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STRUCTURE AND MAGNETISM OF EPITAXIAL RARE-EARTH-
TRANSITION-METAL FILMS

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1. Introduction

Growth of epitaxial transition-metal superlattices has proven essential in elucidating the
role of crystal orientation and structure on magnetic properties such as giant
magnetoresistance, interlayer coupling, and magnetic surface anisotropies.¹³ Extending
these studies to the growth of epitaxial rare earth-transition metal (RE-TM) films and
superlattices promises to play an equally important role in exploring and optimizing the
properties of hard magnets. For instance, Skomski and Coey predict that a giant energy
product (120 MG Oe) is possible in multilayer structures consisting of aligned hard-
magnet layers exchanged coupled with soft-phase layers with high magnetization.⁴
Epitaxy provides one route to synthesizing such exchange-hardened magnets on
controlled length scales. Epitaxial growth also allows the magnetic properties to be
tailored by controlling the crystal orientation and the anisotropies of the magnetic layers
and holds the possibility of stabilizing metastable phases.

Much of the pioneering work on epitaxial growth of films and superlattices
used molecular beam epitaxy (MBE)-growth techniques. However, magnetron
sputtering is increasingly being used for epitaxial growth with results comparable to
those acheived by MBE.¹⁵ Sputtering is a complementary technique to MBE for film
growth with the main difference being the kinetic energy of the deposited adatoms. The
higher adatom energy achieved in sputtering can often have profound effects on the
growth morphology.⁷ A general approach for the epitaxial growth of TM superlattices
(for both sputtering and MBE) is to use epitaxial buffer layers grown onto single-crystal
substrates. The buffer layers are initially deposited at elevated substrate temperature to
establish the epitaxial orientation with the substrate and to relieve the strain induced by
any lattice-mismatch. It can also serve as a diffusion barrier between a reactive rare
earth and an oxide substrate. The buffer layer then provides a template for the subsequent growth of the superlattice which is often grown at a lower temperature to reduce interdiffusion. MgO is a versatile choice for the substrate. We have found, in general, that bcc (100), (211) and (110), and fcc (100), (110), and (111) TM buffer layers grow on MgO (100), (110) and (111), respectively. These epitaxial buffer layers can then be used to control the orientation of the subsequently grown films and superlattices. In many cases, the substrates can be mounted adjacent to each other to grow different orientation simultaneously under identical growth conditions.

Research into the synthesis of RE-TM films for permanent magnet applications mainly has focused on controlling the texture of the films either by varying the growth conditions or using textured buffer layers. Considerably less attention has focused on the growth of epitaxial films. We have examined the epitaxial growth of RE-TM (RE=Sm, Nd, Ho; TM=Fe, Co) thin films by utilizing epitaxial W buffer layers. In this paper we present detailed discussions of the epitaxy and magnetic properties for the following examples: Ho, Ho-Co, Sm-Fe and Sm-Co films onto epitaxial W buffer layers by magnetron sputtering. We find that the use of W buffer layers provides a general technique for controlling the epitaxy of RE-TM films. W is chosen because it is immiscible with the RE elements and therefore should provide a chemically inert template for the RE-TM films during high-temperature growth. Our approach utilizes magnetron sputtering. Previous studies by laser ablation have shown epitaxial growth of Y$_2$Co$_7$(0001) films on W(110). The 100-200 Å W buffer layers are deposited onto MgO(100) and (111) at a substrate temperature $T_s$ of 600 °C. This results in W(100) and (110) epitaxial growth onto MgO(100) and (111), respectively, with typical mosaic spreads of $\sim$1°. The epitaxial relationship for W(100) on MgO(100) is W[001]||MgO[001], and for W(110) on MgO(111) it is W[001]||MgO[011]. For both orientations, the W layers are tetragonally distorted with a 1% out-of-plane expansion. The RE-TM films are deposited by co-sputtering from elemental sources at $T_s$ = 400-800°C and 4 mTorr Ar pressure. The relative deposition rates of the sources were used to adjust the composition of the films. The total RE-TM film thicknesses ranges from 60-6000 Å. The film structure was studied by x-ray diffraction (XRD), transmission electron microscopy (TEM) and with a Digital Instruments atomic force microscope (AFM). The magnetic properties were measured with a Quantum Design d.c. magnetometer equipped with a 9-T magnet, a 5-T SQUID magnetometer equipped with a high-temperature furnace, and by magnetic force microscopy (MFM).

2 Structure

Shown in Figs. 1 and 2 are XRD results for Sm-Fe, Ho-Co, Sm-Co, and Ho films grown on MgO(100) and (111) substrates, respectively. For all cases shown, the films are epitaxial. Rocking curves about the RE-TM peaks have a full width at half maximum $\Delta\theta < 2^\circ$ indicative of a high degree of crystalline orientation. From XRD, a determination of the symmetry and lattice parameters of a film is more straightforward
than an unambiguous identification of the phase since only one direction of the unit cell is probed in the thin-film scattering geometry. The phase identification is further complicated by the thermodynamic stability of many phases with similar compositions, and, for a given composition, there are often polymorphic forms. Therefore, we identify the known phases that most closely match the present XRD results. However, metastable phases may also be present.

2.1 Sm-Fe(001) FILMS

Shown in Fig. 1a is XRD results for a 3000-Å thick Sm-Fe film deposited at $T_s=700$ °C onto a MgO(100) substrate with a W(100) buffer layer. In addition to the expected MgO and W $a$-axis diffraction peaks, a Sm-Fe diffraction peak at 2$\theta=37.44^\circ$ with a higher-order reflection at 2$\theta=79.9^\circ$ and a small Fe(200) peak are observed. The Sm-Fe lattice spacing of 2.402 Å agrees with that obtained from the (002) reflection of SmFe$_{12}$ films (2.403 Å) by Wang et al. The in-plane structure and epitaxial orientation was explored by asymmetric diffraction scans from the Sm-Fe(033) reflections. These and additional scans from the W layer show that the Sm-Fe film is epitaxial and possesses the expected four-fold, in-plane symmetry. The Sm-Fe diffraction peaks are indexed to a tetragonal unit cell with lattice parameters $a=8.42$ Å and $c=4.804$ Å as compared to the result for bulk SmFe$_{12}$Ti ($a=8.55$ Å, $c=4.79$ Å). The epitaxial relation is Sm-Fe[010]/W[011]/MgO[010]. In this orientation, the Sm-Fe surface net is rotated 45$^\circ$ with respect to the W surface with a 4% lattice mismatch. Shown in Fig. 3 is the AFM image which yields a ~30-Å rms surface roughness. The roughness is dominated by Sm crystallites which have segregated to the surface (seen as sharp spikes in the AFM image). An AFM scan of regions of the Sm-Fe film surface devoid of the Sm crystallites yields an rms roughness of only ~8 Å.

2.2 Ho(0001) FILMS

Shown in Fig. 2a are XRD results for a 3000-Å Ho film deposited at $T_s=800$ °C onto a MgO(111) substrate with a W(110) buffer. In addition to the MgO and W peaks, the Ho (0002) and (004) reflections are observed indicating $c$-axis growth. The in-plane epitaxial relation is the same as that observed for Y(0001) grown on Nb(110): Ho[1 1 0]||W[001] and Ho[1 1 0]||W[1 1 0].

2.3 Sm-Co FILMS

Shown in Figs. 1b and 2b are XRD results for ~5000-Å thick Sm-Co films deposited simultaneously onto adjacent MgO(100) and MgO(111) substrates with $T_s=600$ °C. In addition to the single MgO and W $a$-axis diffraction peaks in Fig. 1b, a single Sm-Co diffraction peak is observed at 2$\theta=35.52^\circ$ with higher-order reflections at 2$\theta=75.2^\circ$ and 132.6$^\circ$ corresponding to a 2.526-Å periodicity. This is consistent with the (110) orientation ($a=5.052$ Å) of a number of Co-rich Sm-Co phases. TEM confirms that the film is hexagonal with a $c$-axis periodicity of 4.09 Å and that it grows epitaxially,
Figure 1: X-ray diffraction results for (a) Sm-Fe, (b) Sm-Co, and (c) Ho-Co films grown onto MgO(100) substrates with W(100) buffer layers. The W and MgO peaks are identified by W and M, respectively, in (c). The asterisks identify peaks from impurity phases or orientations. The indexing of the RE-TM peaks are discussed in the text. The corresponding films (b) and (c) grown on MgO(111) substrates are shown in Fig. 2(b) and (c).
Figure 2: X-ray diffraction results for (a) Ho, (b) Sm-Co, and (c) Ho-Co films grown onto MgO(111) substrates with W(110) buffer layers. The W and MgO peaks are identified by W and M, respectively, in (c). The asterisks identify peaks from impurity phases or orientations. The indexing of the RE-TM peaks are discussed in the text. The corresponding films (b) and (c) grown on MgO(100) substrates are shown in Fig. 1(b) and (c).
Figure 3: (a) AFM image of the Sm-Fe film shown in Fig. 1(a). The horizontal scale is 1 μm/division and the vertical scale is 400 Å/division. (b) AFM image of the Sm-Co film shown in Fig. 1(b). The horizontal scale is 1 μm/division and the vertical scale is 1000 Å/division.
although it is twinned due to the two-fold Sm-Co(110) growth alignment with respect to the four-fold symmetry of the W(100) buffer layers. The two epitaxial relations are Sm-Co[001]//W[111]MgO[001] and Sm-Co[001]//W[111]MgO[001] with XRD results indicating that the two orientations are equally populated. In this orientation, the in-plane Sm-Co(110) spacing is lattice matched to the W(111) to within 1%. Figure 3 shows AFM imaging of the Sm-Co film on MgO(100). The surface roughness is considerably greater than that for the Sm-Fe film; the surface topography dominated by domed features with a lateral length scale of ≈2000 Å and an rms roughness of ≈120 Å. These features are considerably larger than the average lateral dimensions of the twins (≈50-100 Å) observed in the TEM image.

Figure 2b presents XRD results for the film grown simultaneously with that of Fig. 1a, but onto a W(111)-buffered MgO(111) substrate. There is a dramatic change in the diffraction pattern in Fig. 2b compared to that of Fig. 1a with a series of peaks which yield a periodicity of 8.19 Å. This is consistent with c-axis growth on W(111) in agreement with the report of c-axis growth of Y$_2$Co$_{17}$ on W(110). The in-plane epitaxy is the same as that observed for the Ho(0001) film. This demonstrates that under identical growth conditions, epitaxial templates can be used to control the orientation of the RE-TM films. The diffraction peaks can be indexed (see Figs. 1b and 2b) to a hexagonal structure with $a=5.052$ Å and $c=24.59$ Å. This most closely matches either the hexagonal SmCo$_3$ ($a=5.055$ Å and $c=24.57$ Å) or $\alpha$-Sm$_2$Co$_3$ phases ($a=5.040$ Å and $c=24.35$ Å).

2.4 Ho-Co FILMS

Shown in Figs. 1c and 2c are XRD results for ≈5000-Å thick Ho-Co films deposited simultaneously onto adjacent MgO(100) and MgO(111) substrates with $T_s=600$ °C. The results are similar to that observed for Sm-Co films: (300) growth on W(100) with a twinned microstructure and (002) growth on W(110). The diffraction peaks can be indexed to a hexagonal structure with $a=8.345$ Å and $c=12.24$ Å. This is consistent with the low-temperature-phase Th$_2$Zn$_{17}$-type Ho$_2$Co$_{17}$ structure ($a=8.332$ Å and $c=12.20$ Å). The XRD pattern could also be indexed to the high-temperature Th$_2$Ni$_{17}$-type or the disordered TbCu$_3$-type structures. The in-plane epitaxial relations are the same as those observed for the Sm-Co films.

3. Magnetization

3.1 Sm-Fe(002) FILMS

Shown in Fig. 4 are room-temperature magnetization loops and MFM images for the same Sm-Fe film as in Fig. 1a. There is a strong perpendicular anisotropy, indicated by the sheared in-plane hysteresis loop, which is consistent with the expected c-axis anisotropy of SmFe$_{12}$. The open squares, taken from the literature, are hard-axis results from a single-crystal SmFe$_{11}$Ti sample which illustrate good agreement with
the present results. The saturation magnetization of our film at 5 K is 21.5 \( \mu_B/\text{formula unit} \) and is slightly above the single-crystal SmFe\(_n\)Ti value of 20 \( \mu_B/\text{formula unit} \) reported in Ref. 18. The lower bulk value most likely results from Ti substitution of one Fe site which otherwise would contribute a moment of 1.2-1.7 \( \mu_B \) depending on the site. The measured Curie Temperature \( T_C \) of our film is 575 K. Another bulk magnetic property that is captured in our films concerns the high-field magnetization behavior. At low temperatures (\( T < 150 \) K), SmFe\(_n\)Ti hard-axis loops show sharp upturns in the magnetization characteristic of a first-order magnetization process for fields in excess of 9 T. The beginning of this behavior is also observed in some of the present films below the 9-T limit of our magnetometer. The high value of the room-temperature anisotropy and the first-order magnetization process are not expected for Sm\(^{3+} \) ions with a 4f\(^3 \) \( J = \frac{3}{2} \) ground-state configuration. However, inelastic neutron scattering has shown that mixing of the \( J = \frac{3}{2} \) and \( J = \frac{5}{2} \) multiplets by the large exchange field due to the Fe sublattice quantitatively accounts for the observed anisotropies. Even though the films have high anisotropy, they are magnetically soft (the remanence is low in both parallel and perpendicular orientations) which suggests magnetic domain formation driven by the shape anisotropy at low fields. The domain pattern, observed by MFM, is shown in the inset of Fig. 4. The magnetization is either in or out of the plane of the film, and the typical domain width is \( \approx 1300 \) Å.

### 3.1 Ho(0001) Films

The magnetic properties of the RE metals have been widely studied for many years. Competition between magnetoelastic energy, the exchange interaction, and magnetocrystalline anisotropy leads to many types of spin configurations, including those with parallel, antiparallel, spiral and conical alignment. In hcp Ho, the spins align in the basal plane and form a c-axis spiral below the 132-K Neel temperature \( T_N \). This spiral has a temperature-dependent turn angle that varies between 50°/layer at 132 K and 30°/layer at the 20-K Curie temperature. At \( T_C \) the spins cant 10° out of the basal plane, resulting in a net magnetization along the c-axis. A magnetic field \( H \) applied along the \( a \) or \( b \) directions distorts the spiral into a fully aligned configuration via some observed states of intermediate magnetization \( M \). A helifan model has been proposed to describe the intermediate states for which the spiral spin structure periodically turns back on itself, yielding a net magnetization in the basal plane.

Shown in Fig. 5 are magnetization results for the Ho film shown in Fig. 2a. \( H \) was applied in-plane. The magnetic behavior is very similar to that observed for Ho single-crystals and Ho(0001) films grown by MBE. The 40-K data shows a first-order metamagnetic phase transition from a helical or conical state with no net magnetic moment to the saturated state. The higher temperature data, for increasing fields, suggest a first-order transition to a partially magnetized intermediate state, which is followed by a gradual approach to saturation. This intermediate state is most clearly evident in the 60-K data as a plateau in the magnetization above the metamagnetic transition. Shown in the inset, is the field \( H^* \) for which the first-order transition occurs.
Figure 4: Room-temperature magnetic hysteresis loops for the Sm-Fe(001) film in Fig. 1(a) with the field either parallel (I) or perpendicular (L) to the film plane. The solid lines are the measured results and the open squares are from Ref. 18 for a SmFe$_{11}$Ti single crystal. The inset shows the MFM image. The horizontal scale of the image is 2 µm.

Figure 5: Magnetization at various temperatures for the Ho film in Fig. 2(a) with the field either parallel to the film plane. The loops are taken at temperatures from 20 - 140 K in 20K steps. The inset shows shows the critical field $H^*$ for the metamagnetic transition in the film (open squares) compared to the results of Ref. 19.
compared to the results from Ref. 19 for hcp-Ho with H along the b axis. The close agreement highlights the bulk-like behavior obtainable in epitaxial RE films by sputtering.

3.3 Sm-Co FILMS

Shown in Fig. 6 are magnetic hysteresis loops for the Sm-Co film shown in Fig. 3a. The film has strong planar anisotropy requiring >9 T to saturate the magnetization perpendicular to the film. In contrast to the Sm-Fe films, the room-temperature coercive fields (H_c) are large and typically exceed 3 T (5 T at 5 K). These values are comparable with the highest H_c values for Sm-Co films of similar composition. In previous studies on Sm-Co films, the high H_c values were attributed to high magnetic anisotropy and fine grain structures. It is therefore somewhat surprising that such large H_c values are obtained for an epitaxial film since the grain size is quite large (~2000 Å). However, the density of twin boundaries is significantly greater than that of grain boundaries and, therefore, the twin boundaries are most likely the microstructural feature that controls the coercivity. This makes the Co-Sm (110)/W(100) system analogous to Co and CoPtCr films with bicrystalline microstructure (for growth on Cr(100) underlayers). It should be possible to control the density of twin boundaries and, therefore, the coercivity, by controlling the initial nucleation density of orthogonal domains by varying growth parameters such as deposition rate.

**Figure 6:** Room-temperature magnetic hysteresis loops for Sm-Co film shown in Fig. 1(b) with the field parallel (∥) and perpendicular (⊥) to the film. The in-plane loop is measured with H ∥ MgO(011).
4. Conclusion

In conclusion, we have presented structural and magnetic properties of epitaxial Sm-Fe, Sm-Co, Ho, and Ho-Co films grown onto MgO substrates utilizing epitaxial W buffer layers. These examples are typical of the epitaxial quality achievable by magnetron sputtering for a variety of RE-TM phases. The use of W buffer layers provides a general technique for controlling the phase and orientation via epitaxial growth.

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5. References


