dependence of the magnetization on temperature was measured in the range of 20-300 K with an in-plane applied field of 2 kOe using a SQUID magnetometer. Hysteresis loops were measured at 300, 150 and 100 K with a maximum in-plane applied field of 20 kOe. Evolution of angular dependence of RT hysteresis loops with the in-plane applied magnetic field was

measured by MOKE. Measurements were performed with angular steps of 4.5 degrees and a maximum applied field of 1.25 kOe.

3. Results

In the present study we first show the results obtained by the different characterization methods, followed by a discussion and the implications on the fabrication of magnetite thin films by PLD.

3.1. Surface structure

The deposits were examined by AFM to characterize the surface structure and thickness. For each sample several scans of $2 \times 2 \mu\text{m}^2$ were acquired. The values of thickness and roughness of the deposits are presented in Table 1.

Table 1. Thickness, roughness and size of nanostructures of deposits obtained upon irradiation at different wavelengths and substrate temperatures, as determined by AFM measurements.

Laser wavelength (nm)	Substrate temperature (K)	Thickness (nm)	Roughness (nm)	Nanostructure size (nm)
213	750	11 ± 2	6 ± 1	30-80
532	750	43 ± 2	9 ± 1	80-120
1064	750	117 ± 20	17 ± 1	100-150
1064	475	128 ± 14	15 ± 9	40-90
1064	300	23 ± 2	14 ± 5	40-90

Examples of AFM height images of the deposits obtained by irradiation at different wavelengths at a substrate temperature of 750 K are shown in Fig. 1. Upon irradiation at 213 nm

(Fig. 1a) the deposits are constituted by round nanoparticles with sizes of few tens of nanometers. The mean diameter distribution can be fitted by a lognormal distribution with an average size of 60 nm and a FWHM of 41 nm. In the case of 532 nm irradiation (Fig. 1b), most of the nanoparticles present a rectangular-like shape with sizes of up to 120 nm. When the deposits are produced under irradiation at 1064 nm (Fig. 1c), the nanostructures appear as a mixture of cubic and orthogonal prisms with straight edges, with face dimensions of 100–150 nm. The characteristic nanostructure sizes at each wavelength are listed in Table I.

Fig 1. Height AFM images of the deposits obtained at a substrate temperature of 750 K and upon irradiation at: a) 213, b) 532 and c) 1064 nm. All the images are 80 nm high and the scale bar is 500 nm.

Fig. 2a displays an AFM height image of the deposits obtained by irradiation at 1064 nm at a substrate temperature of 475 K. In this case, and in contrast with the results obtained at 750 K, the deposit contains round nanoparticles with sizes of few tens of nanometers. When the

substrate is kept at 300 K (Fig. 2b), the deposit is also constituted by round nanoparticles. Some larger aggregates, of up to 200 nm, can be observed in both cases.

Fig. 2. Height AFM images of the deposits obtained upon irradiation at 1064 nm with the substrate at a temperature of: a) 475 and b) 300 K. All the images are 80 nm high and the scale bar is 500 nm.

The results herein indicate that the laser wavelength and substrate temperature exert a strong influence on the morphology and dimensions of the nanostructured films produced by ns PLD from hematite targets.

3.2. Surface crystallinity

Fig. 3 presents XRD patterns of samples grown on a substrate heated at 750 K. The XRD peaks are located at 30.1°, 35.4°, 37.1°, 43.1°, 53.4°, 57°, and 62.6° and are assigned to the Fe_3O_4 (220), (311), (222), (400), (422), (511) and (440) diffraction planes, respectively. This pattern is indicative of the polycrystalline nature of the grown magnetite (Joint Committee on Powder Diffraction Standards Card No. 88-0866). The additional broad band centered at 69.2° (not shown completely) corresponds to the diffraction line (400) of the Si substrate. No diffraction peaks corresponding to hematite are observed. For the deposits fabricated at 213 nm (Fig. 3a), the small peak observed at 44.7° corresponds to the (110) plane of metallic iron.

The average crystalline domain size of the deposits can be estimated using the Scherrer law, $D = 0.9 \lambda / B \cos \theta_B$, where λ is the X-ray wavelength (Cu $K_\alpha = 0.154$ nm) and B is the full width at half-maximum (in radians) of the diffraction peak. The Scherrer law does not include peak broadening due to stress/strain, which is important in the case of thin films, and therefore the calculated crystalline domain sizes are over/subestimated. Nevertheless, the obtained values can be used to assess the influence of deposition conditions on the crystallinity of the deposits. The calculated nanocrystalline domain sizes are 24 ± 3 , 37 ± 6 and 44 ± 4 nm, for 213, 532 and 1064 nm irradiation, respectively, showing larger size upon increasing the deposition wavelength.

Fig. 3. XRD patterns of nanostructured films grown by heating the substrate at 750 K and upon irradiation at: a) 213, b) 532 and c) 1064 nm. The labels of the diffraction peaks correspond to magnetite unless other material is indicated.

Samples grown by irradiation at 1064 nm at different substrate temperatures were also analyzed by XRD. The XRD pattern obtained from the film grown at 475 K (Fig. 4a) reveals that only polycrystalline magnetite is obtained. The diffractogram recorded from the sample grown with the substrate temperature at 300 K (Fig. 4b) shows broad peaks and it resembles that of a poorly crystalline material either with small particle size and/or abundant structural defects. The main peaks correspond to the (220), (311), and (400) diffraction peaks of magnetite. Despite the poor signal-to-noise ratio of the diffraction pattern, the small peaks at around 36° and 42° could be associated with the (111) and (200) diffraction planes of wüstite (Fe_{1-x}O). The nanocrystalline domain sizes estimated using the Scherrer law are as small as 13 ± 3 and 9 ± 2 nm for the samples grown at 475 and 300 K, respectively, by comparison with 44 ± 4 nm determined for the film deposited at 750 K.

Fig. 4. XRD pattern of nanostructured films grown at 1064 nm, with the substrate at a temperature of: a) 475 and b) 300 K. The labels of the diffraction peaks correspond to magnetite unless other material is indicated.

3.3. Micro-Raman spectroscopy

The XRD patterns of magnetite and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) differ only for the presence of few diffraction peaks with intensity lower than 5%. Thus, the absence of these low-intensity peaks from the X-ray diffractograms shown in Fig. 3 and Fig. 4, cannot be considered as a proof of the formation of single, pure, stoichiometric magnetite nanostructured films. An alternative technique is the use of micro-Raman spectroscopy, considered a powerful tool to distinguish the different iron oxides phases,[42] which differ in vibrational frequencies. Micro-Raman spectra of the deposits fabricated on substrates heated at 750 K at different irradiation wavelengths are shown in Fig. 5. Although some bands of magnetite overlap with those corresponding to the Si

substrate, the characteristic magnetite features at 668, 538, 303, and 193 cm^{-1} were observed under all deposition conditions. The pronounced magnetite feature at 668 cm^{-1} , attributed to the A_{1g} mode, is clearly visible in all the spectra, whereas the features at 303 cm^{-1} and 538 cm^{-1} , assigned to the E_g and T_{2g} modes respectively, are weak and overlap with the 519 and 303 cm^{-1} bands of the substrate. A very low intensity feature at 193 cm^{-1} , also assigned to the T_{2g} mode, can be observed in the samples prepared upon 532 and 1064 nm irradiation. For the sample prepared at 213 nm the spectrum displays the substrate features, clearly observed at 623, 519, 435, and 300 cm^{-1} and a broad band in the range of 930–990 cm^{-1} . There is no observable peak shift in the Raman spectra, suggesting the absence of contributions from non-equivalent sites in the magnetite structure.[42]

The micro-Raman spectra of samples fabricated upon irradiation at 1064 nm on substrates at 475 and at 300 K, are rather similar (not shown), with all bands corresponding to magnetite. We could not verify the presence of wüstite in the deposits by micro-Raman spectroscopy probably due to the low intensity of the corresponding feature (at 650 cm^{-1}), consequence of its reduced content (as suggested by XRD), in combination with overlapping of the magnetite band at 668 cm^{-1} .

Fig. 5. Micro-Raman spectra of Fe₃O₄ nanostructured films grown by PLD at 213, 532, and 1064 nm, as indicated, by heating the substrate at 750 K. Micro-Raman spectrum of the silicon substrate is shown for comparison.

3.4. Integral Conversion Electron Mössbauer Spectroscopy (ICEMS)

Magnetite presents an inverse spinel structure, with the $[\text{Fe}^{3+}]_A[\text{Fe}^{3+}\text{Fe}^{2+}]_B\text{O}_4$ formula, where A indicates tetrahedral sites, and B octahedral sites. At RT there is fast electron hopping between the Fe cations at the octahedral sites, giving an average +2.5 valence in Mössbauer spectroscopy.[43] Each different iron cation (Fe^{3+} at tetrahedral sites and $\text{Fe}^{2.5+}$ at octahedral sites) gives rise to a different sextet component. In both cases, the Mössbauer quadrupole shift (2ε), related to the distortion of the atomic environment from the ideal cubic symmetry, is close to 0. The hyperfine magnetic field is smaller for the octahedral site, reflecting the smaller magnetic moment of $\text{Fe}^{2.5+}_B$. For stoichiometric magnetite,[43] the ratio between both components (S_B/S_A) is very close to 2 (1.9) with $\delta_A = 0.29 \text{ mms}^{-1}$, $2\varepsilon_A = 0.00 \text{ mms}^{-1}$, $H_A = 49 \text{ T}$; $\delta_B = 0.66 \text{ mms}^{-1}$, $2\varepsilon_B = 0.00 \text{ mms}^{-1}$, and $H_B = 46 \text{ T}$, where δ is the isomer shift and H the hyperfine magnetic field. Mössbauer spectra recorded from the different samples are presented in Fig. 6 and the parameters obtained from the fits are collected in Table 2.

Table 2. Mössbauer parameters obtained from the fit of spectra recorded from films deposited at the indicated conditions. δ and 2ε are the isomer and quadrupole shifts, respectively, and H the hyperfine field.

Irradiation conditions	Component	δ (mm s ⁻¹)	2ε (mm s ⁻¹)	H (T)	Area (%)	A ₂ /A ₃ area ratio	S _B /S _A area ratio
213nm	Doublet	0.27	0.49	-	2	-	
750 K	Sextet A	0.27	0.00	48.7	37	3.00	1.54 ± 0.22
	Sextet B	0.66	0.00	45.4	57		
	α -Fe	-0.02	-0.12	33.0	4	3.00	
532nm	Sextet A	0.27	0.00	48.7	37	2.3	1.70 ± 0.17
750 K	Sextet B	0.65	0.00	45.4	63		
1064nm	Sextet A	0.26	-0.02	49.3	35	2.75	1.85 ± 0.15
750 K	Sextet B	0.67	0.00	46.1	65		
1064nm	Sextet A	0.25	-0.04	48.4	33	1.00	2.00 ± 0.15
475 K	Sextet B	0.64	-0.04	45.4	67		
1064nm	Sextet A	0.26	0.02	46.6	17	(*)	(*)
300 K	Sextet B	0.59	-0.08	43.9	38		
	Fe 2.5+	0.61	0.06	39.6	30		
	Fe _{1-x} O	0.68	1.67	----	11		
	Fe _{1-x} O	1.02	0.89	----	4		

(*)Not calculated due to the complexity of the spectrum

Fig. 6. ICEMS spectra recorded from nanostructured films deposited at the indicated irradiation conditions.

For the deposits prepared at 750 K, with the exception of the film prepared at 213 nm, where a small ($< 3\%$) additional contribution due to metallic iron is also observed, the spectra contain only the two sextets which are characteristic of magnetite. The ratio between the S_B and S_A sextets, which should be 1.9 for stoichiometric magnetite, is lower than this value for the samples prepared under UV irradiation (213 nm). Non-stoichiometric magnetite can be formulated, assuming the existence of vacancies only in the octahedral sites of its spinel-related structure, as $\text{Fe}^{3+}[\text{Fe}^{2+}_{1-3x}\text{Fe}^{3+}_{1+2x}\square_x]\text{O}_4$ or, taking into account the 2.5+ average oxidation state of iron in the octahedral sites, as $\text{Fe}^{3+}[\text{Fe}^{2.5+}_{2(1-3x)}\text{Fe}^{3+}_{5x}\square_x]\text{O}_4$, where $0 \leq x \leq 0.33$. The end member of the series, corresponding to $x = 0.33$, is maghemite, $\text{Fe}^{3+}[\text{Fe}^{3+}_{5/3}\square_x]\text{O}_4$. This implies that a S_B/S_A area

ratio lower than 1.6 does not make sense within the context of a single phase non-stoichiometric magnetite. The only way to explain the obtained ratio (1.54) in the film prepared at 213 nm (Table 2), is to assume the presence of a small, additional amount of maghemite. The spectrum of maghemite overlaps with that of the tetrahedral component of magnetite and to discern both is, in practical terms, impossible,[43] especially if the amount of maghemite is small, as in the present case. This may be probably the reason why maghemite goes undetected in the micro-Raman experiments.

The S_B/S_A ratio approaches 1.9, i.e. the pure stoichiometric value, as the irradiation wavelength increases, clearly showing that the stoichiometry of the deposited magnetite depends on the wavelength used during PLD: larger wavelengths induce the formation of almost stoichiometric magnetite while shorter wavelengths increase the amount of Fe^{3+} . We can rule out the presence of iron oxides such as hematite, which should show only one sextet with a H of about 52 T and a 2ε of -0.20 mms^{-1} .

Mössbauer spectroscopy also gives information about the average magnetization direction. The spectra have been acquired in the as-grown films. The ratio between the 2nd and 3rd component of each sextet (A_2/A_3 area ratio) should be 2 for random magnetization orientation, and A_2/A_3 larger than 2 should implies a tendency of in-plane magnetization orientation. The obtained results indicate that the film fabricated at 1064 nm and 475 K has out-of-plane orientation whereas all other films have in-plane orientation, without showing a clear trend with irradiation wavelength. The values observed might be related to changes in the microcrystalline texture of the films.

It is observed that the films fabricated at 1064 nm and at a substrate temperature of 475 K (Fig. 6) are exclusively constituted by magnetite although the spectral lines appear to be broader than in the spectrum of the sample prepared at 750 K, what would suggest a slightly larger

degree of structural inhomogeneities. However, the S_B/S_A area ratio is 2.0, i.e., as it would be expected for stoichiometric magnetite. The spectrum recorded from the film deposited at 300 K (Fig. 6) is also compatible with the formation of magnetite. However, in addition to the two narrow sextets corresponding to the A and B sites of magnetite there is a third broad magnetic component with $\delta = 0.61 \text{ mms}^{-1}$, similar to that shown by the $\text{Fe}^{2.5+}$ component but with a much smaller H (39.6 T). The results are compatible with incomplete structural and/or magnetic order at the octahedral sites of the spinel-related structure of Fe_3O_4 . Besides this, the hyperfine magnetic field values of the narrower A and B sextets are smaller than those characteristic of bulk magnetite ($H_A = 49.0 \text{ T}$, $H_B = 46.0 \text{ T}$). Taken together, the results indicate that the film deposited at 300 K is of poorly crystalline character and/or is composed by small particles. The spectrum also shows (Fig. 6) paramagnetic contributions (15%) in its central part which have been fitted to two doublets. The Mössbauer parameters of these two doublets ($\delta = 0.68 \text{ mms}^{-1}$, $\Delta = 1.67 \text{ mms}^{-1}$; $\delta = 1.02 \text{ mms}^{-1}$, $\Delta = 0.89 \text{ mms}^{-1}$) could be associated to the presence of Fe_{1-x}O .

3.5. Magnetic characterization

A plot of the magnetization as a function of temperature for the deposits fabricated at a substrate temperature of 750 K and wavelengths of 213, 532 and 1064 nm is shown in Fig. 7. Magnetization was measured on warming in an in-plane magnetic field of 2 kOe after zero field cooling. A sudden jump in magnetization can be observed when increasing the temperature for all the films as a result of the change in the crystal structure from the low temperature monoclinic phase to the high temperature cubic one. The temperature at which this transition occurs, the Verwey temperature (T_V), has been determined for each film by taking the maximum slope of the magnetization.

Fig. 7. Dependence of the magnetization on temperature (warming curves) with an in-plane applied field of 2 kOe for magnetite films fabricated at a substrate temperature of 750 K and a deposition wavelength: a) 213 nm, b) 532 nm, and c) 1064 nm.

A clear Verwey transition is measured at about 110 K and 114 K for films deposited at 213 and 532 nm, respectively. The Verwey transition for both samples is smeared out possibly due to the interfacial strain induced in the films. The film deposited at 1064 nm (thickest film) with $T_V = 119$ K, shows the sharpest increase of magnetization in the smallest temperature range among the complete series.

Demagnetization curves measured at three different temperatures (300, 150 and 100 K) for samples prepared at a substrate temperature of 750 K and wavelengths of 213, 532 and 1064 nm are shown in Fig. 8. A decrease in coercivity is observed at all measurement temperatures under study with increasing deposition wavelength (Fig. 8d). At 300 K, the largest coercivity (415 Oe) is obtained for the magnetite film prepared at 213 nm by comparison with a minimum value of 232 Oe achieved for the magnetite film grown at 1064 nm. At 100 K, these films achieve coercivity values of 742 Oe and 688 Oe, respectively.

Fig. 8. Demagnetization curves at the indicated temperatures for magnetite films fabricated at a substrate temperature of 750 K and a deposition wavelength of: a) 213, b) 532, and c) 1064 nm. d) Evolution of coercivity vs deposition wavelength measured at different temperatures (lines are guide to the eye).

The large increase in coercivity at $T < T_V$ (Fig. 8d) is a well known result due to the abrupt change in the magnetocrystalline and magnetostriction constants when magnetite transforms from the cubic to the monoclinic phase.[31] The large magnitude of the low temperature monoclinic magnetocrystalline anisotropy constants, compared to the cubic ones, and the abrupt

changes in the magnetostriction constant are considered to be the dominant factors controlling the demagnetizing behavior below T_V .

Fig. 9 shows the dependence of the magnetization on temperature for magnetite films grown at 1064 nm and at substrate temperatures of 475 and 300 K, under the same measurement conditions used to obtain the curves displayed in Fig. 7. The decreased microstructural and morphological quality of these films is evident in the magnetization curves with a decreased T_V of about 109 K and even the absence of a well defined T_V for the films prepared at 475 and 300 K, respectively.

Fig. 9. Dependence of the magnetization on temperature (warming curves) with an in-plane applied field of 2 kOe for magnetite films fabricated with a deposition wavelength of 1064 nm at substrate temperatures of: a) 475 K and b) 300 K.

The above mentioned features for both films correlate well with the hysteresis loops shown in Fig. 10. A decreased substrate temperature of 475 K results in a RT coercivity value (255 Oe) higher than that obtained for the film grown at 750 K (232 Oe), shown in Fig. 8d, as a consequence of a finer microstructure consisting of a larger density of intergranular and defective regions.

Fig. 10. Demagnetization curves at the indicated temperatures for magnetite films fabricated with a wavelength of 1064 nm at different substrate temperatures of: a) 475 K and b) 300 K.

The angular dependence of the films has been studied by MOKE by recording hysteresis loops with angular variation (0–360 degrees with 4.5 degrees steps) in the in-plane orientation of the applied external magnetic field. Fig. 11 shows representative hysteresis loops measured at angular intervals of 90 degrees for a magnetite film deposited at a wavelength of 532 nm and a substrate temperature of 750 K. For all the irradiation wavelengths the loops were identical independently of the in-plane angle indicating that the magnetite films grown at different deposition wavelengths are magnetically isotropic.

Fig. 11. Hysteresis loops measured by MOKE at different angles of the in-plane magnetic field for a magnetite film grown with a wavelength of 532 nm and a substrate temperature of 750 K.

4. Discussion

The properties of the nanostructured films prepared by PLD on Si substrates follow clear trends with laser irradiation wavelengths and substrate temperature, with consistency between the results obtained by the different and complementary techniques used in this study. AFM indicates that, while a shorter wavelength produces a roughly more uniform film, the shape of the grains in such film is less defined, showing less developed facets than for longer wavelengths. Deposition at a lower substrate temperature also reduces the particle size but again at the expense of less defined facets. XRD results correlate with the AFM results: the most crystalline films are the ones grown at elevated temperature and under longer irradiation wavelength. XRD results also show that the films are composed of magnetite (although maghemite could not be ruled out due to overlapping of reflection peaks with the former). The micro-Raman spectra prove the presence of magnetite,[44] and are conclusive on the absence of any relevant features indicating a significant presence of either maghemite or hematite. The ratio of the two cation sites from Mössbauer spectroscopy approaches the magnetite stoichiometric value as the irradiation wavelength increases whilst shorter wavelengths increase the amount of Fe^{3+} .

The Verwey transition is known to be very sensitive to the stoichiometry.[11, 12] While the sharper Verwey transition observed for the film grown under the longer wavelength of 1064 nm can be attributed to the larger thickness of that film, the transition temperature corresponds to high quality magnetite. In fact, lowering the temperature of the substrate during deposition, even for films of the same thickness, results in a less defined Verwey transition (smoothed out magnetization curves, decreased Verwey temperature). The Verwey transition disappears for the 300 K grown film, in agreement with the very wide sextets observed by Mössbauer spectroscopy

which are indicative of small particle sizes or poor crystallinity. Furthermore, for the less crystalline films, an increased number of intergranular and or disordered regions are expected which would pin down the magnetic domains increasing the coercivity[31] as experimentally observed. The lowest coercivity of the higher substrate temperature and irradiation wavelength correlates well with that of bulk magnetite.

The changes in film quality can be discussed in relation to the initial laser-target interaction, the subsequent plume expansion and the nucleation processes that take place on the substrate. In the case of ns laser ablation, the main processes induced during target irradiation are normal vaporization, phase explosion and subsurface heating.[45, 46] The tendency to produce smaller nanoparticles with a narrower size distribution at shorter wavelengths as observed herein has also been reported previously for other solid target materials.[4-7] We note, though, that if the goal is to obtain a crystalline film (as opposed to a film constituted by well defined nanoparticles) the presence of smaller nanoparticles would indicate that these are not the ideal growing conditions. Considering the linear absorption coefficients of the target, $\alpha_{213} \approx 8 \times 10^5 \text{ cm}^{-1}$, $\alpha_{532} \approx 2 \times 10^4 \text{ cm}^{-1}$ and $\alpha_{1064} \approx 1 \times 10^3 \text{ cm}^{-1}$,[47] the heated subsurface layer thickness is only 12 nm at 213 nm, while it amounts to around 500 nm for 532 nm and 10 μm for 1064 nm. Therefore, the experimentally observed tendency to produce smaller nanoparticles at 213 nm irradiation is related to the smaller size of the ejected species (ions, atoms and small atomic clusters) produced in a reduced volume during the relaxation of the ablated target. Further characterization of the energy profile of the emitted species particles from the target as a function of wavelength remains the subject of future studies.

One reason for the complete prevalence in previous works of the use of UV wavelength in the preparation of magnetite films by PLD is the avoidance of target particulate ejection. As the PLD

growth from a hematite target is not congruent, a simple test for such process is the detection of hematite in the grown films. We have not detected any sign of the presence of hematite in the films prepared at the various experimental conditions explored by any of the techniques employed in the present work: XRD, micro-Raman, and Mössbauer spectroscopy.

The role of temperature can be understood considering the mobility of the deposited material on the surface, which is favored by increasing the substrate temperature. This dependence indicates that the thermal annealing of the small amount of material deposited at each laser pulse (a thousand of a monolayer) is also a crucial processing parameter to promote smooth growth, and thus, well defined magnetite crystallites. Work is in progress to use the present parameters in the growth of single crystalline magnetite by the choice of the appropriate substrates.

5. Conclusions

Magnetite nanostructured deposits on Si substrates were obtained by PLD from sintered hematite targets at the wavelengths of 213, 532, and 1064 nm at different substrate temperatures, from a Q-switched Nd:YAG laser. Detailed morphological, microstructural and compositional characterization of the films has been carried out by means of AFM, XRD, micro-Raman and Mössbauer spectroscopy, while SQUID and MOKE techniques have been used for magnetic characterization. Except for the shorter wavelength, the obtained deposits are almost stoichiometric magnetite. In particular no hematite is detected, independently of the laser irradiation wavelength, indicating that hematite **particles clusters** are not present in the ablation plume. The observed trend of stoichiometry improvement of deposits as the laser wavelength increases, and the importance of the latter parameter in the crystalline and magnetic properties of the deposits, provide the possibility of tailoring the properties of magnetic nanostructured films

formed by PLD. The best quality deposits, having the right magnetite stoichiometry as indicated by Mössbauer spectroscopy, with a Verwey transition at 119 K and a coercivity of 232 Oe at RT, were grown by ablation at 1064 nm and at a substrate temperature of 750 K. Thin films fabricated at these conditions simultaneously present magnetite nanoparticles of geometrical shape with well defined edges, in a mixture of cubic and orthogonal prisms, with sizes in the range 100-150 nm. As an alternative to conventional UV ns PLD, the use of IR PLD, together with the use of self-prepared hematite sintered targets, enhances the quality of magnetite thin films and allows preparing low-cost pure magnetite nanostructured thin films for different applications.

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