Soft magnetic thin films: influence of annealing on magnetic properties

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Abstract. Soft magnetic materials are currently used in a variety of applications in electrical machines, sensors and elements of devices. If prepared in thin film form, they can be applied to micro- and nano-patterned devices. However, with respect to ribbons and bulk materials, thin films of the same composition usually display worse soft magnetic properties, thus requiring suitable solutions to restore high permeability and low coercivity. In this review, the magnetic properties of thin films prepared by sputtering are presented. Several compositions of soft magnetic materials are investigated, including Co-Fe-Si-B, Fe-Cu-Nb-Si-B, Fe-Si-B, Fe-Co-Nb-Si-P-B, Fe-Zr-Nb-Cu-B. Their amorphous-to-crystallization processes are studied by means of furnace annealing and Joule heating. Hysteresis loops and magnetic domain imaging, together with structural techniques, are used to follow the effects of annealing, which include stress relaxation and crystallization. The effects of magnetic field annealing are investigated and discussed.

1. Introduction
Soft magnetic materials have been widely studied in the last decades because of their interesting fundamental properties and their important applications in electrical machines, sensors and energy saving technologies [1,2]. The integration with the semiconductors industry and the progresses in the preparation of micro- and nano-devices are stimulating the research on soft magnetic thin films [3,4], which should be prepared with conventional sputtering techniques, coupled with other magnetic materials or non magnetic layers, properly annealed to improve their properties or to optimize interfaces, and ideally preserve the excellent soft magnetic properties of ribbons, microwires or bulks. Within this framework, this review paper discusses some recent results on soft magnetic thin films, prepared by sputtering in an amorphous condition, and subsequently annealed to induce (nano)crystallization and to tailor their properties. Results on selected compositions such as Co-Fe-Si-B, Fe-Cu-Nb-Si-B, Fe-Si-B, Fe-Co-Nb-Si-P-B, Fe-Zr-Nb-Cu-B will be analyzed.

2. Experimental techniques
Soft magnetic thin films can be prepared by means of sputtering on different substrates (e.g. glass, Si-O, Si$_3$N$_4$). Compositions close to those commonly used in amorphous ribbons can be obtained starting from targets made of the desired alloys. It is often possible to prepare these targets directly with amorphous ribbons prepared by planar flow casting. The resulting thin films are usually amorphous to X-ray diffraction, and preserve the same composition as the originating target (as detected e.g. with energy dispersive X-ray spectrography, EDS-EDX). The evolution of their microstructure (amorphous-to-crystalline transformation) can be studied by means of structural techniques (e.g. differential
scanning calorimetry, DSC, X-ray diffraction, XRD) and magnetic measurements (hysteresis loops, magnetization as a function of temperature) on samples which are submitted to thermal treatments. These include annealing in furnace (in vacuum, or in an inert gas), at temperatures at which diffusion of the atoms of the film in the substrate is negligible, or current annealing (Joule heating). Magnetic measurements are usually performed by means of high-sensitivity magnetometry (e.g. vibrating sample, VSM, or alternating gradient field, AGFM, magnetometry) or by optical means (magneto-optic Kerr effect, MOKE). Magnetic domain patterns can be studied by means of MOKE and magnetic force microscopy, MFM.

3. Results
The techniques usually employed for studying amorphous ribbons can be exploited also for thin films. In this case, however, several difficulties arise which need to be addressed. As an example, the amorphicity of a specimen can be investigated through DSC measurements, as reported in Figure 1 [5].

But since in a thin film very little material is available, the contribution of the substrate has to be taken into account. For this reason, it is sometimes preferable to deposit the film on a resist, which can then be chemically dissolved: in this way, small flakes of the film can be put in the DSC crucible, without the substrate. The film thickness has to be of a few hundreds of nanometers to have a reasonable signal, which can then be compared with that of the amorphous ribbon used as target. As evidenced in Figure 1, even when the composition of the film is close to that of the ribbon (as evidenced e.g. by EDX), DSC curves show different features: in thin films, the crystallization peaks are often broader and may occur at slightly different temperatures. Additionally, broad halos at lower temperatures often indicate relaxation, oxidation or early relaxation effects, which are not present in the ribbons.

A technique complementary to DSC and applicable to amorphous magnetic thin films consists in measuring their magnetization at constant field, as a function of temperature, for example by means of a VSM equipped with a furnace. Figure 2 shows an example [6], with a comparison to the corresponding DSC curve.

![Figure 1. Differential scanning calorimetry on a Co$_{67}$Fe$_{4}$Si$_{14.5}$B$_{14.5}$ thin film (blue curve) with a thickness of 360 nm, compared to that of an amorphous ribbon with the same composition (red curve).](image-url)
Figure 2. (a) Differential scanning calorimetry on a Fe$_{84}$Nb$_{3.5}$Zr$_{3.5}$B$_{8}$Cu$_{1}$ thin film, 400 nm thick. (b) Magnetization vs. temperature curve on a film with the same composition and a thickness of 100 nm. The measurement is done under an applied field equal to 1000 Oe.

$M$ vs. $T$ measurements are more sensitive than DSC in detecting the Curie temperature of the amorphous phase. The other features of the two curves are easily comparable: a very early crystallization process occurs slightly below 300 °C according to DSC, and indeed the increase of the magnetization, indicating the precipitation of a crystalline phase from the amorphous matrix, begins at comparable temperature values. Similarly, the onset of crystallization at 440 °C on the DSC curves corresponds precisely with the peak of the magnetization as a function of temperature. Additionally, $M$ vs. $T$ measurements allow the detection of the Curie temperatures of the crystalline precipitates, thus helping in their identification. In fact, in order to identify crystalline phases, XRD spectra are usually analyzed. However, on thin films the results are often hardly decisive, as the contribution of the substrate tends to be dominant, especially for samples thinner than a few hundreds of nanometers. In most cases, only the first diffraction peak can be detected, which can only be used to infer the presence of crystalline precipitates in annealed samples, as shown in Figure 3 [6] where the spectrum of an as-prepared sample is shown for comparison.
Figure 3. X-ray spectra of Fe$_8$Nb$_{3.5}$Zr$_{3.5}$B$_8$Cu$_1$ thin films, 80 nm thick, in the as-prepared state (red curve) and after annealing at 340 °C (blue curve).

Different from the usual practice with amorphous or crystalline magnetic ribbons, measuring hysteresis loops on thin films with an inductive technique is often very difficult, because of the very low amount of material and the fact that most of the cross section is attributed to the substrate. On the contrary, magnetometric techniques making use of a VSM or an AGFM are usually viable alternatives, especially because, given the very low thickness of the samples with respect to their lateral dimensions, demagnetizing coefficients are usually negligible when the field is applied in the sample plane. For very thin films, proper actions need to be applied to compensate the diamagnetic contribution of the sample holder and of the substrate. Figure 4 [5] shows the remarkable effects of annealing on a Co-based alloy in thin films form. The crystallization, induced by means of furnace annealing in vacuum at selected temperatures, causes a significant increase of the coercive field: after annealing at 600 °C, the soft magnetic properties are lost and a very hard loop is instead measured.

However, the opposite may also be true, e.g. with alloys that develop a nanocrystalline structure upon annealing. An example is shown in Figure 5: with respect to the as-prepared state, the annealed samples display a coercive field which is more than halved: this is the combined result of stress relaxation and nanocrystallization, which act to promote the soft magnetic properties of this alloy.

Figure 4. Hysteresis loops of Co$_{67}$Fe$_4$Si$_{14.5}$B$_{14.5}$ thin films, 30 nm thick, in the as-prepared condition (black curve), and after annealing in furnace at 550 °C (red curve) and 600 °C (blue curve).
Figure 5. Hysteresis loops of Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ thin films, 250 nm thick, in the as-prepared condition (black curve), and after annealing in furnace at 350 °C (red curve) and 500 °C (blue curve).

In any case, with respect to nanocrystalline ribbons of the same composition, thin films are usually characterized by worse soft magnetic properties, possibly due to the significant role played by the interface between the substrate and the film. The relaxation of quenched-in stresses by means of low temperature annealing is clearly evidenced in Figure 6 [7]: these amorphous thin films are characterized by a spin reorientation transition effect [8], which is responsible for the development of a perpendicular anisotropy when the sample thickness is within a certain range. The domain patterns detected by means of a MFM demonstrate that at low and high thickness values the component of the magnetization perpendicular to the film plane is negligible. On the contrary, at intermediate thickness values, a dense stripe domain structure develops, which has been demonstrated to be due to the presence of large stresses in the as-prepared materials. These stresses can be attributed to implantation effects during the sputtering process [9], and in materials with a positive magnetostriction constant result in the development of a perpendicular magnetic anisotropy.

Figure 6. (Left) MFM images of Fe$_{78}$Si$_9$B$_{13}$ thin films with thicknesses of 80, 150 and 1000 nm. (Right) For the sample 150 nm thick, hysteresis loops in the as-prepared condition and after annealing at selected temperatures.
This effect is quite common in amorphous magnetic thin films, and can also be observed in other crystalline soft materials such as Ni$_{80}$Fe$_{20}$ for specific thickness values [10]. In presence of this large perpendicular anisotropy, the hysteresis loops display a “transcritical” shape [11] (Figure 6). When submitted to low temperature annealing, which are not sufficient to induce crystallization, the samples are progressively relieved from the stresses, and the perpendicular anisotropy progressively reduces, eventually restoring the soft magnetic properties of the samples. The stress relaxation effects are also shown in Figure 7 [6] for a different composition: the coercive field slightly decreases with respect to the as-prepared state when low temperature annealing is performed.

At temperatures greater than the onset of crystallization, the coercive field suddenly increases, marking a significant change in the sample microstructure. Low temperature annealing can also be performed below the Curie temperature of the amorphous phase in presence of a conditioning magnetic field, which can be used to induce a uniaxial anisotropy in the sample. An example is shown in Figure 8 [5], where the presence of uniaxial anisotropy is clearly shown by the loop shapes along the easy and hard magnetization axes.
Although widely used in ribbons [12], current annealing (Joule heating) techniques have not yet been widespread adopted to tailor the soft magnetic properties of thin films. This kind of annealing is less straightforward in films than in ribbons, because of the difficulty in making electrical contacts and of the presence of the substrate, which strongly affects the dissipation of the heat generated by the Joule effect. Figure 9 shows early data on Joule heating on thin films. In Figure 9a the evolution of the electrical resistance variation as a function of time is reported for selected annealing current intensities. At low current values, a reduction of the resistance is observed, which can be ascribed to stress relaxation effects. At intermediate current values (5 and 7 mA), a subsequent slight increase of the resistance marks the first changes in the sample microstructure, which still need to be investigated. Higher current intensities (10 mA) result in a peak of the resistance, which can be attributed to the crystallization of the sample. The hysteresis loops reported in Figure 9b support this picture, as the samples annealed at 5 and 7 mA display the softest magnetic properties, whereas the sample annealed

![Figure 9. Top: Electrical resistance variation vs. time in Fe\textsubscript{51}Co\textsubscript{22}Nb\textsubscript{4}Si\textsubscript{5}P\textsubscript{4}B\textsubscript{14} thin films 75 nm thick submitted to Joule heating at selected current intensities. Bottom: Hysteresis loops on as-prepared and Joule heated samples with the measurement field perpendicular to the annealing field.]

![Figure 10. Coercive field as a function of annealing current intensity in Joule heated Fe\textsubscript{51}Co\textsubscript{22}Nb\textsubscript{4}Si\textsubscript{5}P\textsubscript{4}B\textsubscript{14} thin films, 75 nm thick. Full symbols: measurement field perpendicular to annealing field. Open symbols: measurement field parallel to annealing field.]


at 10 mA is characterized by a much larger coercive field. Its dependence on the annealing current intensity is shown in Figure 10 for the same samples. A slight anisotropy is induced, as expected, by the annealing technique, which exploits a self generated field, and is evidenced by the slightly lower coercivity value when the measurement field is parallel to the annealing field.

4. Conclusion

In conclusion, amorphous soft magnetic thin films can be prepared by sputtering with the same compositions used for ribbons. Even if thin films usually display worse soft magnetic properties with respect to ribbons with the same composition, thermal treatments can be used to tailor them by relieving the quenched-in stresses, and by inducing (nano) crystallization or a uniaxial anisotropy in the case of field annealing.

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