Local Compositional Analysis of Magnetic Crystal Grain and Boundary in CoCrPt-SiO₂ Granular Perpendicular Recording Media

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Abstract. The compositions of magnetic crystal grains and boundaries of a CoCrPt-SiO₂ granular perpendicular medium were investigated for plan-view and cross-sectional samples by using a transmission electron microscope equipped with an energy-dispersive X-ray spectrometer. The grain boundary composition, which is not easy to measure because of the small width around 1 nm, is estimated from the average composition of magnetic layer and that of crystal grains by considering the grain boundary volume ratio determined by structure observation. The grain boundary is shown to include Si as the major metallic element together with not small amounts of other metallic elements.

1. Introduction

Recording layer of current perpendicular media employs CoCrPt-SiO₂ granular thin films which consist of Co-alloy magnetic crystal grains of sub-10 nm in diameter separated by thin SiO₂-based boundaries of around 1 nm width. The compositions of grains and boundaries are strongly related with the magnetic properties. Although local compositions of Co-alloy recording media have been studied by using transmission electron microscopes (TEMs) equipped with electron energy loss spectrometer or energy dispersive X-ray spectrometer (EDX) [1–4], only few experimental data are reported on the crystal grain compositions of current perpendicular media [5,6]. There are very little data on the compositions of grain boundaries. In the current perpendicular media, nonmagnetic oxide segregation toward the grain boundaries is playing an important role in determining the granular structure suitable for high-density magnetic recording. In the present study, the compositions of magnetic crystal grains and boundaries of CoCrPt-SiO₂ granular perpendicular media were investigated by using a TEM equipped with an EDX. Local compositional distribution in the crystal grain along the film growth direction was also investigated by using cross-sectional samples.

2. Experimental procedure

A perpendicular recording medium sample with a structure of CoCrPt-SiO₂(12 nm)/Ru/underlayer/glass was used for plan-view TEM analysis. For cross-sectional analysis, a 5-nm-thick metallic cap-layer was deposited on the sample to achieve uniform thickness around the medium surface in the
sample thinning process for TEM observation. The specimens were processed first mechanically and then by Ar-ion-beam to be transparent for the TEM electron beam accelerated at 200 keV. In the EDX measurements, electron beams of 50 nm and 2 nm in diameter were respectively employed to measure the average and the local compositions. A 2-nm-diameter electron beam was carefully focused at the middle of crystal grain to measure the grain composition. However, oxygen composition could not be determined in the present experiment due to a lack of EDX sensitivity.

3. Results and discussion

Figure 1 shows plan-view TEM micrographs of the magnetic layer. Small crystal grains are well separated by brighter contrast grain boundaries. The high resolution image of figure 1(b) indicates clearly that the grains are single crystals while the grain boundary structure is amorphous. As the sample gives high-contrast TEM images, it is easy to trace the crystal grain boundaries by using an image analysis software (Image-pro plus). The diameter distribution measured for 300 crystal grains is shown in figure 2. The average crystal grain diameter and the standard deviation values are determined to be 7.9 nm and 1.7 nm, respectively. The average grain boundary width is calculated to be 1.1 nm.

Figure 1. (a) Plan-view TEM image of CoCrPt-SiO$_2$ medium. (b) High-resolution image.

Figure 2. Crystal grain diameter distribution.

Figure 3. Local compositional variation measured for wedge-shaped plan-view sample. (a) Plan-view TEM image and the positions for composition measurements. (b) Compositional variation measured along the sample thickness direction. (c) Cross-sectional model of the medium sample.
Figure 4. Process to estimate the boundary composition. (a) Plan-view TEM image of magnetic layer which includes both the magnetic crystals and the boundaries, (b) digitized crystal grain image, and (c) digitized boundary image. The boundary composition is calculated from the magnetic layer composition subtracting the magnetic crystal composition by taking account the respective volume ratio.

Local compositional variation was studied by using a wedge shaped plan-view sample. The result is shown in figure 3. The sample thickness is increasing from the left toward the right side in the TEM image shown in figure 3(a), where a thinner region gives brighter TEM contrast. The local compositions were measured from the point 1 to 11 using the 50-nm-diameter electron beam which gives the average composition of the respective local area consisting of roughly 31 crystal grains including grain boundaries. No Ru signals were detected for the positions from 1 to 8 whereas Ru signal was detected at positions 9, 10, and 11, which indicates that the wedged sample is thick enough for the area from point 9 to 11 to include the Ru layer. The data shown in figure 3(b) indicates that the Si intensity is decreasing with increasing the sample thickness whereas the Co, Cr, and Pt intensities are increasing. The compositional variation seems to saturate for the sample area with Ru layer (positions, 9-11). Such compositional variation will be understood by considering the cross-sectional sample structure schematically shown in figure 3(c). When the volume ratio of SiO$_2$-based oxide is increasing toward the medium surface, the Si intensity is expected to decrease with increasing the sample thickness whereas the intensities of other metals increase. Metallic elements of Co, Cr, and Pt are presumably included in the crystal grains. Therefore it is apparently necessary to measure the compositions of thicker region in order to accurately estimate the composition of whole magnetic layer consisting of crystal grains and boundaries. The average magnetic layer composition is thus determined to be Co(48.2 at.%), Cr(10.5 at.%), Pt(17.9 at.%), and Si(23.4 at.%) from the compositions measured for 65 points in thick regions by using the 50-nm-diameter electron beam.

Magnetic crystal grain compositions were measured by using the 2-nm-diameter electron beam for 35 crystalline grains in the thicker sample area that includes Ru layer. The average composition is calculated to be Co(54.2 at.%), Cr(9.4 at.%), Pt(19.4 at.%), and Si(17.0 at.%). When the composition is compared with that of average magnetic layer, the percentages of Co and Pt increased whereas those of Cr and Si decreased suggesting that the grain boundary includes much Cr and Si atoms.

Because it is not possible to directly measure the composition of grain boundary of which average width is only 1.1 nm with the 2-nm-diameter electron beam, the composition is estimated from the average composition of crystal grain and that of magnetic layer which includes both crystal grains and boundaries. Figures 4(a), (b), and (c) respectively show the plan-view TEM image of magnetic layer, the digitized crystal grain image, and the digitized boundary image. The ratio of area occupied by crystal grains and boundaries are calculated to be 84 % and 16 %, respectively. By assuming columnar growth of magnetic crystals for the 12 nm thickness, the average grain boundary composition is estimated to be Co(16.7 at.%), Cr(16.3 at.%), Pt(10.0 at.%), and Si(57.0 at.%). The result shows that the major metallic element in grain boundary is Si which presumably exists in the form of SiO$_2$ as expected. Furthermore it is notable that not small amounts of other metallic elements are coexisting with Si. These metallic elements are considered to be dissolved in the matrix SiO$_2$ through forming oxides like CoO and Cr$_2$O$_3$. 
Figure 5. Cross-sectional TEM image of CoCrPt-SiO₂ medium sample. 2-nm-diameter electron beam was positioned at upper (1), middle (2), or lower part (3) of 8 columnar crystals.

Table 1. Local compositions of magnetic crystal grains measured along film growth direction (at.%).

|                  | Co  | Cr  | Pt  | Si  |
|------------------|-----|-----|-----|-----|
| Upper position (1) | 62.3| 11.4| 14.5| 11.8|
| Middle position (2) | 61.8| 9.1 | 17.1| 12.0|
| Lower position (3) | 57.5| 10.6| 18.9| 13.0|

The crystal grain composition was also measured by using the 2-nm-diameter electron beam for cross-sectional samples. The electron beam was positioned at upper, middle, or lower part of columnar magnetic crystal as shown in figure 5. The average compositions measured for 8 crystals are shown in table 1. No apparent compositional gradient is recognized along the film growth direction. When the crystal grain compositions measured for the plan-view and the cross-sectional samples are compared, it may be noted that the Si content is several % higher while that of Co is lower for the plan-view sample. The difference may suggest an existence of oxides in the magnetic layer surface.

4. Conclusion
Compositions of crystal grains and boundaries in CoCrPt-SiO₂ perpendicular medium are investigated. The crystal grain boundary composition is estimated from the average composition of magnetic layer (crystal grains + boundaries) and that of crystal grains by taking account of the respective volume ratio determined by structure observation. The grain boundaries are shown to include Si as the major metallic element together with not small amounts of Co, Cr, and Pt.

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