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Study of cobalt ferrite thin films deposited by laser ablation

–Abstract–

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Content

Introduction

Magnetostrictive materials are extensively used as sensors and actuators in a wide range of applications in automobile and aerospace industry for ultrasound generation and detection, in ultrasonic radiolocation and magnetostrictive filters etc. [1-5]. Thin films present a peculiar interest due to the sensors miniaturization trend. The aim of this study was to investigate the processes that take place during laser ablation so that the structural, electric and magnetic properties of the thin films could be anticipated and controlled.

Chapter 1. COBALT FERRITE BULK AND THIN FILM RESEARCH STAGE

1.1 Ferrimagnetic materials with spinel type structure

Magnetic materials with spinel structure have the chemical formula AB_2O_4, where A represents the divalent cation and B the trivalent cation. The spinel structure can be described as an fcc lattice in which the cations can occupy two types of interstices [6].

1.2 Cobalt ferrite

Cobalt ferrite is a ferromagnetic material with an inverse spinel structure with a lattice parameter of 8.38 Å. These materials have a high anisotropy constant and an elevated magnetostrictive coefficient as compared to other ferrites [7]. The magnetic properties are influenced by the mean particle size [8].

1.3 The influence of dopant with large ionic radii on the properties of ferrimagnetic materials with spinel structure

Changing the chemical composition, some properties of ferrite materials can be improved by inserting different types of ions in the spinel structure. The elements from the lanthanide series have various magnetic properties. Their magnetic moments can vary from 0 to 10.5μ_B and each ion has a well localized magnetic moment. Materials that include rare earth elements have a high spin-orbit coupling because RE elements have a large mass and thus the magnetoscrystalline anisotropy is more pronounced. The main results of other research groups in this field are mentioned in the extended paper [4], [9-19].

Chapter 2. METHODS OF OBTAINING COBALT FERRITE BULKS AND THIN FILMS

2.1 Methods of obtaining bulk ferrimagnetic materials with spinel structure

The cobalt ferrite bulk sample studied in this paper was prepared by coprecipitation method and the RE doped samples by solid state reaction [20],[21].

2.2 Thin film deposition methods

The deposition of dielectric or conductive thin films is very important in fundamental research as well as for device manufacturing.

2.3 Pulsed laser deposition of thin films

Pulsed laser deposition (PLD) is a physical deposition process from vapours which takes place in a vacuum chamber and has some commun characteristics with moleculat beam epitaxy and sputtering. This tehnique can be used to deposit a wide range of materials and ensures the stoichiometry. This chapter describes:

2.3.1 The influence of laser parameters and target properties
2.3.2 The influence of preasure and target-substrate distance
2.3.3 The influence of the substrate type and temperature during the deposition process

2.4 Experimental set-up and deposition parameters description

These results were obtained in collaboration with the Plasma Physics Laboratory from “Al. I Cuza” University, CERLA Laboratory from Lille 1 University – Universite des Sciences et Technologies, France and with DPMC Department from Geneva University, Switzerland.

Chapter 3. LASER INDUCED PLASMA CHARACTERIZATION BY OPTIC METHODS

3.1 Introduction

After Laser discovery, the main aim of the research groups was to investigate its interaction with matter and subsequently to analyze the formed plume.

3.2 Local Thermodynamic Equilibrium (LTE)

The conditions for LTE are: the electronic density of the plume should be greater than the threshold value and the excitation temperature of the species which form the plasma (atoms, ions, molecules) should be equal with the electronic temperature.

3.3 Determination of the excitation temperature of different species found in the plume

Using Boltzmann distribution we obtained the excitation temperature of neutrals and ions of the main elements.

3.4 Description of the used experimental set-up

The studies samples were placed in a stainless steel chamber where the pressure was maintained at $2 \cdot 10^{-2}$torr during experiments. For plasma generation we used the radiation of a Nd-YAG laser (532nm, 10ns, 10Hz, 10J/cm^2). The plasma evolution was investigated using ultrafast ICCD camera placed and the end of a monochromator. For the spatial distribution of several spectral lines we recorded the emission spectra corresponding to just a small strip of the plume.

3.5 Laser induced plasma study

This chapter presents the experimental results obtained by investigating the global evolution of the formed plasma and the spatial-temporal distribution of several species found in the plume.

3.5.1 Global evolution analysis

Plasma dynamic information was obtained by ultrafast photography. For all the studied samples two main structures with different velocities were observed (one "fast" and one "slow"). This plasma splitting was noticed by other research groups [22-24].

3.5.2 Optical emission spectroscopy

By optical emission spectroscopy we can obtain information on the contribution of each present species to the plasma formation and expansion processes. The spectral lines observed in the recorded spectra were indentified using two data bases [25], [26].

The global evolution of the plasma obtained by the ICCD camera and the ToF profiles as well indicated the formations of two main structures: one "fast" represented by the ions and one "slow" due to the presence of neutrals. The Boltzmann distribution was used for the excitation temperature determination.

Chapter 4. THIN FILM AND BULK MATERIALS CHARACTERIZATION METHODS

4.1 **X-Ray diffraction**

X-Ray diffraction is a technique which provides information on the crystalline structure of the different types of analyzed samples (powders, bulks, thin films).

4.2 **Raman spectroscopy**

The vibrational spectroscopy is used to study the chemical bonds present in different types of samples, with micro- or macroscopic dimensions, in a wide range of temperatures.

4.3 **Surface analysis techniques**

The structural analysis of thin films implies two steps: one which determines the crystallographic arrangement and another one which investigated the thickness, morphologic structure, chemical composition and distribution of the main chemical elements found in the thin film.

4.4 Vibrating sample magnetometer

The vibrating sample magnetometer is used to study the magnetic properties of materials. Hysteresis loops of different types of samples can be obtained in various configurations.

Chapter 5. CONTRIBUTIONS TO THE STUDY OF COBALT FERRITE BULKS AND THIN FILMS

5.1 Study of the structural, magnetic, dielectric and magnetostrictive properties of $CoFe_{1.8}RE_{0.2}O_4$ bulk materials

5.1.1 X-Ray diffraction analysis results

The $CoFe_2O_4$ diffractogram indicated the formation of a single spinel type structure but for the RE doped samples another phase with a perovskite type structure was detected [11], [13], [27].

Although sintered at higher temperatures than the cobalt ferrite pellet, the RE doped samples presented smaller densities and higher porosities. As the ionic radius of the RE element increases the sample density augments.

5.1.2 Raman spectra analysis

The Raman spectra of the cobalt ferrite sample present four peaks which correspond with this structure [28], [29]. The Raman spectra of the RE doped samples present additional peaks. These indicate the formation of RE orthoferrite.

5.1.3 EDX analysis results

The results obtained confirmed the presence of the main chemical elements on the sample surface, the as obtained images indicating a uniform distribution. The estimated value of the (FeDy)/Co ratio was 2.1. The oxygen concentration could not be determined accurately.

5.1.4 Hysteresis loops analysis

These results indicated that as the ionic radius of the RE element increases the coercive files increases from 141Oe to 252Oe and the saturation magnetization presents a 56% decrease.

5.1.5 The variation of the magnetostriction coefficient with applied magnetic field

Although the induced maximum deformation decreases as RE elements are added, its value is still greater than the one observed for different types of ferrites [30], [31].

5.1.6 Dielectric properties investigation

The experimental results were obtained in the 20Hz–2MHz frequency range. The dielectric properties of the doped and undoped samples can be explained by the microstructural differences of these pellets [21].

5.1.7 Analysis of the magnetoelectric properties

As the intensity of the applied magnetic field is augmented the magnetoelectric coefficient increases but the maximum values are still smaller than the ones observed in different cobalt ferrite based systems.

5.1.8 Piezoresponse force microscopy results

The presence of regions with "up" or "down" orientation of polarization was not detected when an electric field was applied.

5.2 Study of the structural and magnetic properties of the thin films obtained by laser ablation

5.2.1 Study of the cobalt ferrite thin films obtained using XeCl laser

The aim of this study was to investigate the influence of several deposition parameters like pressure and nature of the used gas, time of deposition and target-substrate distance on the structural and magnetic properties of cobalt ferrite films [32].

AFM images indicated that as the target-substrate distance increases the thin films have a higher uniformity. The XRD diffractograms of the thermally treated thin films (900°C, 1h) confirmed the formation of the spinel structure. The average crystallite size was not influenced by the gas pressure. From SEM images we determined a mean particle size of 40 nm for P004 samples and 60 nm for P002.

The XPS analysis confirmed the presence of Fe, Co and O on the samples surface. The estimated Co/Fe ratio of 0.68 for P002 and 0.62 for P004 indicated the presence of cobalt oxide on the surface of the samples. This result was confirmed by XRD analysis.

For the P004 sample a narrowing of hysteresis loop was observed at small applied magnetic fields. This behavior can be explained by the presence of another antiferromagnetic phase of cobalt oxide at the thin films surface [33].

5.2.2 Study of the cobalt ferrite thin films deposited using Nd-YAG laser

The aim of this study was to investigate the influence of the substrate temperature and RE inclusion in the spinel structure on the structural and magnetic properties of cobalt ferrite thin films deposited by PLD.

The Raman spectra of the cobalt ferrite target and thin films indicate the formation of a single spinel structure. Even the thin film deposited without substrate heating presented the same Raman spectrum as the target. For the thin films deposited at higher substrate temperatures the Raman analysis indicated a decrease in chemical bond, possibly due to the thermal expansion mismatch between the substrate and thin film.

The Raman spectra of the doped thin films present peaks which only correspond to cobalt ferrite indicating also an increase in chemical bond. The $CoFe_2O_4$ thin film deposited at 500^oC and the $CoFe_{1.8}RE_{0.2}O_4$ samples deposited at 600^oC presented additional peaks. The thin film thickness was not greatly influenced by the substrate temperature. The XRD results confirmed the formation of a polycrystalline thin film with spinel structure.

The increase in peak intensities with substrate temperature suggests an evolution in crystallinity [34]. The increase in cell edge confirms the Fe substitution with RE elements. ToF-SIMS images and depth profiles indicate an uniform distribution of Fe, Co and RE ions and of their oxides.

The samples surface microstructure was not significantly influenced by the substrate temperature. For the La doped sample, an increased roghness was observed. EDX images confirmed the ToF-SIMS results. The MFM measurements indicated that for zero applied field the samples present a weak magnetic respose.

For the cobalt ferrite thin films, an increase in coercive field and maximum magnetization in perpendicular configuration was observed. The improved magnetic response of the La and Gd doped samples as the substrate temperature increases can be due to the evolution in cristallinity. The magnetic measurement results indicate a substitution of Fe with RE elements.

5.2.3 Study of the cobalt ferrite thin films deposited using Ti-Sa laser

In collaboration with Lille 1 University (France), another research approach was studied: the influence of laser characteristics (pulse repetition rate and width) on the structural and magnetic properties of the thin films.

The ToF-SIMS images did not reveal the presence of regions with modified chemical composition. The Raman spectra indicated the formation of $CoFe_2O_4$ and an enlargement of the chemical bond. To confirm the formation of the spinel type structure and the presence of internal stress, the thin films were analyzed using XRD technique [35]. The diffractograms indicated the formation of a distorted spinel type structure with preferential crystallographic growth direction. The structural analysis showed that different types of internal stress can be induced by changing the laser parameters. The VSM measurement did not reveal the presence of a magnetic anisotropy.

Conclusions

The experimental results presented and discussed in this thesis bring contributions to the study of cobalt ferrite bulk materials and thin films obtained by PLD.

The XRD diffractograms of the sintered disks indicated the formation of RE orthoferrite in concentrations between 12 to 15%. The lattice parameter of the doped samples spinel structure presents a slight increase compared to the one of the stoichiometric cobalt ferrite and the mean crystallite size decreases once the RE oxide is added in the preparation process. The hysteresis loops indicated a decrease in saturation magnetization and an increase in coercive field as the ionic radius of the RE element augments. The maximum magnetostriction coefficient value of the $CoFe_{1.8}La_{0.2}O_4$ disk is 13% lower than the one of the $CoFe_2O_4$ sample.

Using a monochromator and an ICCD camera we could investigate the plasma dynamic and the spatial and temporal evolution of some present species. Information on the two main structures (one "fast" – given by ions – and another one "slow" – represented by neutrals) was obtained.

Thin films of cobalt ferrite were deposited by PLD in different conditions using a XeCl laser. The XRD analysis of the thermally treated thin films confirms the formation of the spinel structure. Using AFM and SEM images, the variations in structural properties with different deposition parameters were investigated. The magnetic measurements indicated o slight modification of the coercive field with applied magnetic field direction.

Cobalt ferrite and $CoFe_{1.8}RE_{0.2}O_4$ (RE=Dy, Gd, La) thin films were deposited using two types of lasers: Nd-YAG and Ti-Sa laser. Although in bulk materials the RE ions did not substitute the Fe ions, the Raman spectra of the thin films deposited at different substrate temperatures confirmed the formation of a single spinel structure. For the RE doped samples, the Raman spectroscopy analysis indicated a distorted spinel structure. These results were confirmed by XRD. The ToF – SIMS analysis revealed a uniform distribution of the constituent elements in the sample volume.

For the thin films deposited using Ti-Sa laser, the structural analysis results indicated the formation of spinel phase with preferential crystallographic growth directions. Due to the low fluence and high repetition rate we obtained thin films with an improved uniformity in short time.

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Bibliography

[1] E. W. LEE, Rep. Prog. Phys., 18 (1995), 184–229;
[2] Y. Kikuchi, IEEE Trans. on Mag., 4 (2003), 107–117;
[3] S. D. Bhame, P. A. Joy, J. Phys. D: Appl. Phys., 40 (2007), 3263–3267;
[4] F. Cheng, C. Liao, J. Kuang, Z. Xu, C. Yan, L. Chen, H. Zhao, Z. Liu, J. Appl. Phys., 85 (1999), 2782–2786;
[5] J. Ryu, S. Priya, K. Uchino, H. E. Kim, J. Electroceram., 8 (2002), 107–119;
[6] A. Goldman, „Modern Ferrite Technology", 2006;
[7] O. F. Caltun, G. S. N. Rao, K. H. Rao, P. Rao, C. Kim, C. O. Kim, I. Dumitru, N. Lupu, H. Chiriac, Sensor Lett., 5 (2007), 1-3;
[8] N. Moumen, M. P. Pileni, J. Phys. Chem., 100 (1996), 1867–1873;
[9] A. A. Sattar, K. M. El–Shokrofy, J. Phys. IV, C1 (1997), 245–246;
[10] A. A. Sattar, A. H. Wafik, K. M. El–Shokrofy, M. M. El–Tabby, Phys. Stat. Sol. (a) , 171 (1999), 563–569;
[11] N. Rezlescu, E. Rezlescu, Sol. Stat. Comm., 88 (1993), 139–141;
[12] N. Rezlescu, E. Rezlescu, P.D. Popa, L. Rezlescu, J. Alloys Comp., 275–277 (1998), 657–659;
[13] E. Rezlescu, N. Rezlescu, P.D. Popa, J. Magn. Magn. Mat., 290–291 (2005), 1001–1004;
[14] K. K. Bharathi, C.V. Ramana, J. Mat. Res., 26 (2011), 584–591;k
[15] K. K. Bharathi, G. Markandeyulu, C. V. Ramana, J. Phys. Chem. , 115 (2011), 554–560;
[16] K. K. Bharathi, J. Arout Chelvane, G. Markandeyulu, J. Magn. Magn. Mat., 321 (2009), 3677–3680;
[17] K. K. Bharathi, R. S. Vemuri, C. V. Ramana, Chem. Phys. Lett., 504 (2011), 202-205;
[18] F. X. Cheng, J. T. Jia, Z. G. Xu, B. Zhou, C. S. Liao, C. H. Yan, L. Y. Chen, H. B. Zhao, J. Appl. Phys., 86 (1999), 2727-2733;
[19] F. X. Cheng, J. T. Jia, C. S. Liao, Z.G. Xu, B. Zhou, C. H. Yan, L. Y. Chen, H. B. Zhao, J. Appl. Phys., 87 (2000), 6779-6782;
[20] O. F. Catun, M. Feder, Editura Universitatii "Al. I. Cuza" Iasi, 2009;
[21] G. Dascalu, T. Popescu, M. Feder, O. F. Caltun, „Structural, electric and magnetic properties of $CoFe_{1.8}RE_{0.2}O_4$ (RE=Dy, Gd, La) bulk materials", submitted in Journal of Magnetism and Magnetic Materials;
[22] L. D'Alessio, A. Galasso, A. Santagata, R. Teghil, A.R. Villani, P. Villani, M. Zaccagnino, Physics and Chemistry of Advanced Laser Materials Processing, 208–209 (2003), 113–118.

[23] T. Kajiwara, T. Nishiyama, S. Morinaga, K. Nagayama, Appl. Phys. A, 101 (2010), 739–742;
[24] G. D'Amico, A. Di Trolio, A. Morone, S. Orlando, A. Santagata, Appl. Surf. Sci., 208–209 (2003), 96–100;
[25] NIST Atomic Spectra Database, http://physics.nist.gov/asd3;
[26] Atomic spectral line database, http://www.pmp.uni–hannover.de;
[27] J. Sun, J. Li, G. Sun, J. Magn. Magn. Mat., 250 (2002), 20–24;
[28] S. W. da Silva, T. F. O. Melo, M. A. G. Soler, E. C. D. Lima, M. F. da Silva, P. C. Morais, IEEE Trans. Magn., 39 (2003), 2645-264;
[29] J. Barbosa, B. G. Almeida, J. A. Mendes, A. G. Rolo, J. P. Araújo, J. B. Sousa, J. Appl. Phys., 101 (2007), 09M101;
[30] M. Atif, M. Nadeem, R. Grössinger, R. Sato Turtelli, J. Alloy. Compd., 509 (2011), 5720–5724;
[31] V. L. Mathe, A. D. Sheikh, Physica B, 405 (2010), 3594–3598;
[32] G. Dascalu, I. Mihaila, O. F. Caltun, G. Popa, Journal of Advanced Research in Physics, 1 (2010), 011002;
[33] G. Dascalu, O. F. Caltun, J. Optoel. Adv. Mat., 13 (2011), 1145–1148;
[34] G. Dascalu, O. Pompilian, B. Chazallon, V. Nica, O. F. Caltun, S. Gurlui, C. Focsa, in press in Appl. Phys. A;
[35] G. Dascalu, G. Pompilian, B. Chazallon, O. F. Caltun, S. Gurlui, C. Focsa, „Femtosecond pulsed laser deposition of cobalt ferrite thin films", submitted in Appl. Surf. Sci.;