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Epitaxial Growth of Faceted Co Nanoparticles on Sapphire Surfaces

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Crystalline Co nanoparticles with unique faceted structures are synthesized on the sapphire substrate by annealing a sputtered Co film in H_2 atmosphere. The high-temperature sputtering stimulates the epitaxial growth of the Co film, leading to the formation of ordered Co nanoparticles upon H_2 annealing. The crystal structure of the Co nanoparticles is discussed.

Thin films of Co and Co-alloys have been intensively studied because of scientific interest in the phase transition of Co metal from a hexagonal close-packed (hcp) structure to a high-temperature stable face-centered cubic (fcc) structure at a temperature ca. 415 °C and their applications in giant magnetoresistive (GMR) devices and magnetic recording media.[1] Most research has focused on the growth and characterization of epitaxial thin Co films deposited on single crystalline substrates.[2–7]

Recently, metal nanoparticles have attracted great interest because of their unique properties. Co and Co-alloy nanoparticles are especially interesting in terms of the magnetic and catalytic properties. Also, the Co nanoparticles are used for the catalytic growth of carbon nanotubes (CNTs).[8,9] Decomposition of hydrocarbon molecules and formation of graphene structure occur on the Co nanoparticle. However, in contrast to the thin Co films, the Co and related nanoparticles have not been well studied.

In this Letter, we demonstrate that crystalline Co metal nanoparticles are formed epitaxially on sapphire substrates without using capping reagents. The nanoparticles were obtained by simply annealing a sputtered Co film under a H_2 flow. The sputtering temperature and the crystal plane of the sapphire substrate greatly influence the structure of Co nanoparticles.

A 10-nm-thick Co film was deposited on a sapphire substrate by radio frequency (RF) magnetron sputtering with power and pressure of 200 W and Ar 0.6 Pa, respectively. Three different substrate temperatures, room temperature (RT), 300 °C, and 500 °C, were used during the sputtering. Crystal-plane dependence was also studied by using *a*-plane $(11\bar{2}0)$, *r*-plane $(1\bar{1}02)$, and *c*-plane (0001) sapphire substrates. The sputtered Co film was annealed at 900 °C for 10 min in a 80 sccm H_2 flow under atmospheric pressure, which converts the thin film to nanoparticles.

Figures 1a–1c show scanning electron microscope (SEM) images of the Co/*a*-plane surface taken after H_2 annealing. As-sputtered Co films showed a continuous film structure from SEM observation (not shown). Thus, H_2 annealing induced the structural change from the Co film to the Co nanoparticles. Interestingly, the structure of the Co nanoparticles was strongly dependent on the sputtering temperature. The RT-sputtered film gave a disordered film-like morphology together with inhomogeneous nanoparticles (Figure 1a). These nanoparticles showed irregular shapes with broad distribution in their size. The 300 °C-sputtered film gave clearer nanoparticles, as seen in Figure 1b, although the nanoparticle shape and orientation are still not uniform. In addition, the sapphire surface was slightly covered with residual Co metal. We found that a film sputtered at 500 °C gave well-defined nanoparticles. They show a clear faceted structure, which indicates that the Co metal is well crystallized. The sapphire surface was clean, and the particle size was smaller than that prepared at the 300 °C sputtering; the average particle sizes are 300 and 181 nm for the samples sputtered at 300 and 500 °C, respectively (Figure 1d). Our results suggest that sputtering temperature modifies the crystallinity of the original Co film and, consequently, influences the nanoparticle structure. This indicates that high-temperature sputtering stimulates the epitaxial metal film deposition, as reported for the epitaxial Co film deposited on a MgO(001) substrate.[10] Although the Co nanoparticles have faceted structure, their orientation is not uniform. The nanoparticle formation occurs via Ostwald's ripening, i.e., diffusion of Co atom to Co nanoparticles increases their size. As the diffusion occurs in different directions, the as-formed Co nanoparticles have several facet orientations.

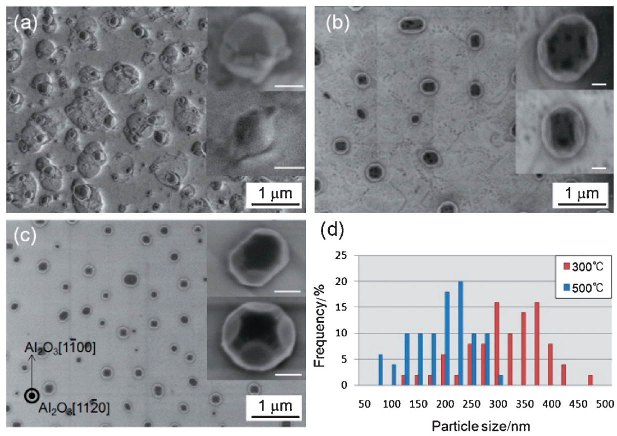

Figure 1. SEM images of Co/a-plane sapphire surface taken after H_2 annealing at 900 °C. The sputtering temperature is (a) RT, (b) 300 °C, and (c) 500 °C. Insets show the magnified images of typical Co nanoparticles (scale bars are 100 nm). (d) Histograms of nanoparticle width determined from the SEM images ($N = 50$).

To investigate the crystallographic orientation, we measured the X-ray diffraction (XRD) profiles for the H_2 annealed samples, as displayed in Figure 2. Typically, two diffraction peaks were obtained from the Co metal; a peak at ca. 44°

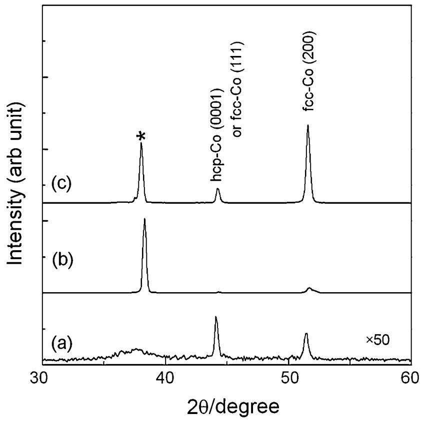

Figure 2. XRD profiles of Co/*a*-plane sapphire samples annealed in H_2 at 900 °C. The substrate temperature during the Co sputtering is (a) RT, (b) 300 °C, and (c) 500 °C. Asterisk indicates the peak from the sapphire substrate.

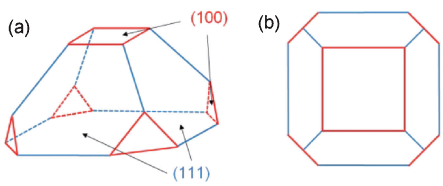

Figure 3. A proposed model of the faceted Co nanoparticles observed for the 500 °C-sputtered sample. (a) Three-dimensional image and (b) top view.

assigned to the hcp(0001) and/or fcc(111) Co diffractions, and a peak at ca. 52° assigned to the fcc(200) Co diffraction. The RT-sputtered sample showed very weak diffraction peaks, which suggests the amorphous and/or polycrystalline nature. Since the nanoparticles showed irregular faceted structures (Figure 1a), we think that polycrystal nanoparticles with very small grain size were formed after H_2 annealing. As the sputtering temperature increases, the diffraction peaks became stronger and sharper. The 500 °C-sputtered sample showed an intense fcc(200) peak. Thus, it is likely that the Co nanoparticles mostly have an fcc structure which is a stable phase at high temperature. Shi and Lederman reported that a thin Co film deposited on an *a*-plane sapphire transforms from fcc(111) to fcc(100) when the film is annealed at >500 °C.[11] Our result is consistent because the annealing temperature (900 °C) is much higher than this transition temperature.

Figure 3 shows a proposed crystal model of the Co nanoparticles expected for the 500 °C-sputtered sample (see Figure 1c inset). From the XRD pattern, the top surface is assumed to be fcc(100) plane. According to Wulff's theorem,[12] the crystalline particle can have an equilibrium form which minimizes the surface energy. In the case of fcc Co metal, the nanoparticle shape is expected to be octahedron consisting of stable {111} planes. The model in Figure 3 is the half-octahedron with truncated with {100} planes at the corner. Thus, our model qualitatively agrees with the Wulff's theorem. In this case, the crystalline orientation is expressed with Co(100)//Al_2O_3(11$\bar{2}$0); Co[110]//Al_2O_3[1$\bar{1}$00].

Finally, we discuss effects of the sapphire crystal plane and annealing atmosphere. On *c*-plane sapphire, unordered Co nanoparticles were mainly obtained. Although some faceted nanoparticles were observed, their orientation was random. The Co nanoparticles formed on the *r*-plane showed a similar structure to that on a-plane. The orientation of the Co nanoparticle against *r*-plane sapphire was assigned as Co(100)//Al_2O_3(1$\bar{1}$02); Co[010]//Al_2O_3[1$\bar{1}$0$\bar{1}$]. We also note that the similar faceted structure was observed when annealed in vacuum (10^{-4} Pa), while Ar annealing gave irregular nanoparticle structures. Thus, the sapphire crystal plane and annealing atmosphere are important for the control of Co nanoparticles.

In summary, crystalline Co nanoparticles with unique faceted structure were obtained on *a*- and *r*-plane sapphire substrates. The nanoparticles showed half-octahedron with truncated edges that can be explained by Wulff's theorem. Our growth method is simple and does not require any capping reagents and solvents. It is reported that the graphene film is formed epitaxially on the Ni(111) surface.[13] The orientation of the graphene coincides with the underneath metal film. Therefore, applying faceted Co nanoparticles to CNTs growth is interesting from the possibility of controlling nanotube chirality, because our method gives the crystalline Co nanoparticle with (111) plane and the growth direction of nanotubes is determined by the sapphire surface.[14] Further study to reduce the Co nanoparticle size is underway to apply to the controlled CNTs growth.

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