Structural and magnetic effects induced by annealing in sputtered thin films of $R_{1-x}Co_x$ amorphous alloys

M L Soltani
Department of Physics, Faculty of Sciences, Annaba University, Annaba, 23000, Algeria
E-mail: ml_soltani@yahoo.fr

Abstract. The objective of this work was to study the thermo-magnetic properties of sputtered $R_{1-x}Co_x$ amorphous alloys ($R=$ Er, Tb, Sm). We have investigated a series of amorphous thin film of $R_{1-x}Co_x$ having a high Curie temperature $T_C$ (above room temperature), which rises with Co content. The desired parameters were $T_C$ higher than in crystalline state and low macroscopic anisotropy. Samples of $R_{1-x}Co_x$ have been prepared by DC triode sputtering from different targets. All of them have been then examined by means of X-ray diffraction for determining the as-cast amorphous structure and after each step of annealing, Rutherford back scattering (RBS) for determining the thickness and chemical composition. Magnetic measurements were taken before and after annealing (up to 400°C) at room temperature by means of vibrating sample magnetometer (VSM). These alloys were initially magnetically hard and characterized by a biaxial anisotropy in the film plane. Field annealing allowed to get both desired effects: first, reduction of internal stresses which were caused by the deposition process; second, producing a well-defined in plane anisotropy.

1. Introduction
Amorphous and nanocrystalline materials are of interest in number of areas, structural, electrical and magnetic, but it is in magnetism where the particular properties (high/low magnetostriction, high susceptibility, coercivity) of these materials in as-cast or devitrified form are most studied and have immediate practical application. This is true for both soft and hard magnetic materials such as in perpendicular magnetic recording media [1, 2], transducers and sensors [3], etc. Especially, the magnetic structure of the rare earth-transition metal amorphous alloys, generally ferrimagnetic, has been intensively studied because of their potential practical applications [4-8].

Amorphous films are usually prepared by physical deposition processes such as sputtering, vacuum evaporation methods, etc. These preparation methods allow to prepare new phases which are metastable, and can widen the ranges of solid solution. In addition, it is possible to prepare nano- and microcrystalline materials with well controlled grain size from amorphous precursor. The studies cover a wide range of saturation magnetisation, permeability, coercivity, and magnetostriction. All of these properties, in particular the shape of hysteresis loops are dependent upon the alloy composition, heat and mechanical treatment.

The random anisotropy model [9] describes the competition between exchange interactions and random anisotropy in amorphous alloys. The model accounts for the ferrimagnetism, i.e., the non
collinear arrangement of rare-earth magnetic moments in 3d-4f alloys due to the large random anisotropy of rare-earth atoms.

These amorphous alloys are characterized by large magnetic domains, so-called Imry and Ma domains [10]. In case of magnetism, the amorphous state changes the magnetic properties due to the close relation between crystallographic and magnetic structure. However, in first approximation the mean magnetic moment does not depend upon the surrounding atomic arrangement but depends upon chemical composition in either crystallized or amorphous state. As an example, compensation point for vanishing spontaneous magnetization in amorphous state is greater than in crystallized state [11].

Thus, it is interesting to consider the RCo$_x$ alloys (R is rare earth) in the crystalline state where their Curie temperatures are below the room temperature, while the reported results show for amorphous state very high ordering temperatures up to 600 K for $x > 0.66$. This has been explained in terms of band narrowing in the amorphous state which renders the Co-sublattice strongly magnetic at room temperature having a well-defined ferromagnetic coupling of the Co moments [12, 13]. The aim of the present work is to study the magnetic properties in the $\text{R}_{1-x}\text{Co}_x$ (R= Er, Tb, Sm) amorphous alloys with nearest RCo$_2$ compositions and the processes which take place during annealing. Their influence upon magnetization process and on magnetic anisotropy will be considered.

2. Experimental Procedure

2.1. Preparation of amorphous films

Rare earth-transition metal amorphous films Sm-Co, Er-Co were prepared from various targets by DC triode sputtering and Tb$_{1-x}$Co$_x$ films were deposited by co-sputtering from two different targets in a DC triode sputtering machine. The thickness was from 2000 Å to 5000 Å. The compositional and depth analysis of samples was made by X-ray diffraction and Rutherford back scattering (RBS). The figure 1 shows the variation of thickness versus position of sample on substrate holder and the comparison between simulation of sputtering and composition from RBS evaluation. Annealing was carried out up to 400 °C of some alloys.

![Figure 1](image)

**Figure 1.** Comparison between simulation and results obtained from RBS: Left: thickness versus position sample on substrate holder. Right: composition versus position sample.

2.2. Structural analysis by X-ray diffraction

All the samples were measured by means of 20 X-ray diffractometer. These as-sputtered films present the common shape of the X-ray patterns for amorphous alloys which consists only of broad maxima without sharp peaks. The Scherrer formula gives an atomic correlation length of about a few interatomic distances, confirming the amorphous character of our samples.

2.3. Compositional analysis by means of RBS

To estimate the thicknesses and chemical composition, the Rutherford back scattering was used. The count rate of energy values corresponds to element content at fixed depth of analysis. Stoichiometry is
deduced from $I_{R}/I_{Co}$. The exact composition depends on vapor pressure, sputtering rate, atomic size, system geometry, sticking probabilities and sputtering coefficients. Analysis reveals a variation in the initial stoichiometry of the starting bulk material. So, in addition to evidence of amorphous quality of the samples, we observed enrichment in Co caused by different sticking coefficients of heavy rare earth and cobalt.

The width of peak gives the thicknesses which were found to be between 2000 Å and 5000 Å. The thicknesses are given also by means $\alpha$-step profilometer. Thickness given by RBS was systematically about 10-15 % smaller than that of the $\alpha$-step and this can be attributed to the lower density of the sputtered films compared to their bulk equivalent.

2.4. Magnetic measurements
Hysteresis loops (in fields up to ± 2 T) were measured in the film plane by a classical axial extraction magnetometer and by a more sensitive VSM with 1 Oersted increment. Two types of measurements were carried out when the magnetic field was applied parallel or perpendicular to the direction of the measurement. The magnetisation M (H) was measured at room temperature 300 K.

3. Results and Discussion

3.1. Amorphous Tb-Co
The samples which were magnetic at 300 K show hysteresis loops characteristic of an anisotropy which is dependent on composition. The loops were measured along easy and hard magnetic axes in plane of film. Anisotropy depends upon composition: for low Co content, the magnetization lies in the plane of the sample with a very small anisotropy (small $M_R/M_S$). On contrary, for higher Co content, competition occurs between well defined in-plane anisotropy and a perpendicular anisotropy. This is a biaxial anisotropy regime where there are competing in-plane and perpendicular anisotropy terms [13, 14]. Some samples were annealed for 1 hour at various temperatures from $T_a=75$ to 400°C under field about 2.5 T applied perpendicular to the length in the film plane. In earlier paper [15] author made X-ray analysis after each annealing temperature and found that the crystallisation begins above 350°C. Thus, the expected annealing effect is below 350°C.

Considering figure 2 (top), one can observe the change of hysteresis loops at 300 K before and after annealing in Tb$_{0.31}$Co$_{0.69}$ alloy. First, the shape of loop in sample annealed at 250°C shows zero plane anisotropy on contrary of as-cast sample which shows a biaxial anisotropy. Near the beginning of crystallization, the magnetic quality is destroyed (increasing of $H_C$ and decreasing of M). For lower x values, as shown in figure 2 (bottom), low annealing temperature $T_a$ can efficiently improve magnetic properties. Stresses are relaxed by annealing which leads to the rapid decrease of $H_C$ and the induced uniaxial anisotropy by field annealing.

3.2. Amorphous Er-Co
The loops for as-cast sample (figure 3) shows the remanence $M_R$ and coercive force $H_C$. This shape of loops can be explained by the competition between a well defined in-plane anisotropy and a perpendicular anisotropy. This is a biaxial anisotropy regime described above [13, 14]. The change of magnetization by annealing the Er$_{0.33}$Co$_{0.67}$ amorphous alloy, under applied field, modifies the loop, resulting in a strongly modified loop area with a weak decrease of both $H_C$ and $M_R$. Effect of annealing produces a uniaxial anisotropy along easy axis.

3.3. Amorphous Sm-Co
The aim was to find the ideal temperature at which the system shows a uniaxial structure. In the case of too high temperature, one can exceed the Curie temperature of alloy; moreover, the crystallization of the layer prevents obtaining a uniaxial anisotropy. Three Sm$_{0.33}$Co$_{0.67}$ samples of various thickness
(between 2500 and 4000 Å) were investigated. One can see in figure 4 that a biaxial regime occurs due to existence of a significant hard magnetic component of $\text{Sm}_{0.33}\text{Co}_{0.67}$.

Concerning the initial sample which is to be annealed at 150°C, the cycle is angular and does not change with the angle when the moments turn sharply. One can say that the moments are in the plane of the layer and are distributed in an isotropic way. For the sample after annealing at 150°C the curve is angular indicating that the moments are in the plane of the layer; one can thus identify a hard direction in addition to one easy direction. (figure 5). Although one can note an easy magnetization direction, the variation of the curve according to the angle is weak. The higher temperature annealing destroys a magnetic quality.

4. Conclusions
We have investigated a series of amorphous thin films $R_{1-x}\text{Co}_x$ ($R=$ Er, Tb, Sm). These alloys are magnetically hard and characterized by a biaxial anisotropy in the film plane. A sufficient field annealing allowed to achieve both desired effects: first, reducing internal stresses which were caused by the deposition processes; second, inducing a well-defined in plane anisotropy. In particular, the magnetic quality of low-cobalt $R_{1-x}\text{Co}_x$ alloys may be improved with a weak annealing.
Figure 5. Hysteresis loops for easy (top) and hard (bottom) magnetization directions in Sm$_{0.33}$Co$_{0.67}$ annealed at 150°C.

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