Topology and elemental distribution in Co alloy:oxide perpendicular media

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This analytical electron microscopy study was performed to understand better the microstructure of CoCrPt:SiO_2 media. The topology of the magnetic Co alloy grains and the distribution of the elements in the thin films were of special interest. High angle annular dark field images revealed that many grains in the range 5–8 nm have a cavity in their center, observed by low mass-thickness contrast. Electron energy loss spectroscopy Co elemental mapping shows Co to be concentrated mainly in the grains with a depleted region in the center. Si, O, and Cr appear to strongly segregate to the grain boundaries and somewhat to the cavities. In this paper we discuss the possible grain growth mechanisms and the effect of the presence of such cavities on recording properties. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3057818]

I. INTRODUCTION

The magnetic recording properties of hard disk drives strongly depend on the topology (grain size or shape) and elemental distribution in the recording layer. The variation of grain size or shape results in a switching field distribution, which, in turn, decreases the signal to noise ratio (SNR) because the effective magnetic anisotropy of each grain varies. In current perpendicular recording media, CoCrPt with an oxide phase for grain isolation is commonly used for the recording layer. The good isolation and uniform distribution of oxide in the grain boundaries are very important factors for intergranular exchange decoupling and switching field distribution. There have been many studies on reducing the grain size and better isolation with various oxides.[1–6] In order to investigate the microstructure including grain size and oxide isolation in media, bright field (BF) conventional transmission electron microscopy (CTEM) has been commonly used. However, these BF images provide superimposed phase, mass-thickness, and diffraction contrast information. In addition, both plan view and cross section views usually look through several overlapped grains. Ion milling procedures during the specimen preparation have limitations to obtain only recording layer or a single grain column, respectively. Therefore, CTEM can lead to misunderstanding on the topology of grain and oxide distribution in recording layer. In this study we utilized three analytical techniques, which supplement BF in CTEM, namely, (1) high angle annular dark field scanning transmission electron microscopy (HAADF STEM) imaging, (2) energy dispersive x-ray spectroscopy (EDXS) mapping (in STEM mode), and (3) elemental mapping and thickness mapping using electron energy loss spectroscopy (EELS) in energy filtered TEM (EFTEM) mode. The intensity in the HAADF image is proportional to Z^2t where Z is atomic number and t is thickness.[7] Both EDXS and EELS elemental mapping mainly show signal characteristics of the elements present, which means the intensity is related to the elemental concentration. The thickness mapping in the EFTEM mode is proportional to t/λ where λ is the mean free path of inelastic scattering and the elemental characteristic.[8] The combination of each technique helps to distinguish the dominant contrast in each mode, providing a better understanding of microstructure that a single technique usually cannot provide. Some researchers conducted TEM studies on plan view of media fabricated with varying oxygen content during reactive sputtering. It was reported that "low mass-thickness pockets" are present in the interior of many grains of the CoPt:TiO_2 media.[1] Other researchers observed "white dots" in BF of CoCrPt:SiO_x media when the oxygen percent is high (21 at. %).[2] It is difficult to identify the nature of these regions with only the BF image: Questions about their nature (Are these voids or oxides?) arise. We have investigated CoCrPt:SiO_x media and also found similar "cavity-like" feature in many grains. In this paper, the nature of the cavity is proposed based on our results and findings obtained by other researchers. Also, the corresponding grain growth mechanism and the effect of the grain morphology on magnetic properties are discussed.

II. EXPERIMENT

The analytical TEM study was carried out for a commercial coupled granular/continuous perpendicular media consisting of a CoCrPt capping layer and a CoCrPt:SiO_x recording layer using the FEI Tecnai F20 TEM/STEM with the acceleration voltage of 200 kV. The thin specimens were prepared by mechanical back thinning, followed by ion milling (PIPS) from the substrate side. The CoCrPt capping layer was removed during the ion milling procedure. The EFTEM mappings were performed with a Gatan image filter. For

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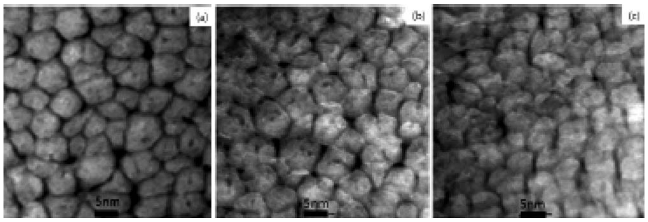

FIG. 1. HAADF images at primary tilting angle (a) $\alpha=15.60°$ displaying region with cavities (b) $\alpha=31.46°$ and (c) $\alpha=40.31°$ showing 3D cylindrical grain topology.

each elemental mapping, the three-window method was used: The background under an energy loss peak was extrapolated with two pre-edge images by a smoothed R power law model and removed from the post-edge image. A different window width was chosen for different elemental edges to prevent the overlapping with other elemental edges and for accurate background subtraction. The exposure time was set between 8 and 10 s and the drift was compensated. The thickness mapping in the EFTEM mode was acquired by dividing a zero loss image by an unfiltered image of the same area.

III. RESULTS AND DISCUSSION

Figure 1 shows the HAADF plan view images of CoCrPt grains isolated with an oxide, taken at different primary (α) tilt angles. The images are in agreement with those of CoPt: TiO_x in Ref. 1 and show best the dark regions ("cavities") in the interior of the grains at $\alpha=15.60°$. As the specimen is tilted by increasing α, the three-dimensional (3D) cylindrical dome shape of grains becomes more apparent. At $\alpha=40.31°$ in Fig. 1(c), the image does not display the cavities in the grains as clearly as in Fig. 1(a). It is hard to identify the nature of the cavities because what contributes to their low intensity can be either low atomic number elements, such as Si and O, or empty voids. However, the images do confirm that the interior of the grains has a discontinuity inside of their volume and the shape of the magnetic grains is not solid cylindrical domes as is often assumed, based on conventional BF images of plan and cross section views.

Figure 2 shows the EELS elemental distribution mapping of each element. The BF image of Fig. 2(a) does not display clearly the regions in the center of grains where dark regions were seen in HAADF images. Co $M_{2,3}$ mapping in Fig. 2(b) shows low intensity regions in many grains, which is consistent with the finding in Ref. 1 and the cavities observed in Fig. 1(a). Cr $M_{2,3}$ mapping was taken on a different area and a higher intensity is observed in the center of grains as well as in the grain boundaries as shown in Fig. 2(c). The Pt mapping is not displayed due to the unavailability of an energy loss peak at the measurable energy range.[9] The obtained Si $L_{2,3}$ core-loss mapping in Fig. 2(d) shows apparently enriched concentration regions in the interior of the grains. The O K elemental mapping in Fig. 2(e) shows an increased concentration of O in the center of grains. Thickness mapping as shown in Fig. 2(f) clearly displays dark regions in the middle of many grains. The low intensity in

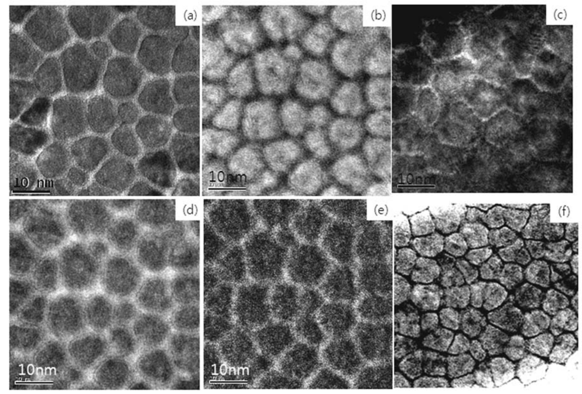

FIG. 2. (a) EFTEM BF image of CoCrPt: SiO_2 perpendicular media (area1) and EELS elemental mapping of (b) Co (area1), (c) Cr (area2), (d) Si (area1), (e) O (area1), and (f) thickness mapping (t/λ map) (area3).

thickness mapping means low thickness or elements with high mean free path of inelastic scattering, such as Si or O, are present. Combining all the observations, the nature of cavities found in the CoCrPt: SiO_x media is a Co depleted region ("low thickness" of Co) filled with Si, O, and Cr. The region is not just low in Z number, because Cr is enriched in the region. The same interpretation can be applied to the CoPt: TiO_x media of Ref. 1. Their ″low mass-thickness pockets″ in the grains are Co and Pt-deficient, and Ti and O-enriched. Ti is not a low Z element; thus, the regions can be concluded to be a "physical cavity" filled with some amount of Ti and O. The creation of these cavities seems to be a common phenomenon in current Co-alloy:oxide perpendicular media, where much effort has been made to reduce the grain size by increasing the oxide content. This can be explained by the nucleation and growth mechanism especially on the domed Ru intermediate layer grown with low mobility condition during the sputtering. Jung *et al.*[4] varied the thickness of the recording layer and found in series of BF plan view images that the subgrains start to form only after a certain thickness. Combining all results, the schematic of a possible "tooth growth" mechanism and shape of the grains can be deduced as shown in Fig. 3. The preferred nucleation sites for the metallic, CoPt, are various places (ledges) on the side of the Ru dome, rather than at the smooth hcp (00.2) on the dome top. As metallic CoPt nucleates preferably first and grows faster from the sides, voids start to be created. The created cavity of CoPt can play a role as a subgrain boundary. Ti, Si, Cr, and O tend to go together either to the "valley" between Ru domes or to the voids created in the middle

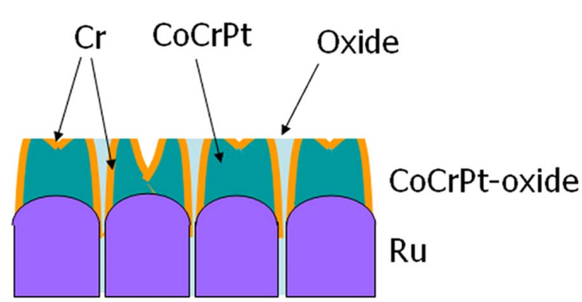

FIG. 3. (Color online) Schematic of a possible mechanism for tooth growth.

of the grains. It is not clear whether the migrating Ti, Si, Cr, and O are in the oxide form or in an ionic form. However, it seems that the elements filling cavities are in oxide form, which have high bonding energy. This can be explained as following: we see from Fig. 1(a) that the population of cavities increases as the observed area approaches the thinner areas (specimen edge, on the right side of the figure). This shows how ion milling (PIPS) may mill off the capping layer and reveal the cavity in recording layer. This can be explained to be due to preferential milling since CoPt metal is milled more easily than the strongly bonded oxide; thus the oxide in the cavity remains while the CoPt is milled away. Zheng *et al.*[2] reported that x-ray photoelectron spectroscopy (XPS) reveals that for CoCrPt:SiO_x media, oxygen contents reached 21 at. % where the "white dots" are found, and the ratio of Cr in oxide to Cr metal form is about 1. Si is mostly in the oxide form. Choe *et al.*[3] fixed the oxygen pressure during reactive sputtering for different oxide media (TiO_2, SiO_2, and Cr_2O_3) and studied the ratio of oxide to metal form using XPS and the oxide segregation using BF TEM. At $P_{O_2}=0.6$ mT, XPS results show that Ti atoms exist in oxide form more likely than Si or Cr atoms. It is also interesting to note that the population of the cavities in the TiO_2 media appears to be somewhat higher than in the SiO_2 media in their BF images.[3] The proportion of each oxide in the cavity or in the grain boundary is governed by sputtering kinetics and relative free energy of oxide formation. A systematic study of oxide formation related to kinetics and thermodynamics is necessary for the better understanding on oxide segregation. Using these microstructural features Zhu *et al.*[10] conducted a simulation study to determine the reasons that SNR does not improve further as the grain size gets significantly smaller. The presence of such regions creates either a free surface or interface with nonmagnetic materials (TiO_x, SiO_x, or CrO_x) in the grains. Such surfaces can cause a decrease in the effective magnetic anisotropy if the surface anisotropy, which is aligned perpendicular to the surface, is significant.[10] As the grain size gets smaller and the surface to volume ratio increases, this phenomenon may be the main reason that SNR does not improve further.

IV. CONCLUSION

The complementary HAADF and EELS analysis on a commercial CoCrPt:SiO_x media found many grains with cavities. The cavities are Co, Pt-depleted, and Cr, Si, O-enrich suggesting a discontinuous topology of the Co grains. Other workers using XPS showed that Si and Cr exist in both metallic and oxide forms. The presence of such cavities filled with oxides in the grains may reduce effective anisotropy and therefore the thermal stability due to the presence of surface anisotropy. In addition, the variation in size and shape of cavity in the grain results in a larger switching field distribution. Therefore, it can be significantly detrimental for recording properties as the grain size gets smaller and the surface to volume ratio increases. To prevent the creation of cavities, it is proposed to deposit an oxide prior to the deposition of the recording layer to fill up the Ru valleys and eliminate the possibility of nucleation sites for the Co alloy on the sides of the Ru domes. The Co alloy grains would then grow as solid cylinders, eliminating cavities.[11]

ACKNOWLEDGMENTS

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