Appl Phys A (2013) 110:949–955
DOI 10.1007/s00339-012-7218-6

Applied Physics A
Materials Science & Processing

Influence of the ion energy on the structure of Bi and Fe_2O_3 thin films

Dagoberto Cardona · Enrique Camps · L. Escobar-Alarcón · Sandra E. Rodil

Received: 27 May 2011 / Published online: 18 September 2012

Abstract Compounds containing bismuth, iron and oxygen (BFO) can result in materials with important magnetic and electrical properties for high-technology applications. We plan to prepare such compounds using the simultaneous ablation of bismuth and iron oxide targets. For that reason in the first part of this work we study the plasmas and the materials produced by ablation of bismuth or Fe_2O_3 targets, and then the two plasmas are combined in order to deposit the BFO compounds. The individual plasmas were characterized using a Langmuir probe, in order to measure the mean kinetic ion energy (E_p) and plasma density (N_p). Bismuth and magnetite-Fe_3O_4 thin films were obtained in high vacuum (2.7×10^{-4} Pa). Meanwhile for the deposition of α-Fe_2O_3 (hematite) or amorphous bismuth oxide thin films a reactive atmosphere ($Ar/O_2 = 80/20$) was used. All depositions were made at room temperature. The bismuth thin films crystallized in the rhombohedral metallic system with preferential orientations that depended on the Bi-ion energy used. Bismuth oxide phases were only obtained after annealing of the Bi thin films at different temperatures. Iron oxide thin films reproducing the target stoichiometry were obtained at a certain value of iron-ion energy. Preliminary structural results of the BFO thin films obtained by the combination of the individual plasmas are presented.

D. Cardona · E. Camps (✉) · L. Escobar-Alarcón
Departamento de Física, ININ, Apdo. Postal 18-1027, México DF 11801, México
e-mail: enrique.camps@inin.gob.mx

D. Cardona
e-mail: dagobe@gmail.com

L. Escobar-Alarcón
e-mail: luis.escobar@inin.gob.mx

D. Cardona · S.E. Rodil
Instituto de Investigaciones en Materiales, UNAM, circuito exterior s/n, CU, México DF 04510, México

S.E. Rodil
e-mail: ser42@iim.unam.mx

1 Introduction

Bismuth ferric oxide (BFO) has five different crystalline phases, which exhibit interesting multiferroic, magneto-optical and opto-electronic properties, making them very attractive for various technological applications [1–3]. The bismuth ferrite ($BiFeO_3$) phase has been specially considered for magneto-electric applications [4], which has drawn large attention in recent years becoming a very important material. The bismuth iron garnet ($Bi_3Fe_5O_{12}$) phase has important applications in the construction of magneto-optical telecommunication devices and lasers [2]. On the other hand, the $Bi_2Fe_4O_9$ and $Bi_{46}Fe_2O_{72}$ phases are thermodynamically stable, and are usually considered as undesired impurities incorporated into the pure $BiFeO_3$ or $Bi_3Fe_5O_{12}$ phases [5, 6]. The synthesis of these two phases is complicated, but in different published works [4, 7] pulsed laser deposition (PLD) has proved to be one of the most appropriate techniques for the deposition of good-quality films obtained from sintered targets having the appropriate stoichiometry, either $BiFeO_3$ or $Bi_3Fe_5O_{12}$. Nevertheless, the synthesis of such stoichiometric targets is expensive and difficult [6]. An alternative to overcome this problem is the simultaneous ablation of two targets in a reactive atmosphere containing oxygen, using a technique we named as reactive crossed beam pulsed laser deposition (RCBPLD). In this technique the variation of the plasma parameters, produced by the ablation of one of the targets, allows changing the composition of the thin films in a controlled manner. This technique has been evaluated with other types of ternary compounds and has been reported elsewhere [8]. The main aim of the present work is the study of the individual plasmas of bismuth and iron oxide created by laser ablation and their influence on the deposited thin films. Moreover, the data that can be obtained are important in order to determine the most suitable experimental conditions for the formation of the bismuth iron oxide (BFO) using RCBPLD.

2 Experimental details

2.1 Thin-film preparation

For the deposition of the bismuth (Bi) and iron oxide (FO) thin films discussed in this paper, a standard laser ablation system (Nd:YAG pulsed laser having emission at the second harmonic with $\lambda = 532$ nm and 5 ns pulse duration) was used. Bi films were deposited without any gas at a vacuum pressure of $P = 2.7 \times 10^{-4}$ Pa. On the other hand, for the FO films, deposition at both vacuum and a reactive atmosphere was carried out. For the latter, the vacuum chamber was backfilled with an Ar/O_2 (80/20) mixture up to the working pressure fixed at 1.33 Pa. In this case (individual plasmas of Bi or Fe_2O_3) the distance between the substrate and the target was varied from 5 to 8 cm.

In order to deposit BFO thin films, the Bi and Fe_2O_3 targets were placed perpendicularly to each other inside the vacuum chamber and were ablated simultaneously. The laser beam was divided into two beams of approximately the same intensity, and each beam was directed towards one of the targets. The ablation process took place in similar conditions as for the FO films (1.33 Pa and Ar/O_2 80/20). The substrates were placed in the zone where the expanding plasmas cross each other. However, two substrate orientations were tested: lateral and frontal. Lateral experiments correspond to the substrates facing the iron oxide target and frontal when the substrates were placed in front of the bismuth target. In all cases, the films were deposited at room temperature onto pieces of Si (1 1 1) and glass substrates of about 3.0 and 4.0 cm^2 respectively and placed at 5 cm from the target.

Samples of Bi, FO or BFO were deposited at different laser fluencies that varied between 2 and 20 J/cm^2 and the plasma parameters for each fluence and target were determined to study their effect on the film properties. In the case of the BFO films, the laser fluence used for ablation of the FO target was kept constant while the fluence on the Bi target was varied.

2.2 Plasma diagnostic

In order to study the influence of the plasma parameters (mean kinetic ion energy (E_p) and plasma density (N_p)), a Langmuir planar probe (a stainless steel disk 6 mm diameter, 2 mm thick) was placed at the substrate position. In all the experiments the probe was biased at −40 V, where the ion current is saturated, monitoring the current from the voltage drop across a 15 Ω resistor. From these measurements, the time of flight (TOF) curves could be obtained and, from these curves, the mean kinetic ion energy and the plasma density were calculated. These calculations were obtained from the standard procedure proposed by Bulgakova et al. [9].

Ablation of the bismuth target in vacuum or at 1.33 Pa of the gas mixture was performed using experimental conditions that allowed variations of the laser fluence from 3 up to 15 J/cm^2 (which implied a variation of the laser output energy from 22 up to 90 mJ), which leads to Bi E_p values in the 40 and 430 eV range and Bi N_p from 8×10^{11} to 3×10^{14} cm^{-3}. These values were obtained from the TOF curves shown in Figs. 1(a) and (c). In this figure there are displayed the TOF curves for some of the regimes used for depositions of the Bi and Bi_2O_3 thin films. For the case of the ablation of the Fe_2O_3 target in vacuum or at 1.33 Pa of the gas mixture, there were used experimental conditions that allowed variations of the laser fluence from 2 up to 20 J/cm^2 (which implied a variation of the laser output energy from 23 up to 90 mJ); the plasma parameters varied between 70 and 200 eV of Fe E_p and 6×10^{12} and 1×10^{14} cm^{-3} for the plasma density. The mean kinetic ion energy and plasma density were calculated from the TOF curves. Figures 1(b) and (d) show the TOF curves for some of the regimes used for deposition of these films. All these experiments and the results shown in Fig. 1 correspond to a standard laser ablation with only one target, placed in front of the substrates at different distances depending on the experiment. For this reason there is no direct correlation between the applied fluence and the variation of the plasma parameters. The experimental conditions were varied so that a sequence of the plasma parameters could be obtained, as is shown in Fig. 1. A straightforward correlation between plasma parameters and fluence can be observed in the experiments shown in Fig. 1(d), where all the experimental conditions were kept constant and only the fluence was varied. In this case a reduction of the fluence yields lower values of ion energy and plasma density.

The values of the mean kinetic ion energy and plasma density have a standard deviation of about 10 %, which is obtained when the TOF curves are averaged.

2.3 Thin-film characterization

X-ray diffraction (XR D) and Raman spectroscopy were used to study the microstructure of the films. For Raman measurements a Nd:YAG laser beam (532 nm) was focused by a 50× microscope objective onto a ≈1 μm diameter spot on the sample surface. The laser power at the sample was regulated by a neutral density filter (OD = 1) to prevent

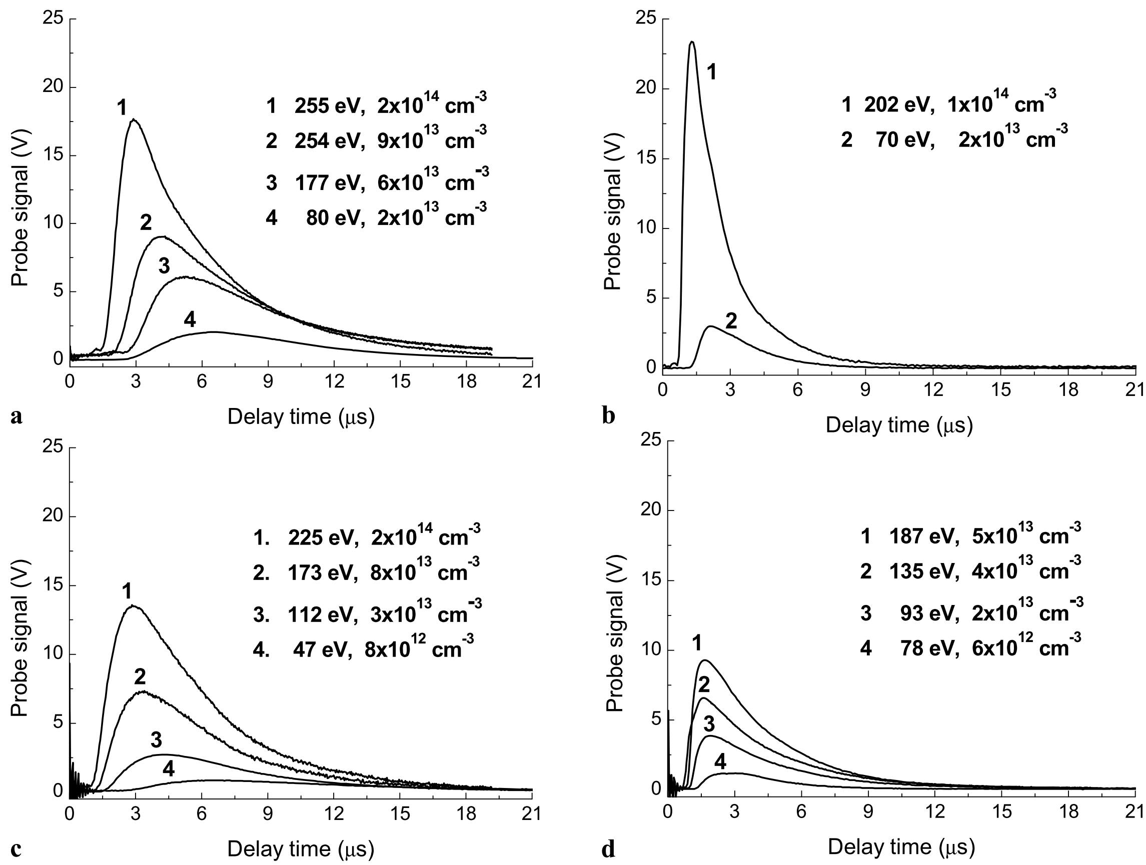

Fig. 1 TOF curves for thin-film deposition of: (**a**) bismuth at base pressure, (**b**) Fe_3O_4 at base pressure, (**c**) bismuth oxide at 1.33 Pa (Ar/O_2, 80/20), (**d**) Fe_2O_3 at 1.33 Pa (Ar/O_2, 80/20). The calculated values of the mean kinetic ion energy and the plasma density are indicated in each of the figures

sample heating and structural changes in the sample. The composition of the films was determined by energy dispersive spectroscopy (EDS).

3 Results

3.1 Bismuth thin films

In this section, the results for the Bi thin films obtained at base pressure as a function of the ion kinetic energy are presented. Films were deposited by changing the mean kinetic Bi-ion energy (Bi E_p), which was done by changing the laser fluence from 3 up to 15 J/cm^2. For each of the experiments Langmuir probe data were collected before deposition, so that it was possible to determine the Bi E_p used during deposition. Figure 2 shows X-ray diffraction data of some of the thin films deposited at different Bi E_p. From this figure it can be concluded that the preferential orientation of the films can be modified when the Bi E_p is varied. In this case, deposits made with Bi E_p lower than 228 eV produced rhombohedral Bi films with preferential growth in the direction Bi (0 0 3). As E_p increases, the intensity of the peak corresponding to the plane Bi (0 1 2) increases, too, as seen in the XRD patterns for the deposit at 291 eV (Fig. 2). For those deposits performed at 350 eV the most intense peak is the Bi (0 1 2).

3.2 Fe_3O_4 thin films

Ablation of a hematite (α-Fe_2O_3) target at base pressure led to the formation of magnetite-Fe_3O_4 thin films. Ablation was carried out using laser fluencies between 3 and 6 J/cm^2, or in terms of the ion energy (Fe in this case) between 70 and 200 eV. XRD data analysis showed that the films deposited under these conditions diffracted only the peaks corresponding to the planes (3 2 0) and (4 0 0), and no clear dependence on the ion energy was detected. Raman spectroscopy was used to confirm the XRD results and it was found that the films are homogeneous. It is clear that the magnetite-Fe_3O_4 phase has lower oxygen content than hematite Fe_2O_3. The oxygen deficit is evident due to the fact that these experiments were made at base pressure. As will be shown below, the oxygen pressure in the chamber is a very important factor for obtaining either of these two phases mentioned

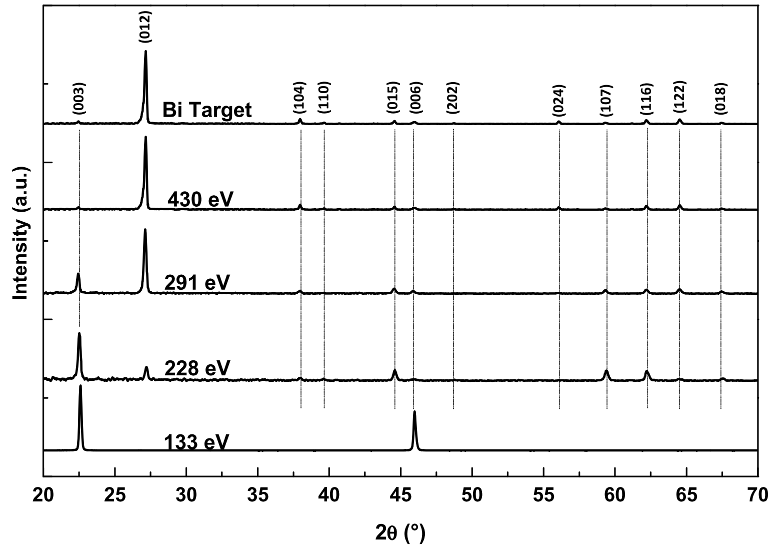

Fig. 2 XRD patterns of Bi thin films deposited at different Bi E_p

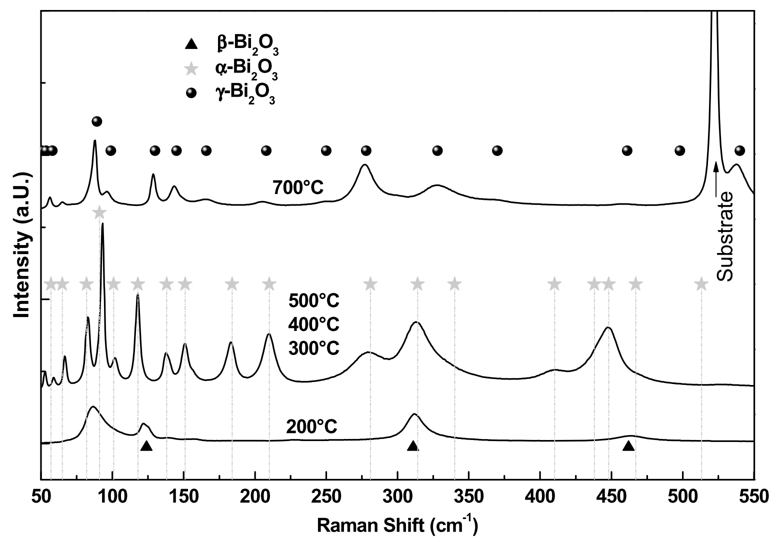

Fig. 3 Raman spectra of Bi thin films annealed at different temperatures

above. This fact has been observed by other authors as well [10, 11].

3.3 Bismuth oxide thin films

Attempts to deposit crystalline bismuth oxide thin films at room temperature with a reactive atmosphere (80/20 Ar/O_2) inside the reaction chamber failed; the produced material was always amorphous, no matter what experimental conditions were used. There are different works in which there is reported the deposition of Bi_2O_3 in different phases; nevertheless, in those cases it was necessary to heat the sample or to use a sintered target with the appropriate stoichiometry previously formed [12, 13]. So, in order to obtain bismuth oxide thin films we used the bismuth thin films deposited as explained in Sect. 3.1 and made an annealing of those samples in air at different temperatures for two hours. The treatments were performed at 100, 200, 300, ..., 700 °C. Figure 3 shows the Raman spectra of Bi_2O_3 films obtained after annealing under different temperatures. The β and γ phases were obtained at temperatures of 200 and 700 °C, respectively, while α phase was observed for the annealed samples at 300, 400 and 500 °C.

3.4 α-Fe_2O_3 thin films

Hematite (α-Fe_2O_3) thin films were obtained by ablation of a hematite target in a reactive atmosphere containing oxygen (Ar/O_2 (80/20) at 1.33 Pa), in order to compensate for oxygen losses. Experiments were carried out at fluencies between 5 and 20 J/cm^2, so that the mean kinetic ion energy (E_p) of the most abundant species (Fe in this case) in the plasma took values between 80 and 190 eV. Deposition of films was done at room temperature. The XRD data revealed that as for the case of Bi thin films, the α-Fe_2O_3 thin

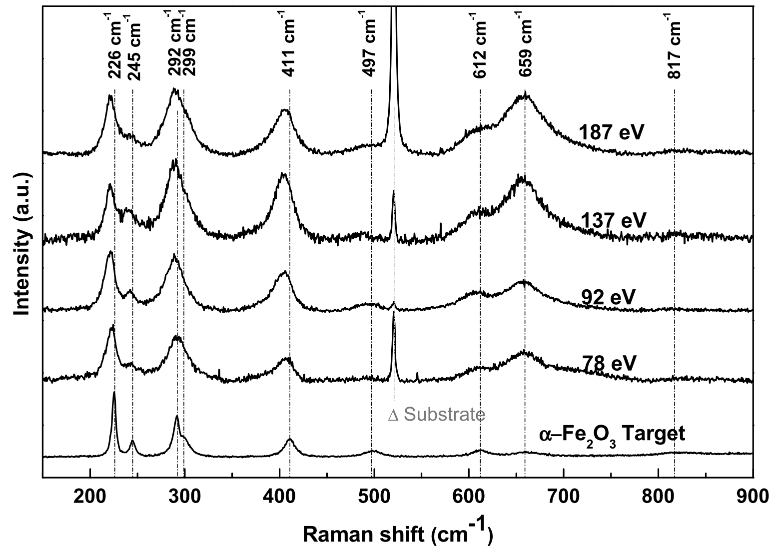

Fig. 4 Raman spectra of Fe_2O_3 thin films deposited at different Fe E_p

films crystallized in the rhombohedral system with preferential orientations that depended on the mean kinetic ion energy used. Ion energies lower than 92 eV tended to form films with (1 1 0) orientation and high energies greater than 137 eV formed films with (1 0 4) preferential orientation. Figure 4 shows the Raman spectra of the deposited α-Fe_2O_3 thin films (similar to those obtained in [10]) as a function of the average kinetic energy of the ions used for deposition. From this figure it can be seen that the deposit made with E_p equal to 92 eV has the most similar Raman spectrum to that of the target.

3.5 Plasma combination

Information obtained in previous deposits was used to combine bismuth and iron oxide plasmas using the RCBPLD arrangement (see Sect. 2.1). In this experiment the laser fluence on the FO target was kept constant, whether for the lateral or for the frontal deposition. The fluence on the Bi target was varied so that the properties of the deposited material were reported as a function of the Bi plasma parameters (E_p or N_p). A set of experiments was carried out in the lateral arrangement, varying the fluence from 4 to 34 J/cm^2, which meant that the Bi E_p could be varied between 40 and 150 eV and the plasma density between 8×10^{11} and 3×10^{12} cm^{-3}. In this case, small quantities of Bi could be incorporated in the films. EDS measurements showed that the Bi content in the films increased when both the ion energy and the plasma density were increased and varied from 2 up to 5 at%.

Another set of experiments was carried out in the frontal arrangement. In this case, the laser fluence on the Bi target was varied from 1 to 15 J/cm^2. With these values of fluence the measured plasma parameters were in the ranges: from 50 to 210 eV for the Bi E_p and from 6×10^{12} to 7.2×10^{13} cm^{-3} for the Bi N_p. It can be seen that using lower fluencies, it is possible to get higher values of plasma density than in the lateral arrangement. In this case, the Bi content in the films also increased with both the energy and the density of the plasma, varying from 13 to 21 at%. It is also worth noting that in all cases the atomic oxygen concentration remained very close to the 60 at% value and only the bismuth and iron contents varied. This is a typical situation for the different BFO compounds (e.g. $BiFeO_3$, $Bi_3Fe_5O_{12}$, $Bi_2Fe_4O_9$, $Bi_4Fe_2O_9$) where the oxygen content remains at a value of 60 at%.

According to Raman spectroscopy and X-ray data, all films deposited either for the frontal or the lateral configuration turned out to be amorphous. It is worth noting that all samples were deposited at room temperature, and the maximum Bi-ion energy used in these experiments was 210 eV. Under these experimental conditions it is not possible to get a crystalline deposit; the ions need more mobility on the substrate surface, which could be achieved through an increase of the energy or by heating the sample. In the first case, an increase of the ion energy is possible but this will lead to an experiment which is difficult to control, as the damage on the Bi target will be very high and the plasma parameters will be changing all the time. On the other hand, there are many reports (see for instance [5, 14]) where the substrate is heated to very high temperatures in order to obtain crystalline films. The use of high temperatures is due to the fact that they usually use very low fluencies, which means very low ion energies. We plan for future work to heat the substrate, combining this with moderately high ion energies, and with this we expect to get crystalline deposits.

Therefore, each of the deposited samples was annealed at 600 °C in air for two hours and slowly cooled to room temperature. The annealed films deposited laterally, i.e. films with a low bismuth content, continued to be amorphous. However, films with a higher content of bismuth (those de-

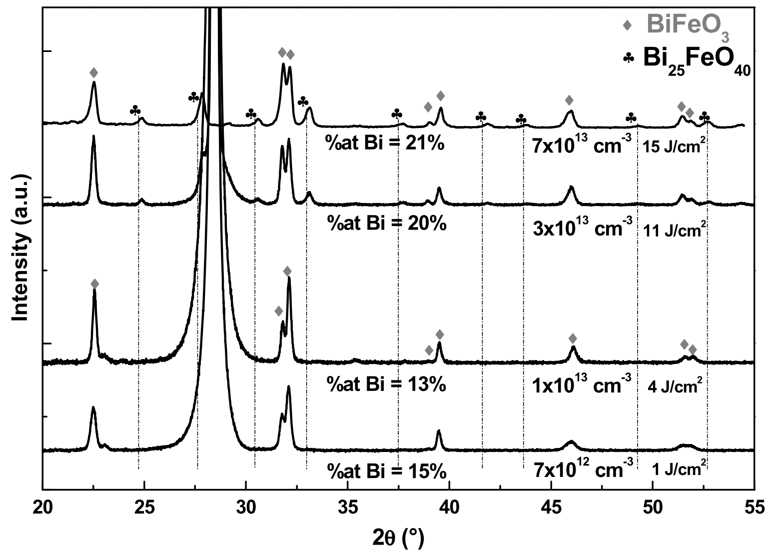

Fig. 5 XRD patterns of annealed Bi iron oxide thin films with their respective plasma density and fluence values

posited in frontal configuration) crystallized in a rhombohedral perovskite structure, which is typical of $BiFeO_3$ phase, independently of the initial Bi content.

Figure 5 shows the XRD diffraction patterns of the thin films deposited in the frontal arrangement after annealing. The obtained diffraction patterns compare well with those reported for the case of $BiFeO_3$ obtained from ablation of a sintered target [4, 15]. Those films with Bi content between 20 and 21 at% were deposited with fluencies of 11 and 15 J/cm^2 respectively and they exhibit reflections corresponding to the $BiFeO_3$ and $Bi_{25}FeO_{40}$ phases. Films with 13 and 15 at% Bi content were deposited using fluencies of 1 and 4 J/cm^2, and in this case reflections corresponding only to the $BiFeO_3$ phase were observed. The mixture of phases observed in samples deposited at higher fluencies is attributed to the presence of droplets (splashing) on the film surface. This splashing is reduced when the fluencies are reduced and only one phase is detected. This fact was confirmed using micro-Raman spectroscopy measuring in the area of the film and on the drops of splashing. The film area has a spectrum corresponding to the $BiFeO_3$ phase, while on the bigger drops the other phase is detected. The Raman spectra obtained from samples prepared in this work have the same shape as those reported for samples obtained from ablation of a sintered target [16].

4 Conclusions

The role played by the plasma parameters in the structural and compositional properties of deposited materials has been shown. Crystalline Bi thin films with different preferential orientations were obtained using different plasma ion energies. The structure and composition of the iron oxide films was varied using plasmas with different ion energies and densities. The composition of bismuth iron oxide thin films was changed using Bi plasmas with different densities; the higher the Bi plasma density, the higher the Bi content in the thin films. There exists a minimum value of Bi content in the films, in order to obtain the crystalline phase, via a post-deposition annealing. The ion energy can play an important role in defining the structure of the films; however, in our case, deposition at room temperature requires much higher energies, which makes the experiment quite difficult. The quality of the films was evaluated only by means of structural and compositional characterization, obtaining results comparable to those previously reported. Magneto-electrical properties of this material are currently being evaluated and will be the subject of a future publication. The RCBPLD configuration eliminates the need for targets with different compositions in order to deposit this type of material with different compositions. The Langmuir probe measurements are useful to control the experiments and give additional information that can be helpful to explain some of the results.

Acknowledgements This work was partially supported by the projects EC263878 and CONACYT 125141 through the BisNano project.

References

1. G.A. Smolenskii, I. Chupis, Sov. Phys. Usp. **25**, 475 (1982)
2. P. Hansen, K. Witter, W. Tolksdorf, Phys. Rev. B **27**, 11 (1983)
3. Ch. Binek, B. Doudin, J. Phys. Condens. Matter **17**, 39 (2005)
4. V.R. Palkar, J. John, R. Pinto, Appl. Phys. Lett. **80**, 9 (2002)
5. S. Fujino, M. Murakami, S.-H. Lim, M. Wuttig, L.G. Salamanca-Riba, I. Takeuchi, Solid State Ion. **178**, 1257 (2007)
6. T.P. Gujar, V.R. Shinde, S.S. Kulkarni, H.M. Pathan, C.D. Lokhande, Appl. Surf. Sci. **252**, 3585 (2006)
7. R. Lux, A. Heinrich, S. Leitenmeier, T. Körner, M. Herbort, B. Stritzker, J. Appl. Phys. **100**, 113511 (2006)

8. L. Escobar-Alarcón, E. Camps, S. Romero, S. Muhl, I. Camps, E. Haro-Poniatowski, Appl. Phys. A **101**, 771 (2010)
9. N.M. Bulgakova, A.V. Bulgakov, O.F. Bobrenok, Phys. Rev. E **62**, 5624 (2000)
10. J. Cao, T. Kako, N. Kikugawa, J. Ye, J. Phys. D, Appl. Phys. **43**, 325101 (2010)
11. M. Lübbe, A.M. Gigler, R.W. Stark, W. Moritz, Surf. Sci. **604**, 679 (2010)
12. B.L. Zhu, X.Z. Zhao, Opt. Mater. **29**, 192 (2006)
13. L. Leontie, M. Caraman, A. Visinoiu, G.I. Rusu, Thin Solid Films **473**, 230 (2005)
14. S. Kahl, A.M. Grishin, S.I. Khartsev, K. Kawano, J.S. Abell, IEEE Trans. Magn. **3**(1), 2457 (2001)
15. A. Lahmar, K. Zhao, S. Habouti, M. Dietze, C.-H. Solterbeck, M. Es-Souni, Solid State Ion. **202**, 1 (2011)
16. H. Béa, M. Bibes, S. Petit, J. Kreisel, A. Barthélémy, Philos. Mag. Lett. **87**(3–4), 165 (2007)