Nanostructure of CoPtCr–SiO₂ Granular Films for Magnetic Recording Media

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Structural properties of CoPtCr–SiO₂ magnetic recording films grown on Ru or Pt seed layers prepared by UHV-magnetron sputtering were studied by high resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS) and energy filtered transmission electron microscopy (EFTEM). CoPtCr grown on Ru seed layers together with SiO₂ forms a well-isolated structure composed of CoPtCr fine grains of 10 nm diameter surrounded by amorphous SiO₂, whereas CoPtCr grown on Pt seed layers together with SiO₂ forms a network structure composed of CoPtCr crystal of 5 nm size. These structural features made differences in their magnetic properties. The HRTEM and EFTEM studies revealed that cylindrical crystalline grains composed of CoPtCr and Ru are formed for CoPtCr–SiO₂/Ru samples, whereas SiO₂ are aggregated around the boundary between relatively large Pt grains and magnetic layers without obstructing the epitaxial growth of CoPtCr on Pt, not resulting in the cylindrical CoPtCr grains. Lattice spacings of CoPtCr grown on Pt with SiO₂ are 0.7% expanded in comparison with CoPtCr grown on Pt without SiO₂. The EELS studies suggested that Co and Cr atoms are partly oxidized by SiO₂ addition for both samples and Cr atoms are more oxidized for CoPtCr–SiO₂/Pt samples.

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1. Introduction

A composite alloy of CoPtCr attracts a great interest for high density magnetic recording media due to its large uniaxial magnetocrystalline anisotropy (1×10^6 [J/m³]).^{1,2)} For realization of high density recording beyond 400 Gbit/inch², the application of higher order terms such as K_{u2} ($K_u = K_{u1} + K_{u2} + \dots$) is advantageous,^{3–7)} where total magnetic anisotropy energy is described as $E = K_{u1} \sin^2 \theta + K_{u2} \sin^4 \theta + \dots$. The alloy CoPtCr is one of the attractive materials from this standpoint because Shimatsu *et al.* recently reported that the value of K_{u2} of CoPtCr could be easily controlled by a choice of seed layers.⁸⁾ In their study CoPtCr deposited on Ru underlayers shows a large K_{u1} value of about 1×10^6 [J/m³] and little K_{u2} , whereas that deposited on Pt layers shows high K_{u2} to K_{u1} ratio, K_{u2}/K_{u1} , of around 20% without significant decrease of total anisotropy K_u . It is recently recognized that CoPtCr is a promising candidate for 1 Terabit/inch² magnetic recording media when it becomes possible to control K_{u1} and K_{u2} values independently.

For the application of CoPtCr to recording media, magnetic grains must be segregated as nanometer sized clusters in non-magnetic materials such as SiO₂ for realizing low noise performance. It was reported that CoPtCr–SiO₂/Ru samples formed a well-defined fine grain structure,^{1,9,10)} but good CoPtCr–SiO₂/Pt grains have not been reported. It is crucially important for design of recording media with higher order term, K_{u2} to clarify the growth mechanism of CoPtCr–SiO₂ on Ru and that on Pt. In the present study we characterized those structures of CoPtCr–SiO₂/Ru and CoPtCr–SiO₂/Pt samples by using high resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS) and energy filtered transmission elec-

tron microscopy (EFTEM), and discussed about the growth feature and the relationship with their magnetic properties.

2. Experimental

CoPtCr–SiO₂ films were deposited on surface-oxidized Si(001) substrates by a co-sputtering method using Co, Pt, Cr and SiO₂ targets in an UHV magnetron sputtering system.¹⁾ Metals as Ta, Pt and Ru were deposited as underlayers or cap layers. In the present study we used two kinds of samples, one was CoPtCr–SiO₂ grown on Ru, [Ta(5 nm)/CoPtCr–SiO₂(10 nm)/Ru(20 nm)/Pt(10 nm)/Ta(5 nm)/Si substrate] and another, CoPtCr–SiO₂ grown on Pt, [Ta(5 nm)/CoPtCr–SiO₂(10 nm)/Pt(20 nm)/Ta(5 nm)/Si substrate], for investigation of the difference of the atomic structures and textures depending on the underlayers. The composition of the magnetic layer was {(Co₉₀Cr₁₀)₇₅Pt₂₅}_{88.8}–(SiO₂)_{11.2} controlled by the deposition rates. We also used the samples without SiO₂, [Ta(5 nm)/CoPtCr(10 nm)/Ru(20 nm)/Pt(10 nm)/Ta(5 nm)/Si substrate] and [Ta(5 nm)/CoPtCr(10 nm)/Pt(20 nm)/Ta(5 nm)/Si substrate] for comparison. In order to prepare cross-sectional and plan-view specimens, the deposited films on Si substrates were dimpled mechanically and polished by Ar ion beam at 3.5 kV.

HRTEM observation and selected area electron diffraction (SAED) study were performed using a 200 kV TEM (JEM-2010). EFTEM observation and EELS measurement were performed using a 300 kV TEM (TECNAI-F30) attached with a Gatan Image Filter (GIF). For the cross-sectional observation, zone axis was set up to the Si[110] direction. Si-mapping image by using EFTEM was obtained by the filtering of Si *L* edge ($\Delta E = 99$ eV), in which the background was subtracted by the 3 window method. EELS were recorded in the image mode with an entrance aperture corresponding to around 50 nm in the sample dimension. In this measurement, energy drift of spectra in EELS was

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corrected by a dedicated software.¹¹⁾ From EEL spectra around Co and Cr $L_{2,3}$ edges (Co: $L_3 = 779$ eV, $L_2 = 794$ eV, Cr: $L_3 = 575$ eV, $L_2 = 584$ eV) acquired from 10 positions, white-line ratio, L_3/L_2 , was then calculated. Magnetization curves were measured by a vibrating sample magnetometer (VSM).

3. Results and Discussion

Figures 1(a) and (b) shows magnetization curves of CoPtCr–SiO₂/Ru and CoPtCr–SiO₂/Pt, respectively. CoPtCr–SiO₂/Ru (a) shows a large coercivity of 2.6 kOe reflecting its large anisotropy. However, very small value of 290 Oe was obtained for CoPtCr–SiO₂/Pt (b), indicating a soft magnetic property, although CoPtCr grown on Pt have a relatively large anisotropy K_u and K_{u2} to K_{u1} ratio. It is considered that CoPtCr magnetic particles were coarsened on the Pt underlayer by the co-sputtering of SiO₂, resulting in their magnetic reversal far different from rotation magnetization of single domain particles.

Figures 2(a) and (b) shows plan-view TEM images and

Fig. 1 Magnetization curves of CoPtCr–SiO₂/Ru (a) and CoPtCr–SiO₂/Pt (b).

selected area electron diffraction (SAED) patterns of the samples and Figs. 2(a') and (b') are the intensity profile of the diffraction patterns from the diffraction center along the radial direction by using pixel numbers. From the TEM observations, it is found that there are some differences in particle shapes of the CoPtCr–SiO₂/Ru and CoPtCr–SiO₂/Pt samples. CoPtCr–SiO₂/Ru (a) forms well-segregated CoPtCr fine grains of less than 10 nm diameter surrounded by amorphous SiO₂ as was reported.^{1,9,10)} On the other hand, CoPtCr–SiO₂/Pt (b) doesn't form an isolated structure but another network structure composed of CoPtCr particles of 5 nm size. Also, diffraction patterns and their intensity profiles show that diffraction rings of CoPtCr–SiO₂/Ru are very sharp, whereas those of CoPtCr–SiO₂/Pt are relatively broad. This means that the crystal grain size of CoPtCr grown with SiO₂ on Pt is relatively small and/or deviation of lattice spacing is relatively large. In relation to the diffraction patterns (a) and (b), enhancement of the ring intensity in some directions may be due to a small selected area aperture picking up local heterogeneity of grain orientations, which does not represent a general structure of the films.

Figure 3 shows HRTEM images and SAED patterns of the present samples in the cross sectional view. It is found that the boundary between the Ru layer and the magnetic layer is not clear and CoPtCr cylindrical small crystalline grains seem to grow on Ru isomorphous crystalline grains sequentially for CoPtCr–SiO₂/Ru. In contrast with this, we can see a bright contrast area between Pt layer and magnetic layer, as indicated by a white arrow, in spite of sequent lattice fringes for CoPtCr–SiO₂/Pt (Fig. 3(c)). Besides the shape of CoPtCr particles grown together with SiO₂ on Pt is not always cylindrical. For underlayers, grain size of Ru and Pt was revealed to be about 10 nm and about 30–200 nm, respectively from their low magnification observation.

Fig. 2 Plan-view TEM images and corresponding SAED patterns of CoPtCr–SiO₂/Ru (a) and CoPtCr–SiO₂/Pt (b). (a') and (b') are intensity profiles of the diffraction patterns along the radial direction from the center with pixel numbers in abscissa, in which reflection indexes of CoPtCr are indicated.

Fig. 3 Cross-sectional HRTEM images of CoPtCr-SiO₂/Ru (a) and CoPtCr-SiO₂/Pt (b), and corresponding SAED patterns. (c) is the magnified image of the area in (b) indicated by a dotted rectangle. There are bright contrast regions at the boundary between Pt and magnetic layers, although lattice fringes of CoPtCr(002) are seen there.

SAED patterns showed that hcp-CoPtCr(002), hcp-Ru(002) and fcc-Pt(111) planes are parallel to Si(002) ones. The easy axis of CoPtCr is oriented to a normal direction of the substrate, which is the ideal orientation for perpendicular magnetic recording. The (001) lattice spacings of hcp-CoPtCr are measured as $d = 0.424$ nm and 0.427 nm for CoPtCr-SiO₂/Ru and CoPtCr-SiO₂/Pt, respectively, on the other hand, $d = 0.424$ nm for both CoPtCr/Ru and CoPtCr/Pt. The lattice spacing of the CoPtCr-SiO₂/Ru sample was not changed from the value of the CoPtCr/Ru sample, whereas 0.7% expanded for CoPtCr-SiO₂/Pt by addition of SiO₂, suggesting an inter-diffusion of impurities such as silicon and oxygen atoms.

Figure 4 shows cross sectional bright field TEM images ((a), (b)) and Si-mapping images by EFTEM ((a'), (b')) at the same position. For CoPtCr-SiO₂/Ru, Si atoms are distributed much in the Ru layer's region, forming a laterally streaky image. This result can be interpreted as that SiO₂ surrounds cylindrical crystal grains composed of CoPtCr and Ru. On the contrary, they are distributed little in the Pt layer's region and aggregated near the boundary between the Pt layer and the magnetic layer, forming vertically streaky structures, which corresponds to the bright contrast seen in the HRTEM image of CoPtCr-SiO₂/Pt (Figs. 3(b) and (c)). This suggests that SiO₂ is rich near the boundary between the Pt and

magnetic layers for CoPtCr-SiO₂/Pt. A bright fringe is seen in Fig. 4. It is also considered as a coagulation of Si atoms, and detailed mechanism is under consideration.

It is suspected here that aggregation of SiO₂ to the boundary obstructs the epitaxial growth of CoPtCr on Pt, but in fact CoPtCr grew epitaxially. In the mechanism of epitaxial growth, however, small nuclei are first formed at the contact with substrate or underlayer, then the nuclei are grown into big clusters.¹²⁾ In the Fig. 3(c), Pt(111) and CoPtCr(002) lattice fringes are continuous even in the above mentioned bright contrast area, so the contact between underlayer and growth layer for epitaxial growth can be considered to be sufficiently close. Therefore, the aggregation of SiO₂ to the boundary is not in conflict with the epitaxial growth.

From Figs. 2, 3 and 4, the growth style of CoPtCr and SiO₂ on Ru or Pt is summarized as follows: In a case of CoPtCr-SiO₂/Ru, Ru underlayer consists of about 10 nm cylindrical crystalline grains and one CoPtCr crystalline grain grows epitaxially on one Ru cylinders taking over their morphological characteristics, and SiO₂ fills in the space between each of the CoPtCr/Ru cylinders. Then, a well-isolated fine grain structure was formed as shown in Fig. 2(a). In a case of CoPtCr-SiO₂/Pt, on the other hand, SiO₂ cannot penetrate into Pt layers because of relatively big crystalline grains and

Fig. 4 Cross-sectional bright-field TEM images of CoPtCr–SiO₂/Ru (a) and CoPtCr–SiO₂/Pt (b), and EFTEM images at the same position (a') and (b'). In EFTEM images, bright areas correspond to a segregation of Si atoms.

SiO₂-rich areas are formed. At the same time, CoPtCr grows epitaxially on Pt and doesn't form well-isolated structures but network structures (see Fig. 2(b)). These differences in the growth feature also might be dependent on the surface energy of Ru and Pt as well as the grain size. Surface energies of Ru and Pt are 3.05 and 2.55 [$\times 10^4$ J/m²],¹³⁾ respectively, and it is considered that Ru surfaces tend to form metallic bonds more than Pt surfaces.

Figure 5 shows white-line ratios of each samples obtained from EELS measurements. The values of the samples without SiO₂ are also shown for comparison. It is known that the more Co and Cr are oxidized, the higher white-line ratio they tend to show.^{14,15)} Compared with the values of CoPtCr/Ru and CoPtCr/Pt, it is found that those of CoPtCr–SiO₂/Ru and CoPtCr–SiO₂/Pt are obviously increased by SiO₂ addition. This means that Co and Cr atoms in both samples are partly oxidized. Especially, Cr shows a high white-line ratio for CoPtCr–SiO₂/Pt, which suggests the preferential oxidation of Cr atoms. In CoPtCr–SiO₂/Ru, the oxidation of Co and Cr can be considered to occur for the surface of the grown particles because the lattice spacing of CoPtCr in CoPtCr–SiO₂/Ru are just equal to that of CoPtCr/Ru. However, lattice spacing of CoPtCr in CoPtCr–SiO₂/Pt is 0.7% expanded by SiO₂ addition, therefore oxygen atoms may exist in CoPtCr particles of CoPtCr–SiO₂/Pt. Then, Cr atoms inside the particles are preferentially oxidized by them due to a relatively high electronegativity in comparison with Co.

Fig. 5 White-line ratios of Co and Cr for each sample.

4. Concluding Remarks

In the present study we analyze the atomic structure of CoPtCr–SiO₂ films, which are candidates for future high density magnetic recording media with higher order anisotropy terms, by using HRTEM, EFTEM and EELS. Plan-view TEM observation revealed that CoPtCr–SiO₂/Ru forms a well-isolated structure composed of CoPtCr fine grains of 10 nm diameter surrounded by amorphous SiO₂, and

CoPtCr–SiO₂/Pt forms a network structure composed of CoPtCr crystals of 5 nm size and amorphous SiO₂. This network structure seems to make a mode of magnetic reversal different from that of isolated single domain particles, resulting in a soft-magnetism. HRTEM and Si-mapping using EFTEM showed that this textural difference is originated from the growth style of CoPtCr–SiO₂ on Ru or Pt. In a case of CoPtCr–SiO₂/Ru, one CoPtCr particles grow on one cylindrical Ru crystalline grain and SiO₂ surrounds these CoPtCr/Ru cylinders. For CoPtCr–SiO₂/Ru, SiO₂ aggregates around the boundary between Pt and magnetic layers and CoPtCr crystalline particles are not cylindrical. White-line analysis using EELS suggested that Co and Cr atoms located at the interfaces are partly oxidized by SiO₂ addition for both samples and Cr atoms inside the particles are preferentially oxidized for CoPtCr–SiO₂/Pt.

For the application of the present materials to magnetic recording media, the isolated cylindrical structure of CoPtCr–SiO₂/Ru is desirable although CoPtCr/Pt have relatively high K_{u2}/K_{u1} , which is advantageous for high density recording. For designing media with K_{u2} using the present CoPtCr–SiO₂/Pt system, it may be required to prevent the network structure by a reduction of Pt grain size or a substrate heating.

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REFERENCES

- 1) T. Oikawa, M. Nakamura, H. Uwazumi, T. Shimatsu, H. Muraoka and Y. Nakamura: IEEE Trans. Magn. **38** (2002) 1976.
- 2) T. Shimatsu, H. Sato, T. Oikawa, Y. Inaba, O. Kitakami, S. Okamoto, H. Aoi, H. Muraoka and Y. Nakamura: IEEE Trans. Magn., **40** (2004) 2483.
- 3) H. N. Bertram and V. L. Safonov: Appl. Phys. Lett. **79** (2001) 4402.
- 4) O. Kitakami, S. Okamoto, N. Kikuchi and Y. Shimada: Jpn. J. Appl. Phys. Part 2 Letters **42** (2003) L455.
- 5) N. A. Usov, C.-R. Chang and Z.-H. Wei: Appl. Phys. Lett. **83** (2003) 3749.
- 6) Q. Peng and H. J. Richter: J. Appl. Phys. **93** (2003) 7399.
- 7) L. Guan, Y.-S. Tang, B. Hu and J.-G. Zhu: IEEE Trans. Magn. **40** (2004) 2579.
- 8) T. Shimatsu, H. Sato, T. Oikawa, Y. Inaba, O. Kitakami, S. Okamoto, H. Aoi, H. Muraoka and Y. Nakamura: IEEE Trans. Magn. **41** (2005) 566.
- 9) H. Uwazumi, K. Enomoto, Y. Sakai, S. Takenoiri, T. Oikawa and S. Watanabe: IEEE Trans. Magn. **39** (2003) 1914.
- 10) T. Kubo, Y. Kuboki, M. Ohsawa, R. Tanuma, A. Saito, T. Oikawa, H. Uwazumi and T. Shimatsu: J. Appl. Phys. **97** (2005) 10R510.
- 11) K. Kimoto and Y. Matsui: J. Microsc. **208** (2002) 224.
- 12) R. Kern, G. L. Lay and J. J. Metois: *Current Topics in Materials Science*, **3**, (North-Holland Publishing Company: Amsterdam, New York, Oxford, 1979) p. 135.
- 13) A. R. Miedema and J. W. F. Dorleijn: Surf. Sci. **95** (1980) 447.
- 14) R. D. Leapman, L. A. Grunes and P. L. Fejes: Phys. Rev. B **26** (1982) 614.
- 15) N. Tanaka, J. Yamasaki, S. Mitani and K. Takanashi: Scr. Mater. **48** (2003) 909.