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Direct observation of magnetically induced phase separation in Co-W sputtered thin films

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Phase separation of Co-W sputtered thin films having a large magnetocrystalline anisotropy energy have been investigated. A nanoscale compositional fluctuation caused by magnetically induced phase separation was directly confirmed in the films deposited on a heated substrate in analogy with Co-Cr-based alloys. The difference between the phase separation features in Co-W and Co-Cr is attributed to the difference in their elastic energy. It is expected that the phase separation is enhanced by selecting optimum sputtering conditions. The Co-W system, therefore, is considered to be a promising candidate as a base alloy system for high-density recording media. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1793354]

Co-Cr-based sputtered films are in the current of high-density longitudinal magnetic recording media,[1] and also promising materials for perpendicular magnetic recording media.[2] The Co-Cr-based film is made up of Co-rich ferromagnetic hexagonal-closed-packed (hcp) nanosized grains surrounded by a Co-poor paramagnetic hcp phase.[3] This unique compositional modulation weakens the interparticle exchange interaction between the ferromagnetic grains, resulting in improvements of recording resolution as well as significant recording noise reductions. Such a compositional modulation due to the magnetically induced phase separation[4,5] in a hcp phase is easily developed during the thin-film growth process on heated substrates around at 500–700 K.[3]

For increase of recording densities, both much higher magnetocrystalline anisotropy and enhancement of magnetic isolation between constituent ferromagnetic grains are required. Therefore, a number of intensive studies have been focused on how to promote the magnetic isolation as well as the enhancement of magnetocrystalline anisotropy energy (MAE) by utilizing high magnetocrystalline anisotropy materials, such as FePt[6] and CoPt.[7] According to systematic studies on the MAE of Co-based hcp alloy thin films, the value of the MAE for Co-Mo,[8] Co-W,[9] and Co-Pt[10] alloy films is larger than that of Co-Cr films. It should be noted that the MAE of the Co-W alloy films is several times higher than that of the Co-Cr films in the composition range Co-(5–20 at. %) W.[9] In addition, the metastable miscibility gap associated with the Curie temperature line has been predicted from the thermodynamic calculations for the Co-W system[11] in analogy with the Co-Cr system. Accordingly, it is expected that a nanoscale compositional fluctuation of W is easily developed during the deposition of Co-W thin films on a heated substrate. Namely, the Co-W thin films are expected to be promising as next generation high-density magnetic recording media. In our recent work,[11] an annealing of Co-W hcp alloy films at 773 K enhances the saturation magnetization and the Curie temperature, suggesting that the magnetically induced phase separation is enhanced by annealing.

In the present study, the nanoscale compositional fluctuation of W developed in Co-W films is directly observed by a scanning transmission electron microscope equipped with an energy dispersive x-ray analyzer (STEM-EDX). Furthermore, the thermodynamic calculations are carried out by considering the effect of elastic energy on the phase separation behavior in the film.

A Cr(100) buffer layer 20 nm in thickness and a Co-W$(11\cdot0)$ layer of 50 nm thickness were epitaxially grown on a NaCl(100) substrate by a sputtering method. The sputtering chamber had a base pressure of less than 5×10^{-7} Torr. The depositions were carried out at an argon gas pressure of 5m Torr. The Cr layer was deposited at 423 K by using a dc sputtering and the Co-W layer was deposited at room temperature and 573 K by an rf sputtering. The Co-W$(11\cdot0)$ layer showed a bicrystal growth on Cr(001) with the crystallographic orientation NaCl(001)[100]/Cr(001)[110]/Co-W)$(11\cdot0)[00\cdot1]$. The film compositions were determined as Co-11.9 at. % W by an electron probe micrcoanalyzer. The magnetic properties were measured with a vibrating sample magnetometer. The STEM-EDX was used to investigate the local compositions in the films. For electron transparency, the substrate was dissolved in water and the Cr layer was removed by ion milling. Each point analysis was conducted at 200 kV with a spot size of 0.7 nm.

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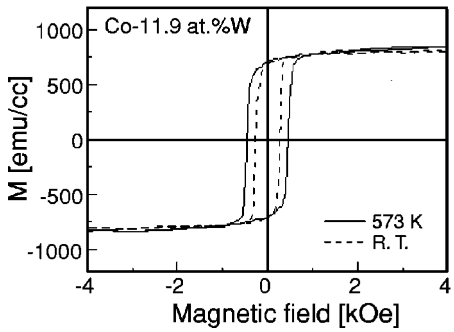

FIG. 1. Magnetization curves of Co-11.9 at % W films deposited at room temperature and at 573 K.

Figure 1 shows the in-plane magnetization curves of the films measured along the NaCl[110] direction. The saturation magnetization Ms and coercivity H_c given by the solid curve for the film deposited at 573 K are slightly larger than those represented by the dashed line for the film deposited at room temperature. Note that the relatively large value of H_c for the film deposited at room temperature is associated with a large value of MAE.[9] The temperature dependence of Ms of the film deposited at 573 K is given in Fig. 2. The Ms curve changes in the slope around at 300 K. Note that the Ms behavior can be well reproduced by superposition of the two Brillouin functions with the different Curie temperature T_c (the dashed line with a low T_c and the solid line with a high T_c), suggesting that two phases with the different T_c coexist in the film. These magnetic properties are very similar to those of Co-Cr sputtered films,[12] regarding as a supporting evidence of the compositional fluctuation in films.

Figure 3 sets out the results of the STEM-EDX observation of the Co-W film deposited at 573 K. For the TEM bright-field image, the corresponding selected area electron-diffraction (SAD) pattern and the indexed electron-diffraction pattern are shown in Figs. 3(a)–3(c), respectively. Because of its bicrystalline structure, the SAD pattern consists of two different types of domains with the *c* axes of hcp, being at right angles to each other, as seen from Fig. 3(c). Only a disordered hcp structure can be identified from the SAD patterns of the film. The local composition was examined at the positions numbered in the STEM bright-field image shown in Fig. 3(d). The nanoscale compositional fluctuation of W is clearly confirmed as shown in Fig. 3(e). The composition analysis was carried out in several local areas in the views. Each position is given by the relative distance from the position 1. The minimum and maximum values are 4.7 and 17.0 at. % W, respectively, bearing out that the two-

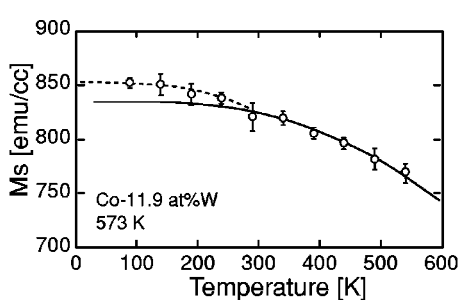

FIG. 2. Temperature dependence of the saturation magnetization M_s of a Co-11.9 at% W film deposited at 573 K.

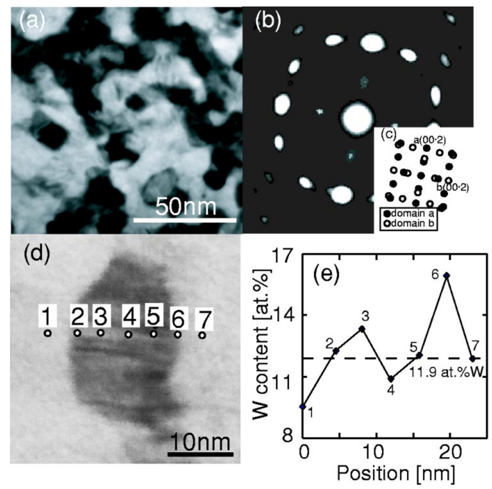

FIG. 3. Several kinds of data for Co-11.9 at % W film deposited at 573 K: (a) TEM bright-field image, (b) the corresponding SAD pattern, (c) the indexed-electron-diffraction pattern, (d) STEM bright-field image, and (e) the local composition at the numbered positions.

phase separation of the hcp phase takes place during the deposition.

The compositional fluctuation of W in the Co-W hcp alloy film was confirmed by STEM-EDX examinations and magnetic measurements. According to thermodynamic calculations,[13] a metastable two-phase miscibility gap of hcp associated with the Curie temperature line has been predicted; that is, this fluctuation is considered to occur due to the magnetically induced phase separation, just as the Co -Cr system.[5,10] However, the spread of the compositional fluctuation of W in the Co-W film is depressed in comparison with that of Co-Cr films,[12] although the calculated miscibility gap of the magnetically induced phase separation in Co-W system is very similar to that of the Co-Cr system.[11] In other words, the phase separation in the film does not arrive at the equilibrium state, which depends not only on the element diffusivity but also on the elastic energy introduced by the coherent lattice misfit between two phases.[14] The composition dependence of the lattice constant of the Co-W system is larger than that of the Co-Cr system,[15] and hence the effect of the elastic energy on the phase separation cannot be ignored. Therefore, the thermodynamic calculations have been conducted by taking the effect of the elastic energy into consideration. The free energy G is given by the sum of the chemical energy, G_{chem}, the magnetic contribution term, G_{mag}, and the elastic strain energy, E_{elastic}, as follows:

$$G = G_{\mathrm{chem}} + G_{\mathrm{mag}} + E_{\mathrm{elastic}}, \tag{1}$$

where G_{chem} and G_{mag} are described by a subregular solution model and the Hillert-Jarl description,[16] respectively, as in the previous reports.[5,11] E_{elastic} is expressed by Cahn[14] as

$$E_{\mathrm{elastic}} = \eta^2 Y (c - c_0)^2 V_m, \tag{2}$$

where η is the linear lattice expansion per unit composition change, V_m the molar volume, c the local composition, and c_0 the average composition. $Y=[2C_{11}+C_{33}+2(C_{12}+2C_{13}) -(C_{11}+C_{12}+C_{33})^2/C_{33}]/2$ is the elastic constant of the elastically soft direction which is the a-axis direction in hcp Co. Here, C_{ij} is the elastic stiffness constant. The values of Y and η are evaluated from the available data as 3.967[17] and 0.1222,[15] respectively.

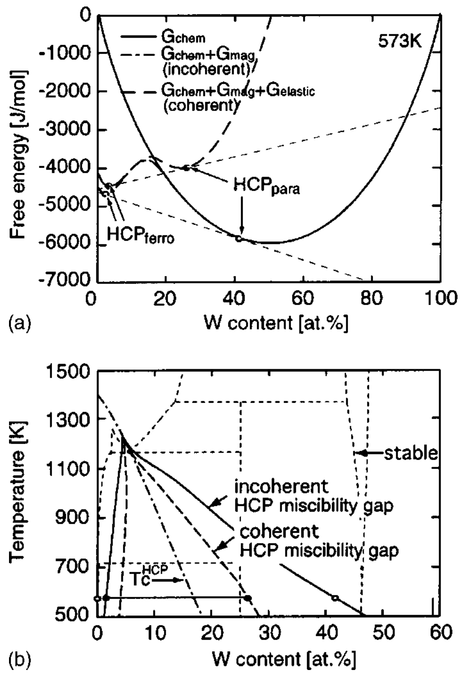

FIG. 4. Free-energy curves and phase diagrams of the Co-W alloy system: (a) Calculated free-energy composition curves at 573 K (details are given in the text), and (b) calculated phase equilibria. The dotted lines represent the stable phase diagram. The solid and dashed lines are the incoherent and coherent magnetically induced phase separations, respectively. The dot-dashed line stands for the Curie temperature T_C of the homogeneous hcp alloy.

The calculated free-energy composition curves are illustrated in Fig. 4(a). Since E_{elastic} is proportional to the square of compositional deviation, the difference between the free energy in the coherent and incoherent states increases with increasing W content. Figure 4(b) contours the calculated coherent and incoherent phase diagrams. The miscibility gap of the coherent phase diagram is narrower than that of the incoherent phase diagram. If the elastic constants vary with the composition, the miscibility gap of the coherent phase diagram should further be depressed, namely, the elastic energy is considered as the main reason for the depression of the magnetically induced phase separation in the film. It is expected that the elastic energy is relaxed by the addition of the third element and the deposition conditions. In addition, for magnetic recording media, it is preferred that a W-rich paramagnetic phase surrounds a Co-rich ferromagnetic phase. The microstructure is sensitive to the volume of each phase. The increase of the W-rich phase would bring about such desirable microstructures by changing the volume ratio of the matrix phase.

In summary, the magnetically induced phase separation of Co-W sputtered thin films has been investigated. The compositional fluctuation of W was directly confirmed in the film deposited on a heated substrate. The difference between the phase separation features in Co-W and Co-Cr originates from the difference in their elastic energy. It is expected that the phase separation is enhanced by selecting optimum sputtenng conditions. Consequently, the Co-W sputtered films are promising as next generation high-density magnetic recording media, because they exhibit the magnetically induced phase separation with a large magnetocrystalline anisotropy energy.

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