In situ growth of Co nanofibers in In_2O_3-SnO_2 matrix during sputtering deposition

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Abstract

Cosputtering onto (001) cubic zirconia from a target of indium tin oxide (ITO) partially covered by cobalt (Co) was carried out at substrate temperatures of 470-770 K in order to investigate the growth of Co nanofibers. During film growth, Co forms fibers in the growth direction in the single-crystalline ITO matrix. The cross section of the Co fibers, the size of which depends on the substrate temperature, was a rectangle with an edge 1-5 nm in length. The edge length of the Co fiber increased with the increase of the substrate temperature. The present method is attractive for application to produce magnetic recording media.

Recently, low-dimensional structures have received considerable attention from viewpoints of both scientific interest and technological application due to their characteristic properties, quite different from those of bulk materials.[1-8] These low-dimensional structures are usually used in fabrication methods such as multi-layer deposition,[2, 3] lithography[4] and so on,[5-8] but the process required to obtain the final form is complicated and entails many steps. In the study herein reported, we have adopted a self-assembling method during deposition to realize formation of an anisotropic nanostructure, which reflects anisotropic physical properties. If we are able to use this method resulting in the anisotropic nanostructure with high-density fibers, it would become a promising method for the manufacture of magnetic recording media. We previously reported a nanostructure formed by phase separation in sputtered Co ferrite ($CoFe_2O_4$) film.[9] In the film deposited at a substrate temperature of 670 K, Co fibers in the Co ferrite matrix grew in the growth direction of the film, i.e., perpendicular to the substrate of MgO. The cross section of the Co fiber was rectangular with a short axis of about 10 nm and a long axis of about 50 nm. This structure is a quite similar to that produced by eutectic solidification and eutectoid decomposition.[10, 11] Srolovitz and co-workers theoretically predicted the growth of fibers perpendicular to the substrate in the matrix during co-deposition of materials with a phase separation system.[12-14] If the phase separation during film growth is controlled by surface interdiffusion of atoms in the surface layer, the diameter of the fiber is proportional to the diffusion length of $\sqrt{D_s\,\delta/v}$, where D_s, δ and v are the surface diffusion coefficient, the width of surface layer and the growth rate, respectively.[12] The simulation of molecular dynamics, in which the bond energy difference due to the type of bonds was taken into consideration, showed that a fibrous structure was formed during film growth of the phase separation system.[13] Although the phase separation and formation of the fibrous structure during deposition have theoretically been predicted, few experimental results have been reported, except for the Co-$CoFe_2O_4$ system.

The purpose of the present study is to fabricate a film consisting of nano-sized Co fibers inside an ITO matrix during in situ film growth by using the cosputtering method and to estimate activation energy from the temperature dependence of the diameter of a Co fiber.

The substrates used in the present experiment were (001) cubic zirconia single crystals. Cosputtering onto a (001) cubic zirconia from an ITO target partially covered by Co was carried out at the substrate temperatures of 470-770 K. The sputtering onto the substrate at a rate of 0.6 nm/s was made in an argon gas atmosphere. The thickness of the films was 300 nm. Transmission electron microscopy(TEM) was employed extensively for examining plan-view of the samples by employing a JEOL ARM 1250. The plan-view samples were made by polishing and ion thinning of the samples from only the back side of the specimens. Magnetization measurements were carried out with a vibrating sample magnetometer (VSM) at a temperature of 293 K.

Shown in Fig. 1 (a) is a TEM image of the plane-view sample of the as-sputtered ITO-30vol%Co film deposited on a polished (001) cubic zirconia substrate of 670 K. The image shows fine dots in the matrix. Analysis of the electron diffraction pattern of an area revealed that the fine dots and matrix are the Co and ITO phases, respectively. This means that phase separation in the as-sputtered film was completed during film growth. Figure 1 (b) shows a bright field image taken with 18-degree tilting of the sample shown in Fig. 1(a). The fine dots observed in (a) were elongated in a one direction due to the tilting. The length of Co in the growth direction of the film can be estimated to be about 50 nm from the length of the elongated dots and the tilting angle. This value is regarded as the thickness of the foil, and then the Co fibers are confirmed as fibers elongating at least 50 nm in length in the film growth direction. The ITO matrix was epitaxially grown on the (001) cubic zirconia. The result of epitaxial growth of ITO on the cubic zirconia substrate implies that the diffusion of sputtered atoms as well as their condensation on the surface is mainly controlled by the interaction with the substrate surface, even though they have high kinetic energy.[15]

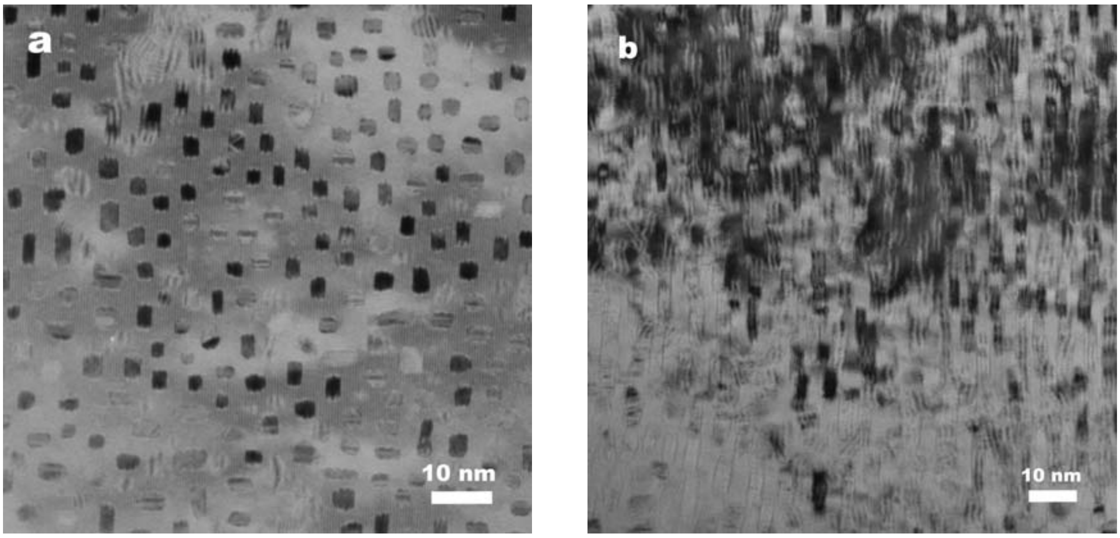

FIG.1. Transmission electron microscope(TEM) images of an ITO-30vol%Co film deposited at 670 K on (001) cubic zirconia. (a) TEM image showing the two-phase structure in a plane-view sample. The incident beam is parallel to the [001] direction of ITO. (b) Bright field image taken with 18 degrees tilting of the sample (a).

Figures 2 (a) and (b) show high resolution TEM images of the thin area of ITO-15vol%Co samples deposited at the substrate temperatures, (a) 570 K and (b) 670 K, respectively. The matrix is the ITO phase and the fibers are Co metal. The length of edge of the fiber regarded as the diameter depends on the substrate temperature. The diameter of the fiber becomes larger when the substrate temperature is higher.

When the substrate temperatures are 570 and 670 K, as shown in Fig. 2, the lengths of an edge of the Co fiber were 1.4 and 2.0 nm, respectively. These values are extremely small in comparison with nanoscale wires and cylinders prepared by an electrodeposition technique in nanoporous templates[4]. According to Atzmon et al., [12] the diameter of the fiber is proportional to $(D_s\delta/v)^{1/2}$, depending on the substrate temperature as mentioned above. Since the surface diffusion coefficient is related to $\exp(-Q/kT)$, the diameter of the fiber is proportional to $\sqrt{\exp(-Q/kT)}$. Here Q, k and T are the activation energy of the surface diffusion, the Boltzmann constant and the substrate temperature, respectively. The temperature dependence of the diameter of the fiber, d, is presented in Fig. 3. The ln d - 1/T plots for the samples with 15 and 30 vol% indicate different straight lines with the same gradient. For these samples, the activation energy estimated from the gradient of the straight lines is to be 0.5 eV, almost the same value each other. Even though there are few data on the surface diffusion coefficient, this estimated value is considered to be reasonable for consideration of the activation energy of the surface diffusion rather than that of the lattice diffusion.[16] These results indicate that the process of the fiber formation is controlled by the surface diffusion. It should be noted that the diameter of the Co fiber increases with the increase of the volume fraction of Co. The decrease of the surface diffusion length due to the decrease of the substrate temperature results in a decrease of the diameter of the fiber, accompanied by formation of a granular structure.

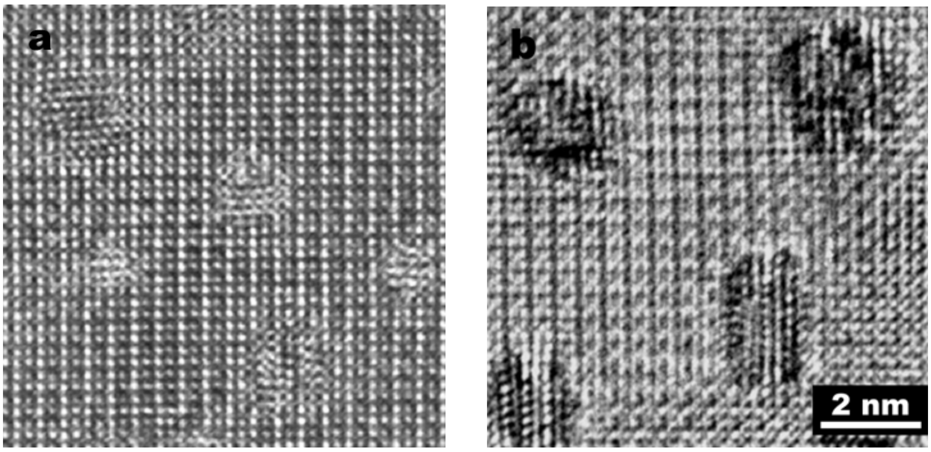

FIG.2. TEM images of a plan-view of the ITO-15vol%Co sample. Films were obtained by deposition on the substrate at temperatures, (a) 570 K, and (b) 670 K.

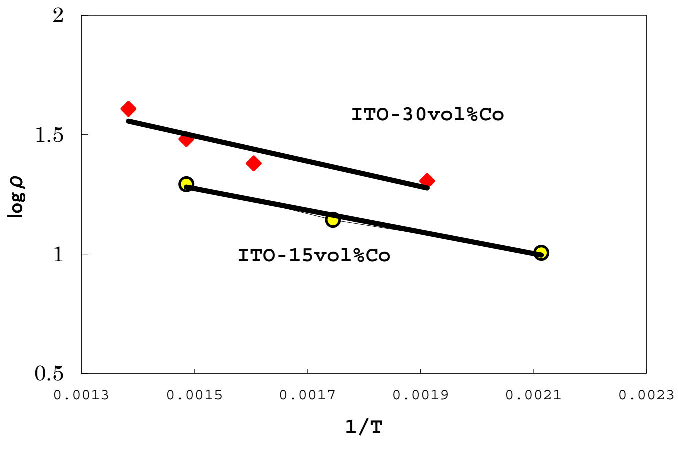

FIG.3. The ln d - 1/T plots for ITO-15 and 30 vol.% samples.

The magnetization curves normalized to the value at 15kOe are illustrated in Fig. 4 for the ITO-15 vol%Co film grown on the (001) zirconia substrate at the substrate temperature of 670 K. Two curves were obtained by applying magnetic fields to the in-plane (parallel) and out-of-plane (perpendicular) directions of the film. From the curves, the magnetic easy direction of the film is the out-of-plane direction. The electron diffraction patterns revealed that the Co fibers are grown in single crystal state in the $[11\bar{2}0]$ or $[1\bar{1}00]$ directions with the hcp structure. Co metal with the hcp exhibits a strong magnetocrystalline anisotropy in the [0001] direction, but the present perpendicular magnetic anisotropy of the film is originated from the shape magnetic anisotropy. Since the ferromagnetic materials are of a needle-like shape, the easy axis of magnetization develops along the long axis of the needle, indicating that the Co fibers are aligned and grow in the direction of growth in good agreement with the image shown in Fig. 1. Arrays of high density of ferromagnetic nanowires have been studied by a process based on electrodeposition of ferromagnetic metals into the nanopores of acid-anordized aluminum oxide (alumite).[17, 18] In comparison with the method mentioned above, the present method is attractive for application to magnetic recording media because of the ability to produce the highly controlled arrays of nanofibers through changing the substrate temperature and the volume faction of metal.

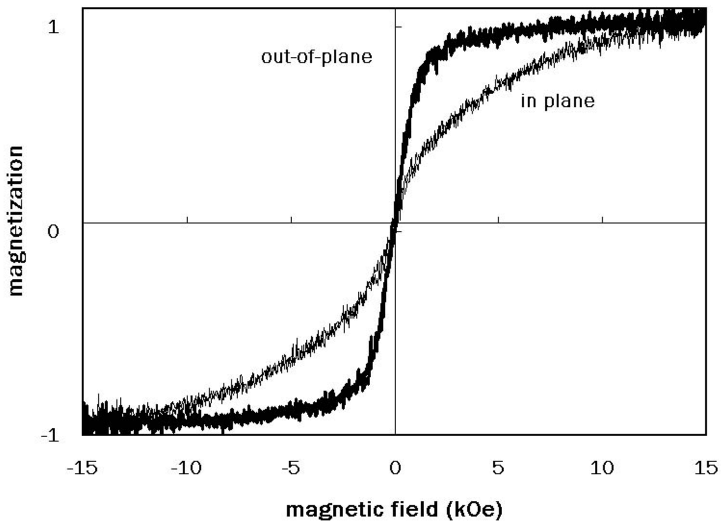

FIG.4. Magnetization curves in-plane and out-of-plane magnetic fields for the ITO-15 vol%Co film grown at 670 K on (001) cubic zirconia.

In conclusion, we have succeeded in preparation of a film having nano-sized *in situ* growth of Co with an edge 1-5 nm in length in the ITO matrix by cosputtering onto a heated single crystal substrate. The cross-section size of the Co fibers is controlled by the substrate temperature as well as the volume fraction of Co.

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