Magnetic anisotropy and its microstructural origin in epitaxially grown SmCo thin films**Mohamed Benaissa* and Kannan M. Krishnan***National Center for Electron Microscopy, Materials Sciences Division, 72-150
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Magnetic anisotropy and its microstructural origin in epitaxially grown SmCo thin films

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Abstract- Microstructural features and magnetic behavior of epitaxially grown SmCo thin films with very high in-plane anisotropy are presented. Transmission electron microscopy was used to characterize the microstructure while magnetic measurements were performed using *dc* and SQUID magnetometers. Two substrate orientations were studied, i.e., MgO(100)/Cr(100)/SmCo(11 $\bar{2}$ 0) and MgO(110)/Cr(211)/SmCo(1 $\bar{1}$ 00). In the former, the SmCo(11 $\bar{2}$ 0) film shows a bicrystalline microstructure, whereas in the latter, a uniaxial one is observed. Both microstructures consist of grains with a mixture of SmCo₂, Sm₂Co₇, and SmCo₅ polytypoids. A deviation from the *c*-axes was observed in the in-plane anisotropy of the SmCo(11 $\bar{2}$ 0) thin film. A strong exchange interaction between the grains would, in principle, explain the observed deviation. On the other hand, both SmCo(11 $\bar{2}$ 0) and (1 $\bar{1}$ 00) thin films show very high coercivity values with pinning-type characteristics. Possible coercivity mechanisms related to intergranular exchange interactions and local variation in magnetocrystalline anisotropy constants are discussed.

Index Terms- anisotropy, coercivity, epitaxy, hard magnet, microstructure, pinning, thin film, samarium-cobalt.

I. INTRODUCTION

Microstructural features such as grain size and shape, phase distribution, grain boundary type, and the mutual crystallographic orientation between grains are parameters that determine the magnetic behavior of modern permanent magnets. Such permanent magnets, generally composed of rare-earth-based compounds, are characterized by high coercivity and energy product. Nowadays, high coercivity values ($H_c \approx 4$ T) are routinely obtained in bulk hard magnetic materials such as SmCo or NdFeB-based alloys. In the case of thin films, such performance was not reached in practice, fundamentally because of insufficient control of

microstructural parameters. Early attempts to grow SmCo in the form of thin films generated large coercivity values [1], although a clear explanation for such an improvement in coercivity forces was not presented. However, it has recently been demonstrated that growth on selective substrates with appropriate surface orientation and temperature, leads to epitaxial Sm-Co thin films with very high coercivity values (comparable to those of bulk hard magnets) resulting from the high in-plane anisotropy [2], [3]. The objective of the present work is to shed light on the microstructural features, such as grains size and their mutual orientation, microstructural imperfection and phase distribution, that induce such a strong in-plane anisotropy and to relate them to the magnetic behavior of the film.

II. EXPERIMENTAL

Sm-Co thin films were prepared by magnetron sputtering as described in [2] and [3]. Cr buffer layers, 200 Å thick, were deposited onto single-crystal MgO(100) and (110) substrates held at a temperature, T_s , of 600°C resulting in Cr(100) and (211) epitaxial growth, respectively. The Sm-Co films were subsequently deposited with a nominal composition of Sm₂Co₇ by co-sputtering from separate Sm and Co sources at $T_s \approx 600^\circ\text{C}$ and 4 mTorr Ar pressure to a thickness of about 750 Å. The Sm-Co thin films were then capped by a thin (50 Å) Cr layer. For plan view transmission electron microscopy (TEM) and microanalyses, disks of three millimeters diameter were prepared, dimpled and ion milled to perforation. The average and local chemical composition of the films were measured using energy dispersive x-ray spectroscopy (EDXS) in an analytical TEM (JEOL 200CX), while electron diffraction and high-resolution TEM (HRTEM) imaging were performed using a Topcon 002B microscope operated at 200 keV. The magnetic properties were measured with a Quantum Design *dc* magnetometer equipped with a 9-T magnet and a 7-T SQUID magnetometer equipped with both longitudinal and transverse coils.

III. RESULTS AND DISCUSSION

The crystal structure of Cr is body centered cubic (bcc) whilst SmCo alloys are generally either hexagonal or rhombohedral. However, when deposited at elevated substrate temperature on MgO, Cr establishes an epitaxial relationship with the substrate providing a template for the subsequent growth of the SmCo film. Fig. 1 shows the microstructure of the as-grown SmCo thin films. For MgO(100) substrates,

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plane view electron diffraction inset in Fig.1a) shows a four-fold symmetry, and an epitaxial relationship given by:

while in the case of $\text{MgO}(110)$ substrates (inset in Fig.1b), the epitaxial relationship is

Since $\text{Cr}(100)$ possesses a four-fold symmetry, the $[0001]$ direction of SmCo_5 grains lie along either the $\text{Cr}[011]$ or $\text{Cr}[0\bar{1}\bar{1}]$ directions (Fig.1a), whereas in the latter case both $\text{SmCo}_5(11\bar{2}0)$ and $\text{Cr}(211)$ adopt a two-fold symmetry which results in a uniaxial structure (Fig.1b).

In the case of $\text{MgO}(100)$ substrate (Fig.1a) the $\text{SmCo}_5(11\bar{2}0)$ film microstructure exhibits small grains (~ 25 - 60 nm in size) with their c -axes normal or parallel to each other resulting in a bicrystalline structure, where the grains are separated by incoherent twin boundaries. In the case of $\text{MgO}(110)$ substrate, the microstructure mainly shows grains (~ 50 nm in size) having their c -axes parallel to each other resulting in a uniaxial structure. Stacking disorder, normal to the c -axis within the grain structure, can be observed in the micrographs (Fig.1). This stacking disorder can be described as an intergrowth of different polytypoids of SmCo alloys. Indeed, close examination using HRTEM (Fig.2), combined with image simulations and measurements of d_{xxx} spacings, shows that the stacking disorder within a given grain corresponds to the difference in stacking between SmCo_3 , Sm_2Co_7 and SmCo_5 phases. The micrograph shows that these SmCo polytypoids have a common c -axis, i.e., their basal planes are parallel to each other. The crystal structures of

Fig.1 Low-magnification HRTEM in-plane view images showing the microstructure of the as-grown (a) $\text{SmCo}_5(11\bar{2}0)$ and (b) $\text{SmCo}_5(1100)$ thin films. The respective electron diffraction are shown as insets.

Fig.2. HRTEM in-plane view image of an individual grain indicating the stacking disorder along the c -axis, or the stacking of different SmCo polytypoids with a common c -axis.

intermetallic Sm-Co phases, ranging from SmCo_2 to SmCo_5 , are closely related and are based on a regular stacking along the c -axis of two kinds of layers. One layer is of the SmCo_2 Laves phase type and the other is that of SmCo_3 type. Since each bilayer is Co -rich, removing one bilayer from Sm_2Co_7 for instance, results in the formation of SmCo_3 stacking type. Furthermore, our chemical microanalyses over either an ensemble of grains or a single grain showed that the thin film contained Sm and Co in an atomic ratio corresponding to the formula $\text{Sm}_{0.24}\text{Co}_{0.76}$, a concentration that is relatively close to the nominal value, within the measurement error. On the other hand, the binary phase diagram of Sm-Co [4] shows that a small excess of $\text{Sm}(\text{Co})$ would push the Sm_2Co_7 phase towards an equilibrium with its adjacent compound $\text{SmCo}_3(\text{SmCo}_5)$. In summary, the growth of Sm_2Co_7 thin films can be described as initiated by an island growth-mode, as indicated by atomic force microscopy images [2], [3], with the basal planes normal to the film surface. Local departure from the nominal stoichiometry may occur during the growth, forming regions with either excess Sm resulting in the formation of SmCo_3 or excess Co leading to the formation of SmCo_5 . To minimize the elastic strain energy, the basal planes of the three phases are driven to be parallel to each other along a common c -axis.

Both $\text{SmCo}(11\bar{2}0)$ and $(1\bar{1}00)$ thin films showed very high coercivity values and seemed to indicate characteristics of pinning-type magnets (Fig.3). Particularly in the former case (Fig.3a), H_c was found to be 25% larger for an external field applied parallel to the $\text{MgO}[011]$ and $[0\bar{1}\bar{1}]$ directions than that for the one applied along the $\text{MgO}[010]$ and $[001]$ directions (parallel to the SmCo c -axes). Due to its bicrystalline microstructure, the $\text{SmCo}(11\bar{2}0)$ thin film exhibits a four-fold symmetry in the in-plane angular dependence of the anisotropy with effective easy axes along the $\text{MgO}[011]$ and $\text{MgO}[0\bar{1}\bar{1}]$ directions. For $\text{MgO}(110)$

substrates with SmCo(1100) thin films (Fig.3b), the in-plane angular dependence of the anisotropy shows a two-fold symmetry (or uniaxial) with the c-axis of the SmCo grains (parallel to the MgO[001] axis) being the easy direction.

The magnetic hardness of SmCo thin films appears to be very sensitive to the crystallography of the phases present as well as the composition and very fine-scale structural details within and at the boundaries of the nanometer-size grains. Two kinds of magnetic interactions exist between neighboring SmCo grains with a given crystallographic orientation. The first is magnetostatic which depends mainly on the shape of the grains, whereas the second, exchange interaction, strongly depends on the grains size. Micromagnetic modeling has shown that for nanometer-scale grains in an isotropic permanent magnet, the exchange interaction between grains is dominant in determining its magnetic behavior [5]. In particular, at the remanent state, the spontaneous magnetic polarization was found to deviate from the easy axes of the grains in the vicinity of the grain boundaries. A similar model, involving strong exchange interactions between the grains in the Sm-Co(1120) film would, in principle, explain the observed anisotropies (Fig.3). Since the epitaxial growth constrains the c-directions of the Sm-Co grains to essentially lie perpendicular (i.e. only two possibilities, in plane) to each other, strong inter-granular exchange interaction would result in the easy direction being at an intermediate orientation, i.e. along MgO[011] or MgO[011]. However, if all the SmCo grains were strongly exchange coupled, individual grain boundaries would not be the likely pinning site to explain the pinning-type coercivity mechanism observed in these films. So the question remains: what is really causing the pinning mechanism in these SmCo hard magnet films? Two alternative explanations can be proposed. It has recently been reported that in Co-based alloy

thin films with a bicrystalline microstructure [6], a "cluster" formed by an ensemble of adjacent grains may lead to an effective anisotropy along an intermediate direction and with a magnitude depending on the strength of the inter-granular exchange coupling. One can possibly assume that due to the ferromagnetic exchange coupling between the grains, a similar type of cluster may form in the case of SmCo(1120) thin films, such that each cluster is considered as a large grain with an effective anisotropy along the MgO[011] or MgO[011]. In such a model, the incoherent twins at the grain boundaries may serve as attractive pinning sites for the magnetic domain walls. The second hypothesis involves the stacking disorder, or the SmCo polytypoids, observed within a given grain with strong variation in local magnetocrystalline anisotropy constants. Although Sm₂Co₇ has a relatively high anisotropy [7], that of SmCo₅ is much higher and hence, it may impede the movement of the domain walls during the magnetization reversal since it has a larger wall energy. This process is only possible if the domain wall motion is parallel to the c-axis. If the magnetization direction is normal to the c-axis, the energy of the wall is independent of the difference in stacking sequence and should not *a priori* act as a pinning center.

IV. CONCLUSIONS

Microstructural features and magnetic behavior of epitaxially grown SmCo(1120) and SmCo(1100) thin films with very high in-plane anisotropy were studied. The SmCo(1120) film showed a bicrystalline microstructure, while the SmCo(1100) film showed a uniaxial one. Both microstructures consist of grains with a stacking disorder, or a mixture of SmCo₃, Sm₂Co₇ and SmCo₅ polytypoids. Although good indications of ferromagnetic interactions between individual SmCo grains were detected, it is still not very clear whether the pinning behavior controlling the coercivity mechanism of the SmCo thin films is due to the incoherent twinning between adjacent grains or to the difference in the magnetocrystalline anisotropy constants of the polytypoids present within the grains. Establishing the validity of either model will involve further studies of the magnetic domain structure in the films. Lorentz microscopy measurements to answer these questions are in progress.

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Fig.3. (a) and (b) show in-plane magnetization loops measured along different axes within the (1120) and (1100) films, respectively. Note the increase in coercivity along MgO[011] in (a).