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# NANOSTRUCTURED FILMS FOR HIGH DENSITY PERPENDICULAR MAGNETIC RECORDING

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Cobalt sulphur, $Co_xS_{1-x}$, is a heterogeneous alloy consisting of nano-size magnetic particles dispersed in an insulating matrix. In this paper we deal with $Co_{0.36}S_{0.64}$ nanostructured thin films prepared by electrolysis deposition method. The films exhibit perpendicular magnetic anisotropy (PMA), which is generally not expected in magnetic thin films. The phenomenon has been observed in a number of granular magnetic systems, but it is not specific to the investigated system. $Co_{0.36}S_{0.64}$ nanocrystalline films have rough surface, where columnar needle-like nanoparticles oriented normal to the thin film plane are separated by amorphous regions. The films consist of randomly oriented ultra-fine particles, quite uniform size and shape with diameter in the range of 3 - 4.5 nm, and well separated from each other. The film morphology is controllable by changing deposition conditions. The inter-particles regions consist of very small magnetic clusters and it is believed that they have a significant role in the matrix-mediated indirect exchange interactions. The observed perpendicular anisotropy is the result of the in-plane biaxial tensile stress and negative magnetostriction.

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## 1. Introduction

Soft magnetic materials besides their classical applications in transformers, transducers and magnetic shields, have become important pre-requisites for sensors and reading heads [1-3]. Amorphous and nanocrystalline alloys are good candidates. Usually, the high-density recording media with low noise characteristics are thin films composed from nanosized particles, each particle being more or less magnetically isolated by a non-magnetic matrix, particularly by an amorphous phase. Many of these materials exhibit perpendicular magnetic anisotropy (PMA) and consequently they can be used as perpendicular recording media (PRM). The interest in these materials is due by the superior writing PMR characteristics. Nanocrystalline materials prepared from amorphous precursors have been intensively investigated in the past, but the role of particle size, compositional fluctuation and internal strains is still not well understood. Therefore, in developing very high-density (ideal) recording media, it is important to clarify the relationship between structure and magnetic properties in these kinds of materials.

In the present work we discuss magnetic hysteresis behaviour that we have been observed in $Co_{0.36}S_{0.64}$ nanocrystalline thin films. These results are correlated with structural characteristics in order to elucidate the origin of the PMA mechanism.

## 2. Experimental

Co - 25 at. % S thin films were prepared by electrolysis deposition method [4]. The substrates used were copper discs 18 mm in diameter. The thickness of the films was determined by X-ray absorption and was compared with that obtained by weighing [5]. The film thickness was in the range of 10-50 μm. The selected films have had Co volume fraction $x = V^{Co} / V^{Film} = M_s^{Film}/M_s^{Co} = 0.36$ and thickness D = 50 μm. The structure of the films was analyzed by X-ray diffraction (XRD) by using Cu-$K_\alpha$ radiation ($\lambda$ = 0.154050 nm) with Ni filter. The morphology and size of the particles were determined directly by means of transmission (TEM) and scanning (SEM) electron microscopy. In addition, the particles size was estimated by using the Scherrer peaks broadening formula to the XRD results [6]. The crystallization

temperature of amorphous films was evaluated from the differential thermal analysis (DTA) curves determined during continuous film heating at a constant rate of 0.27 $Ks^{-1}$. The crystallization temperature was found to be 583 K. Film composition was determined by electron probe microanalysis (EPMA). The saturation magnetization and the effective anisotropy energy of the thin films were determined with a computer assisted automated torque-magnetometer (ATQM) in DC field up to 480 kA/m at room temperature [7]. The DC magnetic hysteresis was measured by using a vibrating sample magnetometer (VSM) in DC magnetic fields up to 600 kA/m at room temperature. No attention was paid to the in-plane film direction of the magnetic field. Saturation magnetostriction was measured employing a B-H loop bending method [8].

## 3. Results and discussion

In Fig. 1 we show the XRD pattern obtained for the $Co_{0.36}S_{0.64}$ thin film. Despite large content of Co no diffraction peaks are observed. The Co-S film is apparently amorphous or heavily structurally disordered.

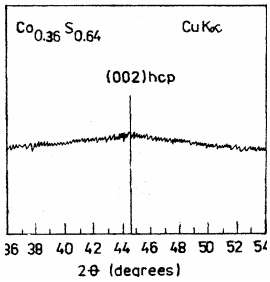


Fig. 1. X-ray diffraction pattern of Co-S thin films.

The TEM image from Fig. 2a indicates that Co-S thin film consists of a small volume fraction of precipitates (particles) with diameters less than 10 nm that cannot be detected by large angle XRD. Therefore, the as-prepared films are "X-ray amorphous", while in reality they consist of ultra-fine particles embedded in a Co-S amorphous matrix. We can notice that the film consists of randomly in-plane oriented ultra-fine particles, quite uniform size and shape with diameter in the range of 3 - 4.5 nm. Particles are well separated from each other. The morphology shown in Fig. 2a is common to many nanostructured materials, and is controllable by changing the deposition conditions [4]. Clearly, the inter-particles regions in Fig. 2a exhibit a lower electron density. This is due to the establishment of the film growth conditions, in which columnar or needle-like microstructural units are separated by less dense cobalt-sulphur amorphous or heavily disordered inter-particle regions. The nanostructured films have rough surface, where columnar nanoparticles normal to the film plane are separated by amorphous regions.

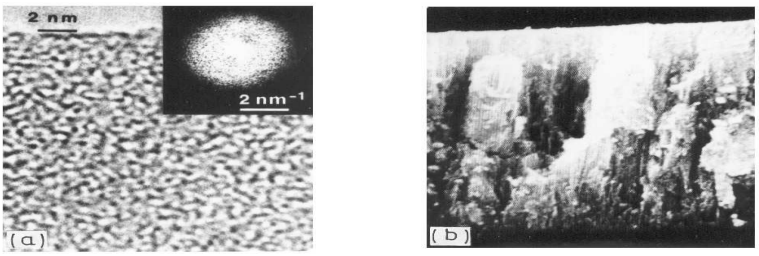


Fig. 2. Transmission electron micrograph and corresponding electron diffraction pattern (a), and scanning electron micrograph of cross-section (b) for the Co-S thin film.

Fig. 3 shows the DC magnetic hysteresis loops at room temperature for Co-S thin films measured by VSM. The DC hysteresis loops were measured in plane (//) and perpendicular ($\perp$) to the film plane, respectively. It is worth to note that magnetization is linear regardless of the direction of the applied field with respect to the thin film plane. The saturation field ($H_{s//}$) required to align the magnetization in the film plane is of about $3 \times 10^5$ A/m, while the saturation field in perpendicular direction to the film plane ($H_{s\perp}$) is even larger of about $5 \times 10^5$ A/m. These features, totally different from those observed in homogeneous or polycrystalline Co films, suggest the existence of a strong perpendicular anisotropy in addition to the usual in-plane anisotropy. Similar behavior was recently observed in sputter-deposited Co-Si thin films [9]. The M-H linear dependence is characteristic for an (ultra)fine magnetic particles assembly that exhibits dipolar

interaction. According to [10], the nanoparticulate Co-S thin films behave as a magnetically disordered system (Fig. 3). The wasp-like shape of the DC perpendicular hysteresis loops (Fig. 3) indicates that Co-S films are not uniformly magnetized but they are divided into magnetic domains with up and down magnetization components.

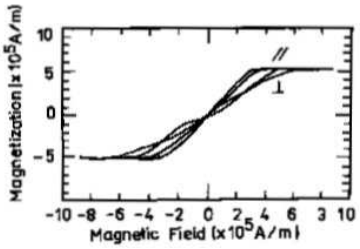


Fig. 3. Magnetic hysteresis loops of Co-S thin films: // - applied field parallel with the thin film plane; ⊥ - applied field perpendicular to the thin film plane

Fig. 4 shows the Bitter-powder patterns on the film surface (a) and in the film cross-section (b). The analysis of the Bitter patterns revealed a maze-domain structure on the film surface (Fig. 4a) and a stripe-like domain structure with closure domains in the film cross-section (Fig. 4b). The magnetization is out-of-plane with a small in-plane component (maze-pattern) and the stripe-like patterns are due to up and down modulation of the perpendicular magnetization component. The perpendicular anisotropy is not high enough compared with the demagnetization field, which implies the closure domain appearance. The closure domains spacing became finer as the depth from the surface became larger and this fact can suggest a certain influence of substrate on the perpendicular anisotropy.

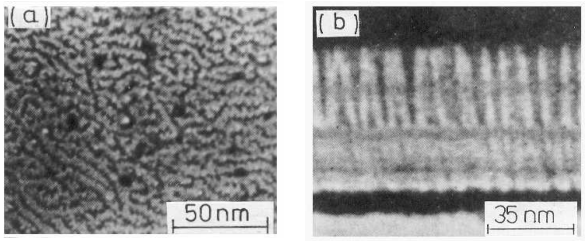


Fig. 4. Bitter-powder patterns on the Co-S film surface (a) and on the Co-S film cross-section (b).

The peculiarity of the observed domain structures is that the domains include a great number of Co particles (magnetic percolation). The measured domain width is W = 3.57 μm while the Co particles size is in the range of 3 to 4.5 nm. Moreover, a maze-domain structure, which is a characteristic of poor soft magnetic materials, is not caused by particles size but probably by the equilibrium between multiple interactions that act in the particles system. By comparing TEM image (Fig. 2a) and its corresponding Bitter-powder pattern (Fig. 4a) for as-prepared film, it is clear that the magnetic domain structures cover the whole sample suggesting magnetic percolation at concentrations much lower ($x_m$ = 0.36) than the volume percolation threshold ($x_v$ = 0.54) [4]. This behavior may be understood as a result of the interplay between: (i) PMA, which tends to orientate the magnetization perpendicular to the thin film plane; (ii) dipolar interactions, which favor flux closure; (iii) exchange interactions mediated by amorphous matrix, which tend to align parallel the magnetic moments [11, 12]. Therefore, the simplest anisotropy that accounts for stripe-like domains in our nanoparticulate Co-S thin films should be an out-of-plane or oblique (tilted) anisotropy K with an angle θ with respect to the thin film normal direction [13, 14]. The effective value of the perpendicular anisotropy was determined by torque measurements (ATQM) and was found to be $K_\perp = 9.18 \times 10^4$ J/m$^3$. The key question is the source of this high perpendicular anisotropy. All results indicate that the perpendicular anisotropy is related to the nanostructure and not the material. Then, the anisotropy constant should be the magnetocrystalline anisotropy of Co, certainly modified and far from the ideal orientation. Since the magnetocrystalline anisotropy for bulk Co is $K_{Co} = 6 \times 10^5$ J/m$^3$ [15], the K ($9.5 \times 10^4$ J/m$^3$) deviation from $K_{Co}$ is too large. Consequently, it is supposed that there is another more important contribution to the perpendicular anisotropy. In the metastable Co-S alloys with no phase separation one does not observe the unusual hysteresis loops [4]. Since the phase separation is a prerequisite for PMA [16], the nanostructure must contain unusual arrangement for Co phase. One can see from the cross-section SEM image (Fig. 2b) that the as-prepared Co-S thin films have a columnar microstructure. Thus, the perpendicular anisotropy appears in the samples as a combined result of strain and texture. The strain and texture can be the result of the combined effects of the induced stresses.

Sulphur atoms in the Co matrix induce a grained structure because S atoms tend to segregate to the grain boundaries. The large difference between the surface free energies of S ($8 \times 10^{-2}$ J/m$^2$ [17]) and Co (2.25 J/m$^2$ [18]) forces S to remain on the surface of the crystallites. The S grain boundary segregation could cause strongly elastic distortions of the Co crystalline lattice near the grain boundary accompanied by an exchange coupling between neighboring grains. Due to texture, the <111> hcp Co direction is thus compressed and, therefore, these films display negative magnetostriction, $\lambda_s = - 4.2 \times 10^{-6}$ [4]. When a thin film is subject of the in-plain strain an out–of–plane strain appears frequently [19], due to the continuum elasticity such as a Poisson–type reaction of the in-plane strain. It seems that columnar growth is imposed by the necessity of the in-plane internal stress equilibrium whatever its nature is [16]. The magnetic anisotropy is along the compressed direction, i.e. perpendicular to the thin film plane. The films present weak dipolar and exchange interactions leading to a relative long-range out-of-plane striped-like domain structure and a closure domain structure in the film plane. The interactions are always strongly influenced by the demagnetization due to the flux closure between anti-parallel neighboring domains [14], [20].

## 4. Conclusion

The Co-S thin films display unusual hysteresis loops characterized by large saturation fields and a linear magnetization dependence on the applied field, both in-plane and perpendicular to the film plane, nearly zero remanence and coercivity. Long-range striped-like magnetic domain structures (magnetic percolation) appear due to the interplay between perpendicular anisotropy and dipolar and matrix-mediated (indirect) exchange interactions. The weak ferromagnetic matrix in which Co nanoparticles are embedded is an amorphous or highly disordered cobalt-sulphur phase that contributes to the stabilization of the domains structure. The perpendicular magnetic anisotropy (PMA) is a structural induced anisotropy and appears as a result of an in-plane biaxial tensile stress and negative magnetostriction. The results suggest that nanocrystalline Co-S thin films displaying long-range domain-like structures share some features of both continuous and discontinuous magnetic systems. The very high value of PMA in Co-S thin films suggests that this material may be used as perpendicular magnetic recording media.

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