LASER INDUCED CRYSTALLIZATION IN SPUTTERED FeSiB THIN FILMS

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Filme subțiri cu compoziția nominală $Fe_{78}Si_9B_{13}$, produse prin pulverizare în radio-frecvență pe substrat de Si cu orientarea (100) au fost iradiate cu un laser cu excimeri la o fluență de 130mJ/cm^2. Informațiile asupra modificărilor structurale induse au fost obținute prin difracția de raze X şi microscopia electronică de baleiaj, iar curbele de magnetizare au fost determinate prin experimentul de efect Kerr magneto-optic. S-a evidentiat ca efectele iradierii asupra filmelor subtiri sunt formarea de graunti cristalini, generarea de zone topite si inghetate ultrarapid, oxidarea suprafetei si schimbari in proprietatile magnetice ale filmului subtire.

Thin films with nominal composition $Fe_{78}Si_9B_{13}$ generated by radio-frequency (rf) sputtering on Si substrates with (100) orientation were irradiated with an excimer laser with 130mJ/cm^2 fluence. Information on the induced structural changes were obtained by X-ray diffraction and scanning electron microscopy, while the magnetization curves were determined by the magneto-optical Kerr effect. The effects of the irradiation consist in the growing of crystallites,appearence of melted and ultra-fast frozen zones, surface oxidation and changes in the magnetic properties of the thin films.

Keywords: laser induced crystallyzation, thin films.

1. Introduction

Thin films based on Fe with both amorphous and nanocrystalline structure are frequently used in miniature devices as magneto-impedance and magneto-elastic sensors (e.g. [1]) . The properties of these materials are strongly dependent on their microscopic structure (crystallite dimensions) which is rather difficult to controle. However, by specific thermal treatments realized (classically) in programable temperature ovens or by laser irradiation, good results can be obtained [1,2,3,4,5] .

In this paper we present microscopic effects of excimer laser irradiation of thin films with nominal composition $Fe_{78}Si_9B_{13}$ generated by rf sputtering on Si

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substrates with (100) orientation and compare with results of classical Joule treatment on identical films.

Thermal laser treatment of ferromagnetic alloys can induce the following effects: crystallization [1,4,5,6,7,8], changes in the magnetic anisotropy, sometimes without induced crystallization [9,10], generation of melted zones followed by "freezing" due to quick cooling [9,10,11] and surface oxidation [1,4,9,10,11].

Pulsed excimer lasers have been frequently used for semiconductor irradiation, however they can be also used in the processing of amorphous alloys due to the uniform energy distribution across the laser spot, high pulse energy and high repetition rates.

2. Experimental procedure

For generation of thin films by rf sputtering commercially available Fe_3B targets are used. Carefully selected Si pieces are placed on these targets and the sputtering is carried out for 90 minutes at 150W in a protective argon atmosphere ($5.33 \cdot 10^{-2}$ mbarr). Previously, the enclosure was evacuated to a pressure of $6.6 \cdot 10^{-6}$ mbarr. The resulted films have square shape with an area of 1x1cm^2. The laser radiation has the wavelength 308nm characteristic to the excimer generated in a He, Xe, HCl mixture. The laser puls characteristics are: 130mJ energy, 9ns duration and 5Hz frequency; the fluence of 130mJ/cm^2 was obtained by focusing the laser beam in a spot of 1x1cm^2 area using two cylindrical lenses.

For comparison, similar samples were treated in an oven at 500^{o}C for 15 minutes and for 2 hours.

The thickness of the films is determined by Atomic Force Microscopy (AFM).

The structure analysis is performed by X-ray Diffraction (XRD) using a Seifert diffractometer and a Bruker diffractometer both in the Bragg-Brentano geometry with the Cu characteristic radiation $K\alpha_1 = 1.540562\,\overset{0}{\mathrm{A}}$.

The laser generation of crystalline precipitates is detected by XRD and by Scanning Electron Microscopy (SEM). The presence of chemical elements in various zones of the film is revealed by Energy Dispersive X-ray Analysis (EDX). The magnetization curves were obtained by the experiment on the Magneto-Optical Kerr Effect (MOKE).

3. Results and Discussions

The measurement of the thickness of the sputtered films as performed by AFM is presented in Fig.1. As observed the films are about 300nm thick.

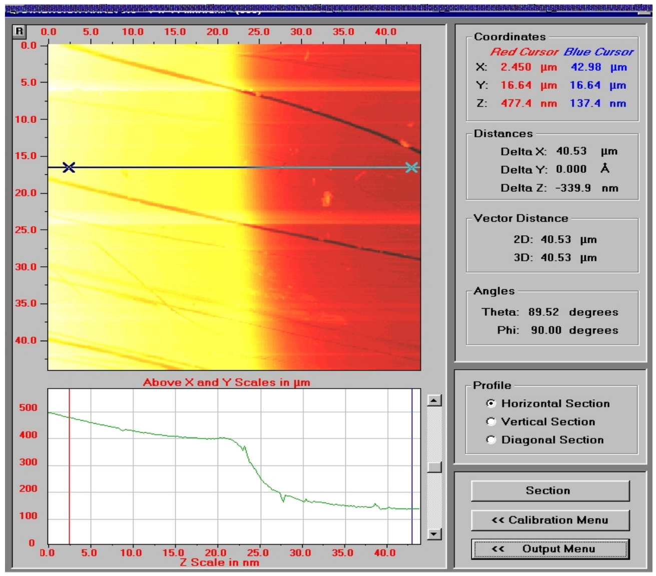

Fig.1. Measurement of the film thickness by AFM

The XRD diffractograms of films submitted to various treatments are presented in Fig.2. The curves corresponding different situations are displaced along the vertical such that the numbers on the intensity axis exactly characterize the bottom curve only. This curve corresponds to the as sputtered films and reveals that these are in an amorphous state.

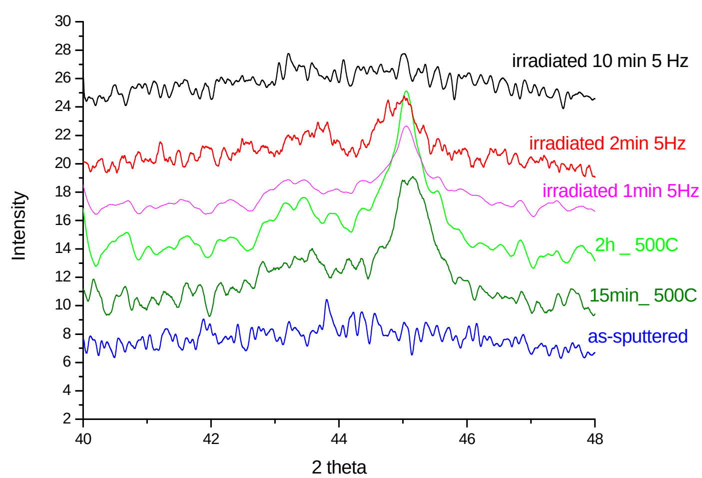

Fig.2. Diffractograms of samples (in the upwards order): as sputtered, thermally treated in the oven for 15 min and 2h or treated by laser radiation for 1min, 2min and 10min at the same frequency, 5Hz and the same fluency, 130mJ/cm^2.

The following two diffractograms, in the upwards direction correspond to samples classically treated in an oven at 500^{o}C for 15 minutes and for 2 hours respectively. The following three diffractograms show the effect of various laser irradiation regimes. We notice two completely different effects. The response corresponding to the crystallized phase increases with the time of thermal treatment in the oven (during the considered interval). Unlike this, in the case of laser irradiation, crystallization is induced for a reduced number of pulses (about 300) while for longer irradiation the crystallized phase diminishes, and for about 3000 pulses the film becomes amorphous again. As shown by the pictures obtained by SEM presented in Fig.3, this behavior is caused by the melting of crystallites formed during the early stages of irradiation (as observed from Fig.3d).

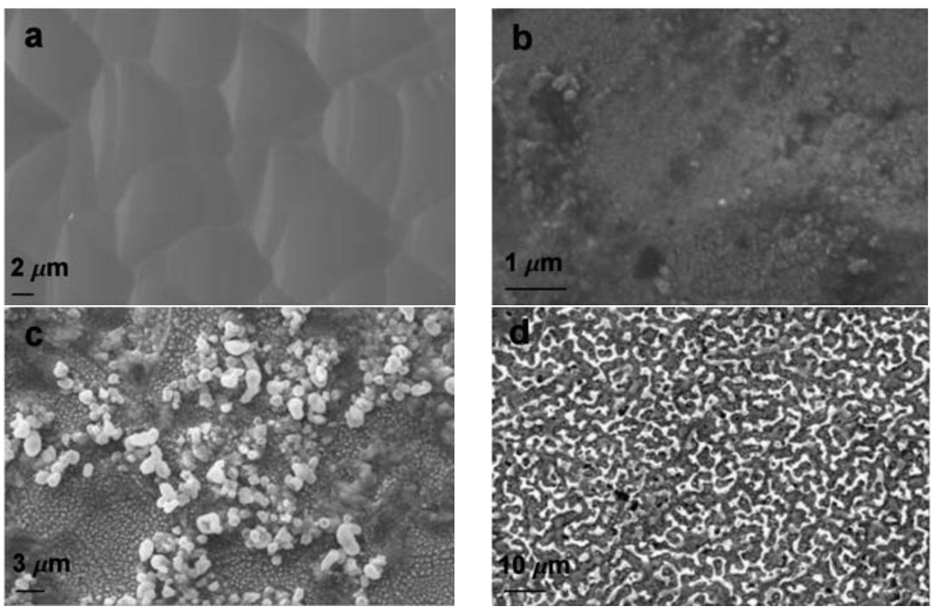

Fig.3 SEM pictures for four samples: as sputtered – a), treated in the oven 15 min at 500^{0}C – b), laser irradiated for 2 min at 5Hz – c) and laser irradiated for 10 min at 5Hz – d) the same fluency, 130mJ/cm^{2}.

Another interesting effect is observed on the SEM pictures. In the case of the sample irradiated for 2 minutes, the size of the formed crystallites is between 0.5 and 1 μm in the zone of full laser irradiation while, in the peripheral zone, where the irradiation is reduced, the size of crystallites is about 200nm. This shows that the fluency is also very important and, for generation of nanometric size crystallites as required in some of the applications, careful balance between fluence and irradiation time has to be observed.

The EDX analysis allows the determination of the stoichiometric composition of the materials. However, this technique is not sensitive enough for chemical elements with small atomic number, Z<11 and in cannot reveal the precise amount of boron and oxygen present in the FeSiB studied. This shortcoming can be circumvented by using the “mapping” procedure. In this type of analysis, a complete X-ray spectrum is computed for each pixel in the film image and the element to which this spectrum corresponds is presented in a conventionally chosen color attributed to that particular pixel. In the images shown on Figs. 4, 5, and 6 obtained by the EDX mapping for three different situations, the color code is mentioned in the corresponding caption. In Figs 5 and 6 the Si distribution is not shown because it is the same as in Fig.4.

Pictures in Figs.4, 5 and 6 reveal the presence of a large proportion of boron in laser treated samples, both before laser irradiation (43.01%) and after laser irradiation (52.05%). These figures are in agreement with usual X-ray diffraction analysis that indicates that laser irradiation causes the generation of a Fe_3B crystalline centered body tetragonal (b.c.t.) phase.

In this case, the energy required for the initiation of the body centered cubic (b.c.c.) crystallization phase of Fe (and Si) is much larger than the energy required for the nucleation and developing of the Fe_3B b.c.t. phase. This means that the local conditions are by far more favorable for the crystallization of the Fe_3B b.c.t. phase. This result was also observed in this type of materials under ribbon shape [12] and testify that at high boron concentrations the crystallization of the (b.c.c.) Fe (and Si) is inhibited while the formation and stability of the Fe_3B (b.c.t.) is favored.

The presence of oxygen can be noticed from the above images. The oxygen is present on the surface of the sample both before and after the laser irradiation; the thermal treated samples are also oxydated. This is explained by the oxydation of the samples due to their interaction with the atmosphere after preparation.

The method of generation of this type of thin films by rf sputtering seems not to be very convenient because although the required stoichiometry was carefully observed, the result is not the expected one. The inconvenient is related to the fact that the evaporation of various elements takes place at different temperatures; one component can be completely exhausted before the start of the evaporation of another one. Moreover, because of chemical reaction of the Si substrate with Fe due to local heating it is possible that the FeSi alloy to appear, which is detrimental for the experimental measurement of the composition of the film.

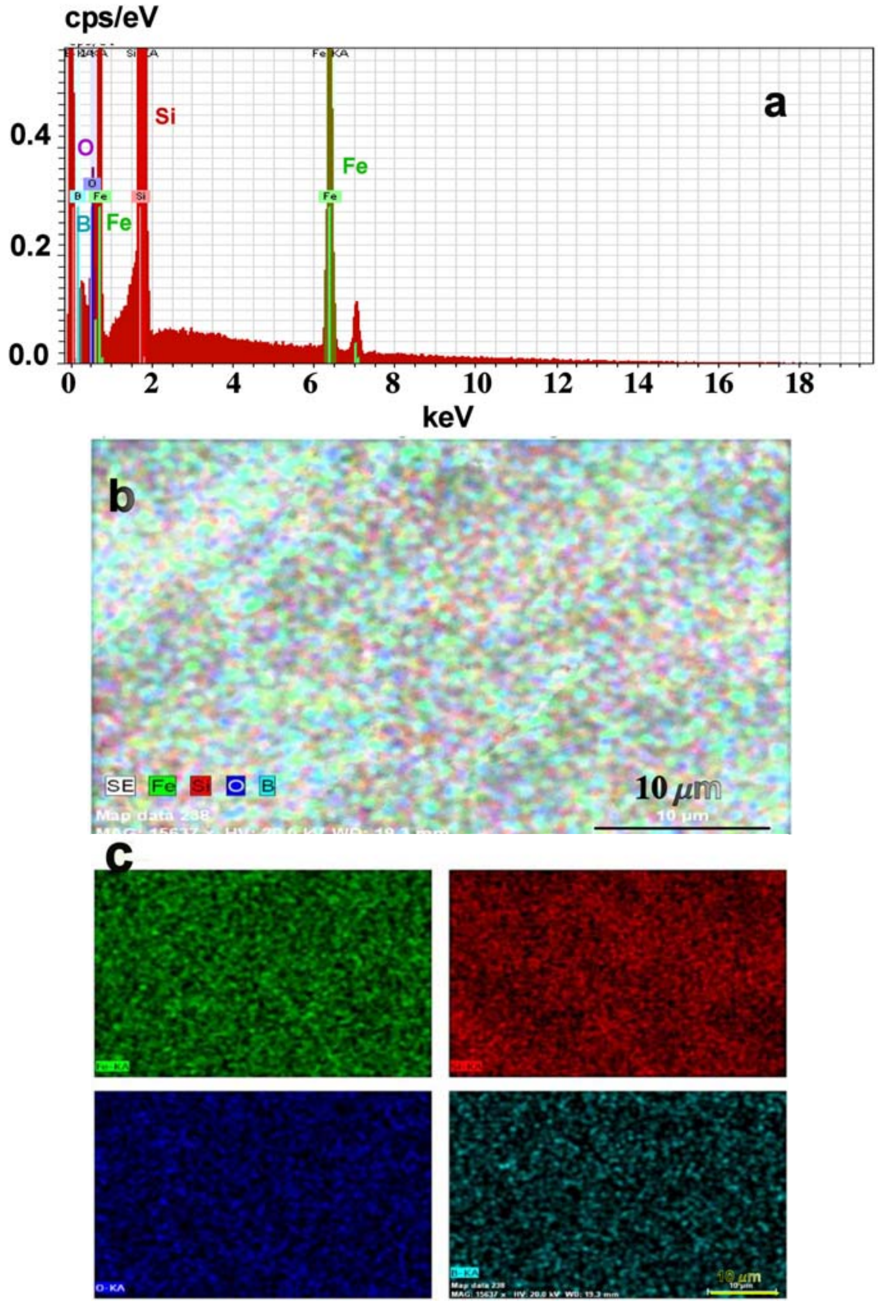

Fig.4 The as sputtered sample. On the top (a) is EDX spectrum. Middle(b): the EDX mapping for the sample. Bottom figure (c): EDX image obtained by the mapping procedure for the as sputtered sample; the color code is: Fe – green, Si – red, O – blue and B – turquoise.

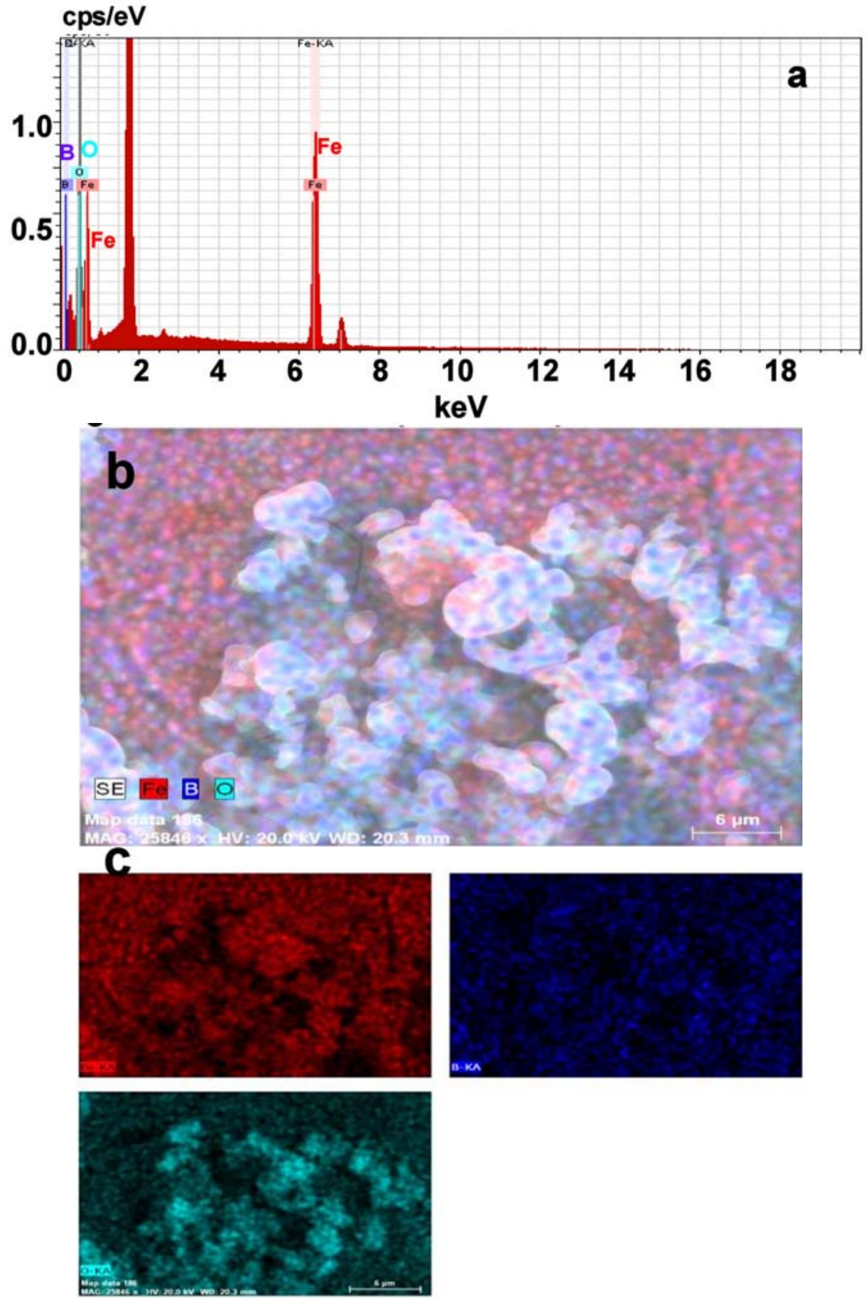

Fig.5: The (2 minutes, 5Hz, 130mJ/cm^2) laser irradiated sample. On the top (a) is EDX spectrum. Middle(b): the EDX mapping for the sample. Bottom figure (c): EDX image obtained by the mapping procedure; the color code is: Fe – red, O – turqoise and B – blue.

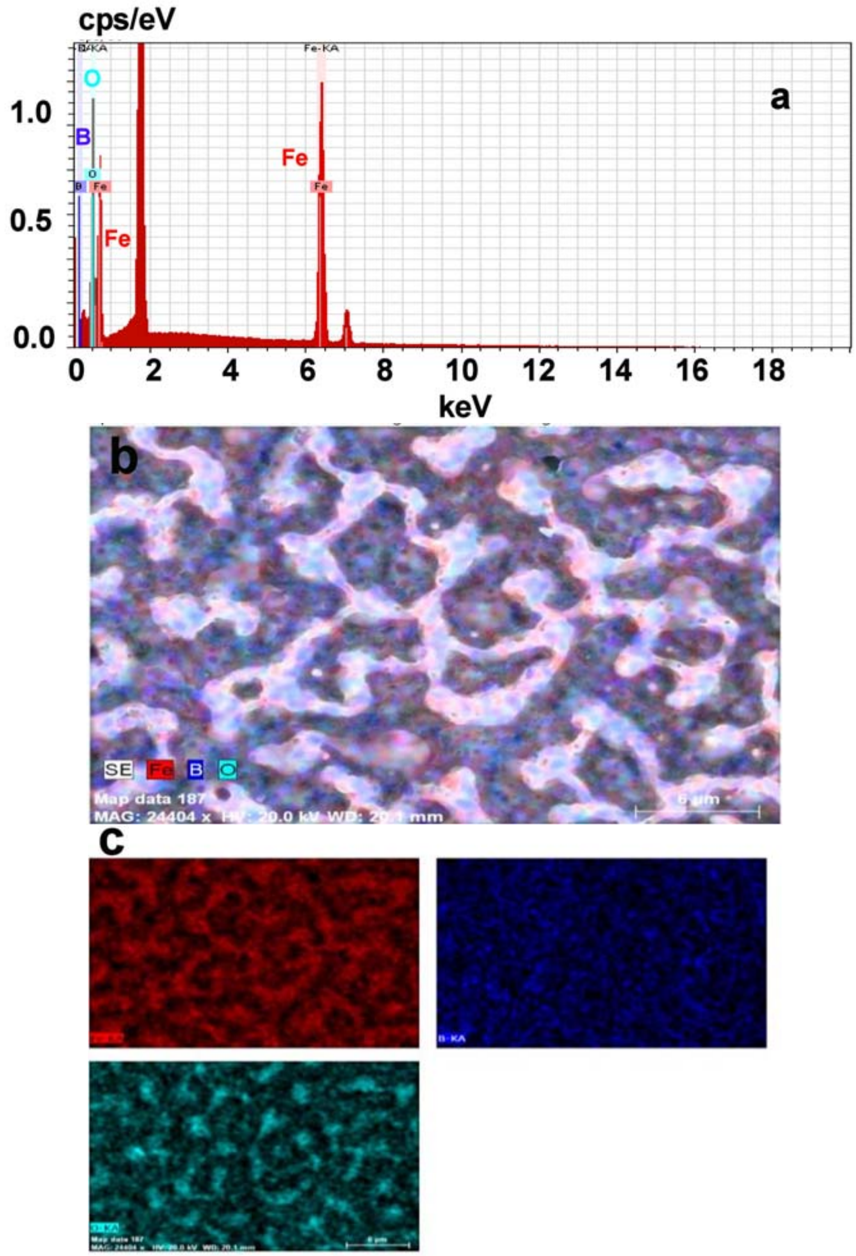

Fig.6: The (10 minutes, 5Hz, 130mJ/cm^2) laser irradiated sample. On the top (a) is EDX spectrum. Middle(b): the EDX mapping for the sample. Bottom figure (c): EDX image obtained by the mapping procedure; the color code is: Fe – red, O – turqoise and B – blue.

Many experimental studies on laser thermal treatments [6,7,8] are in agreement with our observation that the crystallization degree depends significantly on the energy of the laser pulses used for irradiation. This is a factor that demonstrates the degree of dependence of the effect on the temperature. It is extremely difficult to measure the temperature of thin films that are not in thermal equilibrium with the surroundings, as the in the case of pulsed laser thermal treatments. We tried to estimate the time dependence of the temperature by placing a small cromel-alumel thermocouple in contact with the film, immediately outside of the irradiated zone. While the response give some indication on the temperature change, showing it to be much faster than in the case of oven heating, the results are not conclusive enough to be presented in this paper.

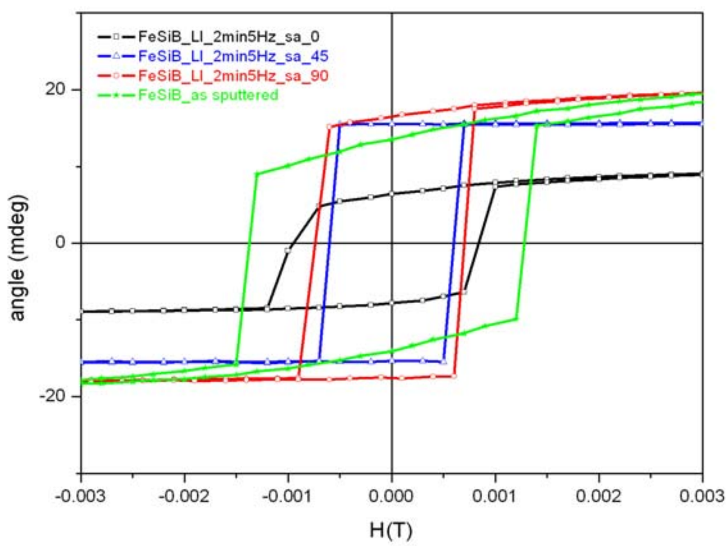

Fig.7 Hysteresis curves measured by the MOKE experiment

We also studied the change in the magnetic anisotropy induced by laser treatment [9, 10, 13]. The hysteresis curves obtained by the MOKE experiment show the presence of a planar anisotropy. This is observed by measurements performed in various directions by rotating the sample with 45 and 90 degrees. The changes in the magnetic properties with orientation are presented in Fig.7. The irradiated sample has smaller values of the saturation magnetization, the remanent magnetization and the coercive intensity than for the as sputtered sample (before laser irradiation). This can be explained by the presence of the generation of the crystalline Fe_3B phase (as demonstrated by the XRD and the

ESM) which has reduced magnetic properties. At present, we have no clear explanation for this planar anisotropy, is might be related to the polarization of the laser beam.

4. Conclusions

The effect of excimer-laser-induced crystallization in amorphous FeSiB sputtered thin films is reported. The laser-induced phase transformation consists of partial crystallization (precipitation of crystallites from the amorphous matrix) accompanied by some surface oxidation.

The fluency is also very important and, for generation of nanometric size crystallites as required in some of the applications, careful balance between fluence and irradiation time has to be observed.

Due to high boron concentrations the crystallization of the (b.c.c.) Fe (and Si) is inhibited while the formation and stability of the Fe_3B (b.c.t.) is favored.

The irradiated sample has smaller values of the saturation magnetization, the remanent magnetization and the coercive intensity than for the as sputtered sample (before laser irradiation).

The advantages of laser annealing consist in the heat up of the materials in a very short time and only the selected area of the material is annealed.

R E F E R E N C E S

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