Glancing XRD and XRF for the Study of Texture Development in SmCo Based Films Sputtered Onto Silicon Substrates

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Abstract

Simultaneous XRD and XRF measurements as a function of the glancing angle of irradiation have been used to study texture and compositions of SmCo based films sputtered onto Si (100) substrates. The films formed a disordered TbCu$_7$-type structure for a range of Sm concentrations with an accompanying variation in the crystallite lattice parameters. Since in a film the $2\theta$ positions of the X-ray diffraction lines stayed constant, it is reasoned that the films do not exhibit composition segregation as a function of film thickness. XRD and XRF gave consistent composition measurements for the Sm at.% in the films. Variable angle XRD measurements showed that the film texturing changed to eliminate crystallite growth with c-axes skewed out of the film plane once the magnetization became established. This was the result due to the demagnetization energy for films directly crystallized onto heated substrates at temperatures below the ferromagnetic Curie point of the magnetic phase.

INTRODUCTION

Previously it has been shown that polycrystalline permanent magnet films can be sputter deposited onto a number of different substrate materials such that the crystallographic axes of crystallite grains exhibit a preferential alignment. (Cadieu, 1992, 2000) Such films are said to be textured. For permanent magnet films such a textured growth is particularly important since there is often a high anisotropy energy for the magnetization to align along a particular crystallographic axis. It follows that if the crystallites can be preferentially aligned or textured during the film growth process then the magnetic properties can be controlled or ideally optimized. The growth of textured magnetic films has been the subject of a number of review articles. (Cadieu 1992, 1995, 2000) Generally the magnetic properties and crystallographic texturing of relatively thick films have been studied. A missing element has been actual studies of the texture growth change and development from an initial growth mode. In this paper we have used variable incidence angle X-ray diffraction and fluorescence to study film texture and composition as a function of film thickness. These relatively new techniques have proven very useful for the study of growth and segregation effects in thin films. (van Brussel and De Hosson, 1994) In this variable incidence angle X-ray diffraction the angle between the substrate plane and the incident beam, $\omega$, is held constant for a series of different $2\theta$ scans, with $2\theta$ defined as the angle between the incident beam and the diffracted beam. Simultaneously at each fixed $\omega$ value an energy dispersive X-ray detector was used to collect X-ray fluorescence data excited by the same beam giving the X-ray diffraction counts. For low $\omega$ angles, corresponding to grazing incidence, the X-ray beam samples only the outer surface region of the film. At higher $\omega$ values for sufficiently thin films the X-rays diffract as well as cause fluorescence from deeper regions down to the region of the initial crystallite growth. There is thus an expectation that variable...
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angle X-ray diffraction can be used to show the development of film growth from an initial mode to that of a particular texture. The X-ray fluorescence data can be used to see if any composition changes were correlated to possible changes in crystallite texturing.

In this paper we are primarily concerned with SmCo based films with a nominal composition of $\text{Sm}_{13}\text{Co}_{58}\text{Fe}_{20}\text{Cu}_{7}\text{Zr}_{2}$ (Hegde, 1992) that can be directly crystallized by sputtering onto heated substrates into a single phase TbCu$_7$-disordered type structure. (PDF 71-0641, hexagonal, $a = 4.942 \, \text{Å}$, $c = 4.164 \, \text{Å}$, $c/a = 0.843$) In this disordered structure transition metals can occupy rare earth crystallographic sites for rare earth to transition metal ratios of less than 1 to 5. In films single phase deposits can be formed for Sm concentrations from about 5 to 16.7 at.%. At the upper Sm concentration corresponding to 1:5 ratio a CaCu$_5$-type structure phase starts to form. Over the range of Sm concentrations for the disordered structure there are increasing lattice parameters as the Sm concentration increases since the Sm atom volume is larger than the corresponding transition metal volumes. This change in volume provides a useful check on the measured Sm XRF concentrations.

The disordered TbCu$_7$-type films form a hexagonal uniaxial high Curie point, $\approx 800 \, ^\circ\text{C}$ (Parker, 1990), permanent magnet material in which the relative amounts of Fe can be changed to vary the total magnetization, and in which the relative amounts of Sm can be changed to vary the intrinsic coercivity. The ferromagnetic Curie point is sufficiently high so that the material can be directly crystallized at substrate temperatures below the Curie point where the crystallites are magnetic. The interest in growing such films onto Si substrates is motivated by recent applications for such films. (Cheung et al 2009) Several sputtering process control parameters can be utilized to produce magnetic films with specifically textured structures to affect the resultant magnetic properties of the films. Here only process control parameters pertaining to sputtered films are considered. Three principal process control parameters can be used to synthesize preferentially textured magnetic films. Only one of these requires that the material being deposited be magnetic. The other two principally affect the relative probability for the growth of crystallites with various lattice parameter considerations. The three principal process considerations are

(1.) The demagnetization energy required to produce a net magnetization perpendicular to the film plane versus in the film plane;
(2.) $c/a$ crystal structure ratio effects; and
(3.) The crystal-structure stacking-sequence complexity factor.

The SmCo based films of interest here are a uniaxial hexagonal single phase deposits crystallizing into the disordered TbCu$_7$-type structure. These are squat structures with a $c/a$ ratio $\approx 0.8$. Growth factor (2.) alone would favor the growth of crystallites with $c$-axes pointing out of the film plane since that allows the most symmetric growth. But here once magnetic crystallites become large enough to be magnetic and since the deposits are being directly crystallized at temperatures below the ferromagnetic Curie point, growth factor (1.) favors the growth of crystallites with $c$-axes aligned onto the plane of the films. Most tetragonal uniaxial ferromagnetic structures such as Nd$_2$Fe$_{14}$B and Sm(Fe,Ti)$_{12}$-phases have $c/a$ ratios $> 1$ and relatively low Curie points so that the deposits are crystallized at temperatures above the Curie point. These conditions favor the growth of crystallites with $c$-axes directed out of the film plane to maintain growth symmetry. (Navarathna et al., 1992, Cadieu, 1992, 2000)
Growth modes only start to exhibit the effects of demagnetization energy after a certain size has been reached to exhibit the magnetic properties. Initially a certain crystallite size has to be reached known as a growth coherence area to exhibit magnetic properties. (Cadieu, 2000) Once a certain crystallite size is reached a demagnetization energy becomes manifest that opposes the growth of crystallites with c-axes skewed out of the film plane. There is an expectation that from an initial growth mode expected to be (002), the growth of crystallite with a particular texture, or c-axis orientations, will become favored. Initially the (002) texture is favored because of the symmetry that mode exhibits in the film plane. In this paper variable angle x-ray diffraction is used to study the transition from an initial growth to that of a particular texture.

**EXPERIMENT**

X-Ray diffraction was collected with a 4-axis PANalytical Materials Research Diffractometer with a Cu tube. A 20 μm thick Ni filter was used at the tube exit to reduce the Cu Kβ intensity (99% Cu Kβ intensity reduction). Programmable divergence slits, PDS, and programmable receiving slits were used to maintain a constant irradiation width on the film surface as a function of θ. A diffracted beam monochromator was used to eliminate fluorescence counts from the diffraction detector. SmCo based film thicknesses were measured by measuring the attenuation of the Si (400) reflection by the film. The films were rotated about the φ axis perpendicular to the film plane to first maximize the Si (400) reflection. X-Ray diffraction measurements from the polycrystalline SmCo based films were independent of φ rotations.

The SmCo based films with a nominal composition of Sm₁₃Co₅₈Fe₂₀Cu₇Zr₂ (Hegde, 1996) were RF diode sputter deposited in a cryopumped vacuum chamber with a base pressure of 3-9 x 10⁻⁸ Torr. The films were sputtered at relatively elevated Ar pressures to thermalize the sputtered atoms before their arrival at the substrates to allow the growth of specifically textured films. All the Si (100) substrates were precoated with a boundary layer to allow the adhesion of the magnetic film to the single crystal silicon substrates. Several different boundary layers with thicknesses of 10-30 nm were used in these studies. Boundary layers of Ta, Ta + N₂, Ti, and Al + O₂ were used with no discernable differences observed in the magnetic film properties. For the majority of the films discussed here a boundary layer made by sputtering Al in an Ar + O₂ mixture was utilized. Although the boundary layer thickness can be measured by X-ray reflectivity measurements, it was too thin to affect the X-ray diffraction measurements discussed in this paper.

X-Ray fluorescence measurements for film composition determinations were made with a Peltier cooled Amptek XR-100T energy dispersive detector. X–Ray fluorescence measurements were taken simultaneously with the X-ray diffraction data for different ω values. Since in 2θ scans the angle ω was held constant for a given ω values, the excitation conditions are constant for a given diffraction as well as fluorescence scan. Bulk SmCo 2-17 and SmCo₅ samples were used as composition standards. Mass absorption coefficients for various film compositions were calculated as a linear composite of the elements present. Mass absorption coefficient values for the elements were obtained from the PANalytical High Score program.

**RESULTS AND DISCUSSION**
A normal X-ray diffraction trace, $2\theta$-$\theta$, is shown in Fig. 1 for a relatively thin SmCo based film sputter synthesized onto a heated Si (100) single crystal substrate. The polycrystalline deposit formed a single phase TbCu$_7$-type structure with 4 reflections evidenced for the (110) at $2\theta = 37.7^\circ$, (200) at 43.9°, (002) at 45.1°, and (102) at 49.3°. For this scan the average angle $\omega$ between the incident X-ray beam and the substrate plane is approximately 22°. For this relatively steep incident angle, for this relatively thin film, the diffraction intensity arises from the entire depth of the film. From the diffraction trace shown in Fig. 1 there is no indication that the diffraction intensity for the different reflections may be occurring from different crystallite texturing as a function of the film thickness.

![EC227d graph](image)

Fig. 1. A normal 2q-q diffraction scan, Cu Ka radiation, is shown for a relatively thin SmCo based film sputter synthesized onto a heated Si (100) substrate is shown.

Figure 2 shows a $2\theta$-$\theta$ X-ray diffraction scan for a Si (400) substrate from the film side and backside uncoated substrate surface. This measurement is for the same film as depicted in Fig. 1. The thickness of the SmCo based film was computed from the attenuation of the Si (400) reflection and using the X-ray mass absorption coefficient from the measured film composition. (Vander et al. 2010a, 2010b) The determined thickness for this film labeled as EC227 was 0.23 µm. It has been previously been shown that the Si (400) reflection intensity from the front and backside are the same within statistical uncertainty whether or not the front side is polished or not.

Figure 3 shows $2\theta$ scans for different $\omega$ values for the same mounting of the film of Fig. 1 on the diffractometer. For larger $\omega$ values the diffraction intensity arises from the entire thickness of...
the film, but for small $\omega$ values only the outer surface region of the film contributes to the diffracted intensity. The relative intensities of the respective reflections for different $\omega$ values are shown in Fig. 4. This data shows that initially the growth modes (102) and (002) are dominant, but as the film thickness increases the growth of crystallites with c-axes aligned onto the substrate become dominant, the (110) and (200) crystallites, become the sole mode of subsequent film growth. For the sputtering conditions employed, the (200) growth mode becomes dominant compared to the (110) growth. The stacking sequence for the (200) corresponds to a (100) vertical stacking length of the $a$ lattice parameter equal to $0.866a$. The stacking length for the (110) crystallites is much shorter at $0.5a$. Sputtering parameters that limit the mobility of incoming atoms, such as lower substrate temperatures, higher deposition rates, and higher pressures are expected to favor the growth of (110) over (200) crystallites. X-Ray fluorescence measurements collected at the same $\omega$ values as the 2$\theta$ scans do not show any composition differences greater than $\pm0.3$ at.% Sm, the major element that determines the properties, as a function of $\omega$. Thus differences in the crystallite texturing cannot be caused by a composition difference as a function of growth thickness.

Fig. 2. The Si (400) reflection from the film and back side of a Si (100) substrate is shown. The film was rotated about the $\phi$ axis to maximize the intensity. The two peaks are from Cu K$\alpha_1$ and Cu K$\alpha_2$. 
Fig. 3.  $2\theta$ diffraction scans for different constant values of $\omega$ are shown. The count values for the respective traces have been offset by 200, 400, 500, 600, 700 counts to prevent overlap of the traces.

Fig. 4. The relative intensities of the (110), (200), (002), and (102) relative to the (200) intensity are shown as a function of $\omega$ for the traces of Fig. 3.

Figure 5 shows counts for the (200) reflection as a function of $\phi$ rotation about an axis perpendicular to the film plane. This shows that the crystallite c-axes are randomly splayed
about the film plane without any preferred orientation. This trace is for the same sample as depicted in Figs. 1-4.

**EC227 I(200) Reflection**

![Graph of X-Ray diffraction counts for the (200) reflection as a function of \( \phi \) rotation about an axis perpendicular to the substrate plane.](image)

Fig. 5. X-Ray diffraction counts for the (200) reflection are shown as a function of \( \phi \) rotation about an axis perpendicular to the substrate plane.

Figure 6 shows \( 2\theta \) X-ray diffraction scans using Cu Ka radiation for a relatively thicker SmCo based film crystallized in the TbCu7-type structure. The film thickness was measured by measurements of the same type for this film as depicted in Fig. 2 was 0.41 \( \mu \)m. At this thickness the (200) reflection arising from crystallites with c-axes aligned onto the plane of the substrate dominates over the entire range of \( \omega \) measurements. It is still evident from these traces that the (002) and (102) intensities arise from crystallites as part of the initial growth next to the substrate. The intensity of the (102) reflection to the (200) intensity as measured from different \( 2\theta \) scans is shown as a function of \( \omega \). It is expected that a normal \( 2\theta-\theta \) X-ray diffraction scan for this film would show a trace similar to the \( 2\theta \) scan for \( \omega = 22^\circ \), but very different from that collected at \( \omega = 2^\circ \).
Fig. 6. 2θ diffraction scans for $\omega = 22^\circ$ and $2^\circ$ are shown for a SmCo based TbCu$_7$-type structure film with a thickness of 0.41 µm.
Fig. 7. The relative intensity of the (102) to the (200) reflection is shown as measured from 2θ scans as a function of ω for the film of Fig. 5.

Figure 8 shows 2θ X-ray diffraction traces for ω values of 22°, 15°, and 10° collected from a thick sputtered SmCo based film. The film thickness at 5.6 µm is sufficiently thick so that the Cu Ka X-rays do not penetrate down to the initial growth region so that the established (200) texture mode is the only mode observed. It was previously shown that sputter process control can be used to grow highly textured films with thicknesses up to at least 120 µm.
Fig. 8. 2θ diffraction scans for ω = 22°, 15°, and 10° are shown for a SmCo based TbCu7-type structure film with a thickness of 5.6 μm.

The films mentioned up to this point have been sputter deposited onto heated Si substrates so that material is directly crystallized upon deposition. By this method films can be grown that have the crystallite c-axes aligned onto the substrate plane. In this case a uniaxial magnetic phase has been directly crystallized so that there is demagnetization energy favoring the growth of crystallites with c-axes aligned onto the film plane. Sputter process control to grow textured films thus allows a higher magnetic energy density to be obtained as would result from a random crystallite growth mode. An alternative method to grow crystalline films is to first make an amorphous deposit be sputter depositing the material onto cooled substrates and then to subsequently crystallize that deposit by heating it at least briefly to a temperature to cause crystallization, ≈500 °C. For the SmCo based films considered here substrates held near room temperature are sufficiently cold so that an amorphous deposit can be obtained. In this case it is not expected that a particular growth mode will be favored by a demagnetization energy to favor (200) or (110) crystallite growth. In Fig. 9 2θ scans for several different ω values are shown for a SmCo based film that was initially made amorphous and was then subsequently crystallized. For this relatively thin film with a thickness of 0.094 μm these traces all show a dominant (002). Thicker films that were first made amorphous and then subsequently crystallized usually exhibit reflection intensities close to that expected from a random powder pattern.
Fig. 9. 2θ diffraction scans for ω = 22°, 15°, 10°, and 5° are shown for a SmCo based TbCu$_7$-type structure film with a thickness of 0.094 µm. This film was first made amorphous and then subsequently crystallized. Here the only strong reflection is from the (002) reflection of the TbCu$_7$-type structure.

Simultaneously for each ω value for which X-ray diffraction was collected, XRF data was collected with an energy dispersive Peltier cooled X-ray fluorescence detector. The fluorescence counts collected for 1000 s intervals for sample DM127, 5.6 µm thick, are shown as a function of ω. This graph shows that the PDS is working properly and that the depth of film sampled decreases as ω decreases. Ideally the same area of the sample is irradiated as ω is changed so that the fluorescence counts should extrapolate to zero which is consistent with this graph.

Multichannel analyzer counts for 9 channels centered about the respective peaks with Cu Kα centered in channel 388. Corrections for peak overlaps were made by determining overlap counts for the Sm Lβ with Fe Kα, and for Sm Lγ with Co Kα, and for Fe Kβ with Co Kα by measurements on pure Sm, Fe, and Co standards. A set of coefficients giving the reciprocals of the detector efficiencies for Sm La, Fe Ka, and Co Ka was then determined by composition comparisons to a known bulk SmCo based bulk standard. The reciprocals for the detector efficiencies for Sm La, Fe Ka, and Co Ka were 1.379:1.184:1.000. These numbers indicate that the detector efficiencies are proportional to the X-ray energy; an expected result. Alternatively a set of coefficients could be determined by forcing the fluorescence composition to agree with the bulk standard. In this case the coefficients do not have any simple relation to the physical counts but the determined compositions are still the same to within about 0.1 at.%. The composition total for the three major magnetic elements was set to 91 at.% as in the standard. The relatively
A large Sm coefficient was required because of the lower sensitivity to Sm counts. The composition of sample TD409 for Sm, Fe, and Co as a function of the angle $\omega$ is shown in Fig. 11. The most important number in determining the film magnetic and X-ray diffraction properties is the Sm at.%. Fortunately the Sm at.% is very much independent of the $\omega$ angle, even though the values for Fe and Co change in opposite manners as a function of $\omega$. Sample TD409 from these measurements had a Sm concentration of 8.9 at.%. This sample exhibited an intrinsic coercivity value of 7.5 kOe for in the film plane magnetic measurements and the magnetization easy direction of magnetization very much lied in the film plane. In this case the dominant TbCu$_7$-type structure lines are the (110) and (200) reflections. Both of these reflections correspond to c-axes aligned onto the substrate plane.

For a wide range of samples that exhibit differing Sm at.% values, the $a$ lattice parameter values determined from the (110) and (200) reflections give the same $a$ lattice parameter value for a given film. This indicates that the indexing used for these reflections is correct. In Fig. 12 the $a$ lattice parameters values as determined from the (200) reflection for a set of samples with differing Sm at.% values is plotted. For increasing Sm concentrations it is expected that the lattice would at first expand as Sm occupy more of the rare earth atomic sites and then saturate as the Sm at.% approaches 16.7 at.%, the highest rare earth concentration that the structure can contain. This graph is useful in that even for a film that does no exhibit (110) or (200) reflections an $a$ lattice parameter value can be determined from the measured film Sm at.%. The indexing for the (002) and (102) has been checked by calculating the $c$ lattice parameter. If these respective reflections are indexed as (111) and (201) then the calculated $c$ lattice parameters fall near 3.7 Å which is unreasonably small. The expected $c$ lattice parameters should be in the range 4.1 – 4.2 Å.

Since the lattice parameters are a strong function of the Sm at.% and the fact that for example from Fig. 2 and 3 that the angular position of the diffraction lines do not shift as a function of $\omega$, it is argued that for a given film the Sm at.% is uniformly distributed through the thickness of the films.
Fig. 10. Fluorescence counts as a function of \( \omega \) angle are shown for a relatively thick film sample.

Fig. 11. Apparent compositions for a 2.3 \( \mu \)m thick sample, TD409, determined from XRF measurements as a function of glancing angle \( \omega \).
CONCLUSIONS

Variable incidence angle X-ray diffraction in which $2\theta$ is scanned for different $\omega$ values has been shown useful for the study of textured film growth. For the case of the SmCo based films studied here it has been shown that the growth of crystallites with c-axes randomly splayed about the substrate plane becomes favored after an initial (002) growth mode favored by symmetry. Thus it has been possible to selectively study the evolution of the textured film growth as a function of the film thickness. For this hexagonal structure the $a$ lattice parameter is strongly correlated to the Sm at.% as shown in Fig. 12. From studies such as shown in Figs. 3, 6, 8, and 9 it is seen that $2\theta$ value of a particular diffraction peak are independent of $\omega$ or sampling depth into the film. It then follows that within a particular film the composition is uniform as a function of film thickness. This is also directly shown in Fig. 11. The simultaneous XRF and XRD strongly correlate to each other and give an absolute composition check of the Sm at.% to within at most ±0.3 Sm at.%.

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