Additive Effects of AlN and MgO on FePt Nanoparticle Assembly

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We have studied the additive effects of AlN and MgO on $L1_0$ -FePt nanoparticles by co-sputtering FePt and AlN (or MgO) on MgO(100) substrates at 973 K. Good epitaxial growth of FePt was confirmed both for AlN and MgO. With the increase of the additive content, the long range order (LRO) of $L1_0$ phase appeared to increase for AlN, whereas it was suppressed for MgO. Morphological observation by addition of AlN, well-isolated FePt particles became to connect each other, and finally formed a maze-like structure. On the other hand, the morphology of FePt particles was hardly affected by addition of MgO.

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1. Introduction

$L1_0$ type ordered alloys, such as FePt and CoPt, have attracted much attention in the field of magnetic recording, due to their very high magnetic anisotropy of more than 10^6 J/m^3 .^{1,2)} In order to achieve high recording density beyond 1 Tbit/in^2 , these magnetic materials must be in the form of well isolated nanoparticle assembly with small dispersions of their size and c -axis orientation. We have previously fabricated the $L1_0$ -FePt nanoparticle assembly on MgO(100) substrate at elevated temperature.³⁾ It has been confirmed that $L1_0$ -FePt nanoparticles exhibited excellent c -axis orientation without any crystal domain variants. However the particle size distribution was quite large due to coalescence of smaller particles during the growth process. If such coalescence is suppressed, smaller and narrower size distribution would be realized simultaneously. One of the possible methods is to use the substrate with some kinds of nanostructured surface. In our previous work,⁴⁾ FePt nanoparticles grown on a self-grooved MgO(110) substrate were as small as 2–4 nm in diameter and showed sharp size distribution, probably due to suppression of surface migration of sputtered particles on the nano-scale groove structure. Another approach is to adopt a composite of FePt and ceramics. This is a so-called granular structure. Numerous studies on FePt granular films have been conducted so far.^{5–7)} However, most of the films reported so far were with random crystal orientation and too thick, obviously inappropriate for magnetic recording.

In order to achieve well oriented and uniformly dispersed FePt nanoparticles, we have studied epitaxial growth of FePt–AlN (or MgO) granular films on MgO single crystal substrates. In this paper, we report the structures and magnetic properties of epitaxial FePt–AlN, MgO granular films.

2. Experiments

Samples were deposited on polished MgO(100) substrates by co-sputtering FePt and ceramics (AlN, MgO). Sputtering

chamber was evacuated to $5 \times 10^{-7} \text{ Pa}$ prior to deposition. Nominal deposition thickness and rate of FePt were fixed at 3 nm and 0.06 nm/s, respectively. By varying the deposition rate of the ceramics, the film composition was controlled. The deposition rate was monitored by a well calibrated quartz crystal oscillator. In order to simultaneously obtain the well isolated and fully ordered $L1_0$ -FePt nanoparticles, the substrate was heated to 973 K. After cooling the sample to the ambient temperature, a 5 nm thick C film for scanning electron microscopy (SEM) observation and an Al 10 nm for anomalous Hall effect (AHE) measurements were deposited as overcoat layers.³⁾

Crystallographic structure and their orientation were studied by reflection high energy electron diffraction (RHEED) and X-ray diffraction (XRD) with Cu- $K\alpha$ radiation. Morphological surface structure was observed by SEM. Vertical magnetization curves are measured by AHE.

3. Results

Figure 1 shows the RHEED patterns for FePt 3 nm thick films co-deposited with AlN and MgO. All the patterns are spotty or streaky, indicating that good epitaxial growth of FePt on MgO(100) is sustained. In addition, by comparison with the reciprocal spots of $L1_0$ -FePt(001) along [110] direction, very clear superlattice spots can be seen in all the observed RHEED patterns in Fig. 1. This result indicates that the epitaxially grown FePt is in the $L1_0$ order phase for both AlN and MgO. However, there are some differences between AlN and MgO. For MgO, spotty patterns are almost unchanged up to the MgO content of 22 vol%. On the other hand, for AlN, the spotty pattern gradually changes into a streak-like pattern as the AlN content increases, suggesting that the surface morphology varies from bumpy to smooth. Moreover, diffractions with half period can be seen in Figs. 1(c), (e), and (f), indicating that a small amount of $L1_0$ -FePt with (100) orientation or another phase exists. Note that this half period diffraction appears above 9 vol% for AlN, whereas above 22 vol% for MgO.

Figure 2 shows XRD profiles for same samples in Fig. 1. Only FePt 001 and 002 diffractions can be observed except from MgO substrate. Figures 3(a), (b), and (c), respectively,

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Fig. 1 RHEED patterns of epitaxial FePt–AlN and –MgO granular films grown on MgO(100). Images were taken along [110] direction. (b) is the reciprocal lattice of L_{10} -FePt(100) along [110]. The solid and open circles indicate the fundamental and superlattice spots, respectively.

Fig. 2 XRD profiles of epitaxial FePt–AlN and –MgO granular films grown on MgO(100).

show the c -axis parameter, coherent length ξ along the film normal, and integrated diffraction intensity ratio $(I_{001}/I_{002})^{0.5}$ as a function of volume fraction of AlN and MgO. Surprisingly, with the increase in the ceramics content, the c -axis parameter decreases for AlN, whereas increase for MgO. The vertical coherent length ξ of FePt determined from the 002 diffraction by using the Scherrer's equation.⁸⁾

Fig. 3 Structure data of epitaxial FePt–AlN and –MgO granular films grown on MgO(100). (a) c -axis parameter, (b) the vertical coherence length ξ of FePt, and (c) the square root intensity ratio of 001 and 002, respectively, as functions of ceramics content. The broken line in (c) indicates the theoretical value of $(I_{001}/I_{002})^{0.5}$ for fully ordered L_{10} -FePt.

As seen in Fig. 3(b), ξ decreases steeply for AlN, but very gradually for MgO. Figure 3(c) shows the square root intensity ratio $(I_{001}/I_{002})^{0.5}$ of FePt 001 to 002. If these two diffractions are attributed to a single L_{10} -FePt phase, the value of $(I_{001}/I_{002})^{0.5}$ should be proportional to the long range order (LRO) parameter. The broken line in Fig. 3(c) indicates the theoretical value of $(I_{001}/I_{002})^{0.5}$ for fully ordered L_{10} -FePt.⁹⁾ As the ceramics content increases, $(I_{001}/I_{002})^{0.5}$ increases for AlN, whereas decreases for MgO. These opposite behaviors of c -axis parameter and $(I_{001}/I_{002})^{0.5}$ seem to be plausible, because the LRO promotes the tetragonality of lattice, resulted in reduction of c -axis parameter. Therefore, it would be said that AlN additive promotes the LRO. However, this simple hypothesis is questionable as discussed later. On the other hand, MgO additive seems to simply suppress the LRO.

Figure 4 shows the SEM images of the FePt–AlN, MgO samples. For no additive, FePt is in the form of well isolated nanoparticle assembly with the average diameter D of 23 nm. With the increase in AlN content, the FePt islands tend to contact each other and form the maze-like structure at 25 vol.%, indicating that addition of AlN promotes two dimensional growth of FePt. These observations are qualitatively coincident with the change in the RHEED patterns in Fig. 1 from spotty to streaky and the reduction of the vertical crystalline coherent length ξ [Fig. 3(b)]. On the other

Fig. 4 SEM images of epitaxial FePt-AIN and -MgO granular films grown on MgO(100).

Fig. 5 H_c of epitaxial FePt-AIN and -MgO granular films grown on MgO(100) as functions of ceramics content.

hand, the particle shape remains almost unchanged for MgO except slight decrease in the particle size.

Figure 5 shows the vertical coercivity H_c at 10 and 300 K as a function of ceramics content. As the ceramics content increases, H_c gradually decreases for MgO, being consistent with gradual decrease of $(I_{001}/I_{002})^{0.5}$ in Fig. 3(c). However, H_c for AlN steeply decreases with AlN content, which seems to be opposite to slight increase of $(I_{001}/I_{002})^{0.5}$ shown in Fig. 3(c), if $(I_{001}/I_{002})^{0.5}$ for AlN corresponds to the degree of LRO.

4. Discussions

We have found different structural and magnetic properties

of epitaxial FePt-AIN and -MgO granular films. MgO simply reduces the LRO of the $L1_0$ phase but gives little influence on the film morphology. The reason for the reduction of LRO is not clear. One would point out the particle size effect on LRO.^{10,11)} However, the particle size in the present study is much larger than the experimentally determined critical size of about 3 nm for FePt/MgO.¹²⁾ Another possible explanation may be slight interfacial reaction between MgO and FePt. As for AlN, the structural analysis in Fig. 3(c) suggests that its addition promotes the LRO, while H_c significantly decreases. If we assume decomposition of AlN during sputtering, Al would form alloy with FePt although crystal structure is unknown. However, since there exist several stable compounds in Fe-Al and Pt-Al systems, such as FeAl ($B2$), Fe_3Al ($D0_3$), PtAl ($B2$ or $B20$), and Pt_3Al ($L1_2$),¹³⁾ it is likely to form some kinds of compounds in FePt-AIN granular films. Therefore, the diffractions with the half period in Figs. 1(c) and (e) and FePt 001 in Fig. 2(a) might be attributed to an uncertain compound consisting of Fe, Pt, Al. If it is so, enhanced coalescence of FePt particles in Fig. 4(d) may be explained by reduction of the melting point due to alloying with Al. The reason for alloying of FePt with AlN additive but not with MgO may be related to the difference of the free energy of formation of ceramics. The free energy of formation for AlN (-287 kJ/mol) is almost half as much as that for MgO (-596 kJ/mol).¹⁴⁾

5. Conclusions

We have studied on epitaxially grown FePt-AIN, MgO granular film on MgO single crystals. For MgO additive, the long range order (LRO) of $L1_0$ phase monotonously decreases with MgO content. This behavior of LRO well corresponds to decrease in coercivity H_c . As for the morphological structure, the shape of FePt particle remains almost unchanged with slight decrease in size. Therefore, it can be roughly concluded that addition of MgO simply degrades the LRO of $L1_0$ -FePt but gives little influence on the morphological structure. On the other hand, by addition of AlN, the LRO seems to be enhanced, while H_c steeply decreases. The morphological structure is also quite different from the case for MgO. With increasing AlN, particles tend to coalesce and form maze-like structure. This behavior is considered to be related to the formation of an uncertain compound consisting of Fe, Pt, Al.

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