Structural and magnetic changes in CoAlZr thin films upon post annealing

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Abstract—**We present a study of the effect of annealing amorphous ferromagnetic thin films of $Co_{0.85}(Al_{0.7}Zr_{0.3})_{0.15}$, post deposition. The annealing was done in vacuum with no applied magnetic field. We find that already at a relatively low annealing temperature of 130 °C there is crystallite formation that introduces both structural and magnetic inhomogeneity. This does not affect the saturation magnetization strongly, but strongly affects the switching behavior and the overall effective anisotropy of the films. Further, there is a dramatic increase in magnetization damping. Thus, the annealing has a profound effect on both static and dynamic magnetic properties of the material. This is important to keep in mind for potential applications using these materials.**

Keywords—**MOKE, FMR, VSM, crystallinity, amorphous, CoAlZr, magnetic anisotropy, coercivity**

1. Introduction

CoAlZr amorphous alloys have been shown to have highly tuneable magnetic properties. They are ultrasoft, with coercivity of the order of 0.2 mT, their ordering temperature and magnetization can be controlled over a large continuous range by composition and they have been shown to sustain large magnetic proximity effects in heterostructures [1], [2]. Many of these features are rooted in the disordered atomic arrangement.

Here, we present a study of the annealing of amorphous thin films of $Co_{0.85}(Al_{0.7}Zr_{0.3})_{0.15}$, hereinafter CoAlZr, which is a ferromagnet with an ordering temperature well above room temperature. We examine the effect of the post annealing treatment on the film structure and how structural changes affect the static and dynamic magnetic properties.

2. Experimental

The CoAlZr films were deposited on polished Si, with 2 nm of native oxide, in a DC magnetron sputtering system with a base pressure of 1×10^{-9} mbar. The films were deposited at room temperature at an Ar (99.999% pure) pressure of 3×10^{-3} mbar. The sputter pressure is controlled by a mass flow controller and a butterfly valve in front of the turbo pump. The samples were deposited by co-sputtering from circular $Al_{0.7}Zr_{0.3}$ and Co (99.9% pure) targets. The CoAlZr films were grown on a 10 nm AlZr wetting layer and capped with a 5 nm AlZr layer, both amorphous. Two samples were sputtered simultaneously, one rectangular 10×10 mm^2 and one circular of diameter 4 mm, using a shadow mask mounted on the sample holder. The samples were deposited in a uniform in-plane 130 mT magnetic field, from four SmCo magnets fixed on either side of the samples. This has been shown to induce a uniaxial anisotropy with an easy axis along the field direction [2]. The sample holder was rotated continuously during sputtering, to ensure that anisotropy is defined solely by the applied field and not by the sputter geometry (see e.g. [2], [3]). The thickness of all the CoAlZr films was 60 nm. The precise composition was $Co_{0.85}(Al_{0.7}Zr_{0.3})_{0.15}$, chosen for its high Curie temperature of 700-850 K, and for its amorphous structure [2] facilitated by the amorphous wetting layer and the composition chosen.

The samples were annealed in a rapid thermal annealing system, Jetfirst 150 RTA, with a base pressure of 1×10^{-4} mbar. The samples were annealed for a duration of 15 minutes each at different temperatures of 110, 130, 150, 170, and 190 °C. No external magnetic field was applied during annealing. The films were annealined in vacuum to avoid oxidation since oxygen during annealing has been found to have a substantial effect on Co alloys [4].

Grazing incidence X-ray diffraction (GIXRD) and X-ray reflectivity (XRR) measurements were used pre and post annealing to examine changes in structure. Details of the system and optics used for GIXRD and XRR measurements can be found in [5].

Static and dynamic magnetic properties were measured by magneto-optic Kerr effect (MOKE) magnetometry, vibrating sample magnetometry (VSM), and broadband ferromagnetic resonance (FMR) [2], [6]–[8]. The samples analyzed by FMR were circular disks with a diameter of 4 mm, in order to reduce the occurrence of domain formation in corners and to exclude in-plane shape anisotropy effects.

3. Results and discussion

A. Structural characterization

The results of the GIXRD and XRR measurements confirm that the sample fabrication is very reproducible, yielding films of the desired thickness with an amorphous structure upon repeated depositions with the same sputter settings. Further, it is evident that upon annealing layer roughness increases, and thereby the total roughness of the films.

Fig. 1 displays GIXRD measurements of samples annealed for 15 minutes each, at different temperature. The as-grown sample has one broad peak, characteristic of the mean atomic separation in the amorphous material. Annealing at temperatures up to 110 °C causes no apparent change, while at temperatures of 130 °C and above there is a clear transition from the broad amorphous feature to a sharp crystallite peak with increased intensity. The curves are offset for clarity, the two lowest curves by 200 and the four above by 300 counts/s each. Also, there are two less pronounced peaks forming at 2θ angles equal to 65.2° and 82.35°. Based on comparison with ICDD reference patterns we infer that the crystal peaks could correspond to a Co_xAl_{1-x} cubic crystal phase (space group Pm-3m) with a near equiatomic composition. The ICDD reference patterns corresponding to the measured data are 00-044- (1115, 1264 and 1266) [9], with $x = 0.5$, 0.53 and 0.48 respectively. The crystallite peak positions are indicated by dashed vertical lines.

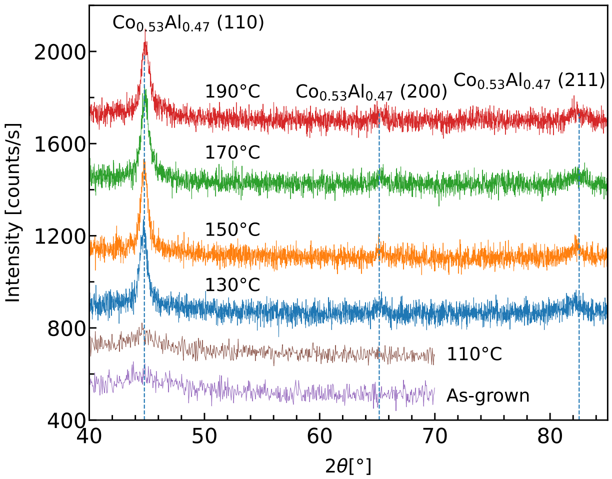

Fig. 1. GIXRD measurements of amorphous $Co_{0.85}(Al_{0.7}Zr_{0.3})_{0.15}$ annealed at the labeled temperatures for 15 minutes. CoAl crystal peaks are included to show that the crystallites that form match CoAl.

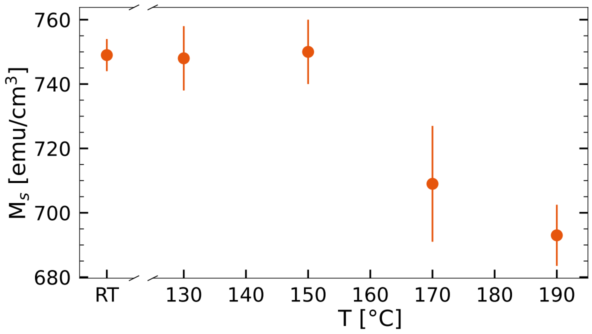

Fig. 2. Saturation magnetization measured by VSM shown as a function of annealing temperature.

B. Static magnetic properties

Accompanying the crystallite formation upon annealing the samples, there is a slight decrease in the saturation magnetization as depicted in Fig. 2. However its onset is not until at higher temperature than where we first detect crystallites. The first sign of a significant drop in saturation magnetization is at 170 °C. The difference in onset temperature could be a difference in sensitivity of the detection methods, or it could be that crystallites formed have either lower magnetization than the bulk film, or are superparamagnetic, but a proximity effect helps maintain the magnetization to higher temperature [1]. Rhee *et al.* [10] observed that Co_xAl_{1-x} alloys are non-magnetic at $x = 0.5$ or below, but on the Co-rich side they are ferromagnetic. They found that $Co_{0.54}Al_{0.46}$ is a disordered B2-phase, space group Pm-3m, that has ferromagnetic properties and a saturation magnetization of 424 emu/cm^3. This is almost an identical composition to the database entry matching our GIXRD data discussed above.

Hysteresis loops measured by MOKE confirm an apparent "ideal" uniaxial anisotropy in the as-grown samples, induced by the magnetic field during growth. They display a sharp rectangular easy axis loop and a completely closed, linear hard axis magnetization trace [11]. The orange data in Fig. 3 exhibit the magnetic remanence at different measurement angles, maximum along the easy axis (0°) and zero when measured in the hard axis direction (90°). After annealing at 130 °C there are already dramatic changes in the magnetization switching behavior. Coercivity in the easy axis loops increases ten-fold (red dots in Fig. 3) and there is an anomalous opening of the loops in the hard axis direction, evident both in coercivity and remanence values and the effective easy axis tilts away from 0° by some random angle. This shows as the protrusion in the hard axis direction (tilted toward 100°) shown in the blue data in the inset of Fig. 3. Such anomalous opening has been observed multiple times [12], [13], usually in Co alloys but has also been observed in pure Fe [14], and has been referred to as anomalous magnetization reversal. It has been studied thoroughly by Idigoras *et al.* [15], who ascribe it to disturbance of the uniform rotation reversal in easy axis samples, by disorder in the material. In our case the disorder arises from crystallites, that also increase the coercivity, either by contributing areas with higher coercivity or acting as pinning centers, which also tilt the effective easy axis. Our annealing process is without external magnetic field, and it seems that upon annealing the effective easy axis can wander away from the field-set easy axis in the as-grown samples. We observe changes to varying degrees, both with positive and negative angular deviation.

C. Dynamic magnetic properties

Broadband FMR measurements of as-grown CoAlZr yield sharp resonance peaks, as the peak in the imaginary part of the susceptibility in Fig. 4 bears witness. We estimate the Gilbert damping of our as-grown CoAlZr to be $\alpha = 0.01$. The effects of annealing on the FMR response are immediately visible, and quite dramatic. The resonance peaks of annealed samples shift to much lower frequency and become quite small already upon annealing at 130°C. At 100 Oe applied field the as-grown resonance frequency is 3.35 GHz, compared with values in the figure of around 2.2-2.6 GHz! This is in stark contrast with the results of saturation magnetization measurements, where there is no noticeable difference until at 170 °C annealing. Angular dependent FMR measurements confirm uniaxial symmetry of all samples. The anomalous effects in remanence and coercive field measured by MOKE are not detected in FMR, as the measurements are carried out in a saturated state and disorder during reversal is not an issue. The angle dependent FMR measurements confirm exactly the tilt in easy axis detected by MOKE. It is quite possible that by annealing in a strong applied field one could affect, or prevent such easy axis tilt [16].

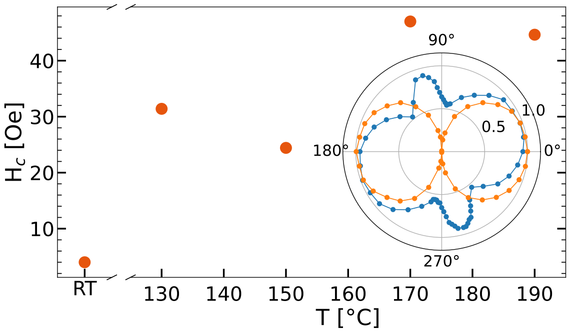

Fig. 3. Coercivity as a function of annealing temperature. The inset shows magnetic remanence for the as-grown (orange) and the sample annealed at 190 °C (blue). The direction of the EA shifts with annealing and the HA opens up.

Alloying has been proven to be a successful method to increase magnetization damping, e.g. in permalloy. However, in most cases this comes at a cost of significant lowering in the saturation magnetization [7]. It is apparent that the increased damping, evident as line broadening, is connected with structural inhomogeneity on the formation of crystallites. FMR damping has been shown to correlate to magnetic and structural homogeneity. The effect of homogeneity has been observed [17], [18] and theorized to be caused by two-magnon scattering [19]. The formation of crystallites introduces both structural and magnetic inhomogeneity as observed by MOKE in the appearance of the anomalous magnetic reversal.

4. Summary

We observe that annealing uniaxial amorphous CoAlZr films at temperatures far below their crit-

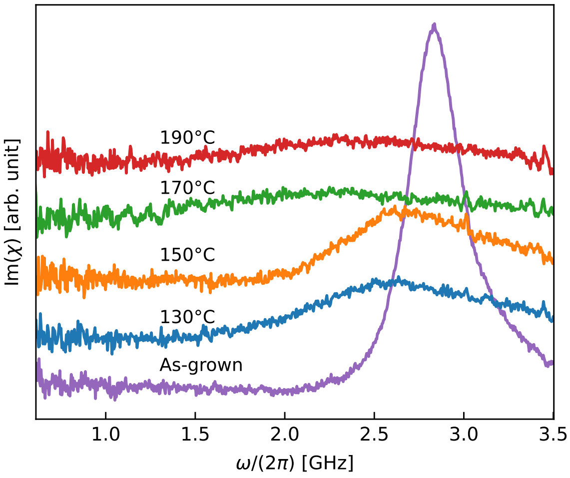

Fig. 4. FMR measurements along the easy axis pre and post annealing. Post annealing measurements are performed with 100.0 Oe applied field along the easy axis while as-grown only had 60.0 Oe field, in order to keep the resonance peak within the same frequency range. Traces are offset vertically for clarity.

ical temperature without external field produces crystallites with disordered grain orientation. This crystallization starts at a temperature as low as 130 °C, far below the critical temperature of about 550 °C. It presents itself in structural data, as well as in changes in hysteresis loops, increased coercive field and opening of hard axis loops. It also causes a dramatic shift in resonance frequency and increase in magnetization damping. We attribute this to loss of structural and magnetic homogeneity in the CoAlZr films upon crystallization.

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