Preparation and Coercivity of Cobalt Ultrafine Particles by Reduction of Multilayered CoO–SiO Films

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Films containing Co ultrafine particles were prepared by hydrogen reduction of periodically multilayered CoO–SiO films which were formed by alternating deposition of CoO and SiO. The films containing Co particles maintained the periodicity similar to the original films. Using samples of CoO single layer sandwiched between SiO layers, highly dispersed Co particles in the reduced sample were observed by transmission electron microscopy. The average size of the Co particles was almost as large as the thickness of CoO layer. The coercivities of the multilayered films containing Co particles were measured at room temperature and 77 K; they decreased with decreasing particle size from 20 nm to 3nm. Superparamagnetism was observed for the Co particles with average sizes below 4nm at room temperature. The formation and the magnetic property of the Co ultrafine particles in the Co–SiO system is dicussed.

Periodically multilayered films composed of two substances have been investigated as a means of producing materials having unusual properties.[1–4] Studies of multilayered films have been limited to their structure and physical properties such as their magnetic, electric and mechanical behavior. The present paper deals with chemical change of multilayered films of CoO–SiO. Silicon oxide ($SiO \sim SiO_2$) has been used as a coating for passivation of semiconductor devices and for coating ultrafine particles.

It has been reported that the coating of precursor particles, such as hydroxides and oxides with silicon compounds frequently has a great effect on the shape and size of metallic or oxide particles prepared by reduction or decomposition of the precursor.[5,6] The role of the silicon oxide in the reduction or decomposition process has not been made clear.

In multilayered CoO–SiO films, a CoO layer is coated with SiO layers. The reduction of the CoO layers in the multilayered film may therefore be similar to that of oxide precursor particles coated with silicon compounds which change into silicon oxide. Investigations of the reduction of multilayered CoO–SiO films contribute to the elucidation of the role of silicon oxide in the preparation of ultrafine particles.

SiO is readily evaporated and the deposited SiO is amorphous. SiO films have strong adhesion to various substrates, environmental stability, and superior mechanical properties. These properties improve the quality of the the multilayered films. Silicon oxide is oxidized during deposition process and its composition (SiO_{1+x}) depends on deposition parameters such as the evaporation rate, the substrate temperature and the degree of vacuum. Hereafter, SiO_{1+x} will be expressed as SiO. Since the thickness of the silicon oxide coating on the oxide or metal particles is considered to be below 2 nm, it is desirable that the SiO layer used in the present experiment be as thin as possible within the limits of a continuous films. We chose 1.5 nm as a suitable layer thickness of SiO.

Fine particles of Co are readily prepared by hydrogen reduction of CoO at a low temperature. Furthermore, Co ultrafine particles have many interesting properties as magnetic materials and catalysts. Therefore, CoO is the most suitable as a constituent of multilayered films for our purpose.

CoO ultrathin films can be prepared by reactive evaporation.[7] Periodically multilayered films may be prepared by alternating deposition of CoO and SiO.

Experimentals

SiO was deposited by evaporation of SiO in a vacuum of 10^{-4}Pa and CoO was reactively deposited by evaporation of Co metal in oxygen at a pressure of 5×10^{-2}Pa. The thickness and deposition rate of each layer were monitored by an oscillating quartz sensor. The deposition rates of both CoO and SiO were 0.1 nm s^{-1}. The thickness of the SiO layers was chosen to be at 1.5 nm and those of CoO layers were designed to be 1.5 to 20 nm. Glass plates and polyimide films were used as substrates (glass for X-ray diffraction and polyimide films for magnetic measurements). During deposition, the substrate was kept at room temperature by water cooling. Reduction of the multilayered films was achieved by heating them in a hydrogen atmosphere at 200 °C for 1 h. The CoO–SiO films and the reduced films were examined by X-ray diffraction (RIGAKU ROTAFLEX RU-200) using Cu $K\alpha$ radiation and transmission electron microscopy (JEOL JEM-100CX and JEM-200CX). The magnetic properties of the reduced films were measured by a vibrating-sample magnetometer (TOEI VSM-3).

Results

Reduction of the Multilayered CoO–SiO Films. The cobalt oxide layers in the as-deposited film were identified to be CoO by X-ray diffraction, as shown in Fig. 1(a). As-reduced films were black and lustrous. X-ray diffraction showed that there was mainly hcp Co metal in the reduced films as shown in Fig. 1(b). However, the existence of the fcc phase was confirmed by electron diffraction of the reduced film as shown in Fig. 1(c); this includes the (200) ring of fcc Co. These results of X-ray and electron diffractions thus showed that both hcp and fcc Co exist in the reduced films, but the amount of the fcc phase is small.

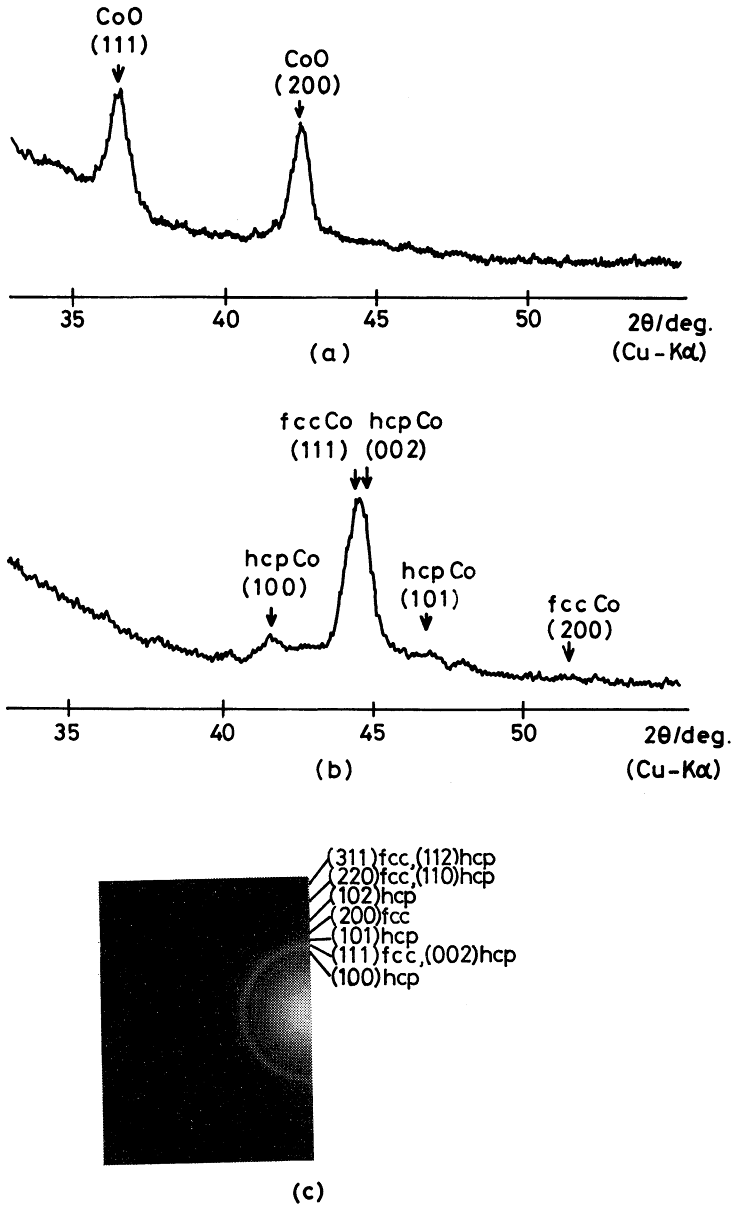

Fig. 1. (a) X-Ray diffraction pattern of the as-deposited [CoO(13.5 nm)-SiO(1.5 nm)]×10. (b) X-Ray diffraction pattern of the reduced [CoO(13.5 nm)-SiO(1.5 nm)]×10. (c) Transmission electron diffraction pattern of the reduced [SiO(10 nm)-CoO(15 nm)-SiO(3 nm)].

Periodicity of the Multilayered Films Before and after Reduction. The periods of composition modulation in the multilayered films were determined by low angle X-ray diffraction. The 2nd and 3rd Bragg diffraction peaks for the as-deposited film were observed as shown in Fig. 2(a), and the period calculated from diffraction angles was in good agreement with the designed period.

As shown in Fig. 2(b), the value of period of the reduced film is almost the same as that of the as-deposited films. This means that the periodicity persists during reduction and the thickness of the Co layers is similar to that of CoO layers, as the thickness of SiO layer should be invariable.

Reduction of Single CoO Layer Sandwiched in between SiO Layers. The samples of single CoO layer sandwiched in between SiO were prepared as follows. The CoO layer was deposited on SiO support film on a mesh for electron microscopic observation and was coated by a SiO film. The single CoO layer was directly examined by TEM, as shown in Fig. 5. The electron diffraction pattern shows CoO and the micrograph shows a continuous film consisting of microcrystallites. Results of TEM examination for the sample after heated in H_2 at 200 °C are shown in Fig. 6. The diffraction pattern indicated metallic Co with the hcp and fcc structures; this is consistent with the pattern in Fig. 1(c). Co ultrafine particles with

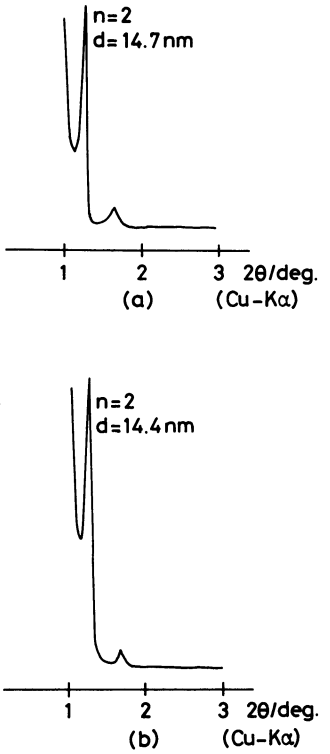

Fig. 2. (a) Low angle X-ray diffraction pattern of the as-deposited [CoO(13.5 nm)-SiO(1.5 nm)]×10. (b) Low angle X-ray diffraction pattern of the reduced [CoO(13.5 nm)-SiO(1.5 nm)]×10.

sizes ranging from 4 to 20 nm were clearly observed in microphotograph of a sample prepared by reducing the 9 nm thick CoO layer. For the 5 nm thick CoO layer, the size of the Co particles in the reduced sample ranged from 2.5 nm to 8 nm, as shown in Fig. 7(a). The average size of the Co particles is close to the value for the thickness of the original CoO layer. The lattice image of a Co particle shown in Fig. 7(b) indicates that the particle is a single crystal.

Magnetic Measurement of the Reduced Films. The reduced films showed ferromagnetism with typical hysteresis loops. Figure 3 shows the coercive force *Hc* measured at room temperature as a function of the thickness of Co layer. *Hc* decreased with decreasing Co layer thickness and became zero below 4 nm thick. The magnetic curves of films with 4 nm or less thick Co layers were superparamagnetic. When the magnetic curves were measured at 77 K, *Hc* for the film containing 4 nm thick Co layers was as high as 63 kA/m, as shown in Fig. 4. These magnetic data for the reduced films show that they contain metallic Co which is highly dispersed in ultrafine particles.

Discussion

It is clear from the experimental results that ultrafine Co particles are prepared by reducing the CoO–SiO multilayered film in H_2. Furthermore, it is surprising that the reduced films containing Co particles have the periodicity of composition modulation. This means that SiO layer as thin as 1.5 nm supports the multilayered structure during reduction, as shown in Fig. 8. The reduction of CoO to Co would not occur at once. When a CoO layer sandwiched between SiO

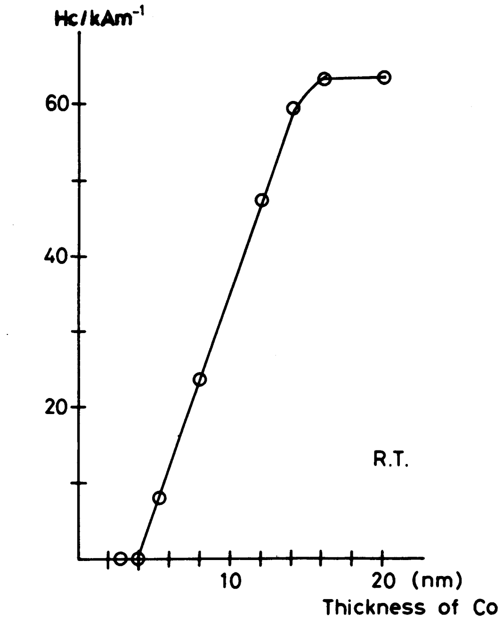

Fig. 3. Coercive force *Hc* measured at room temperature as a function of thickness of Co layer. Total thickness of Co layers in each film was fitted to be about 100 nm.

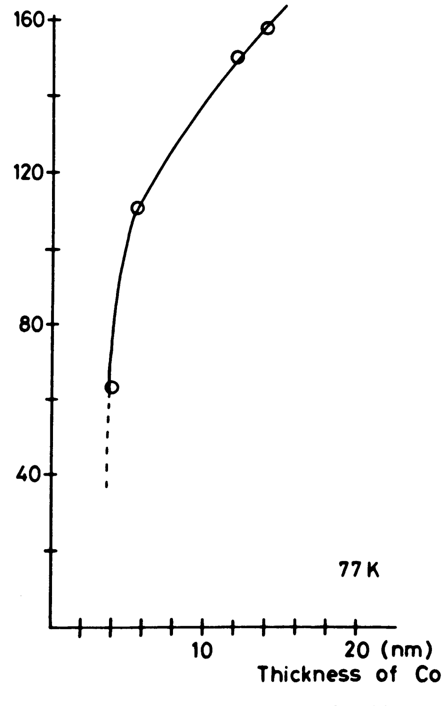

Fig. 4. Coercive force *Hc* measured at 77 K as a function of thickness of Co layer.

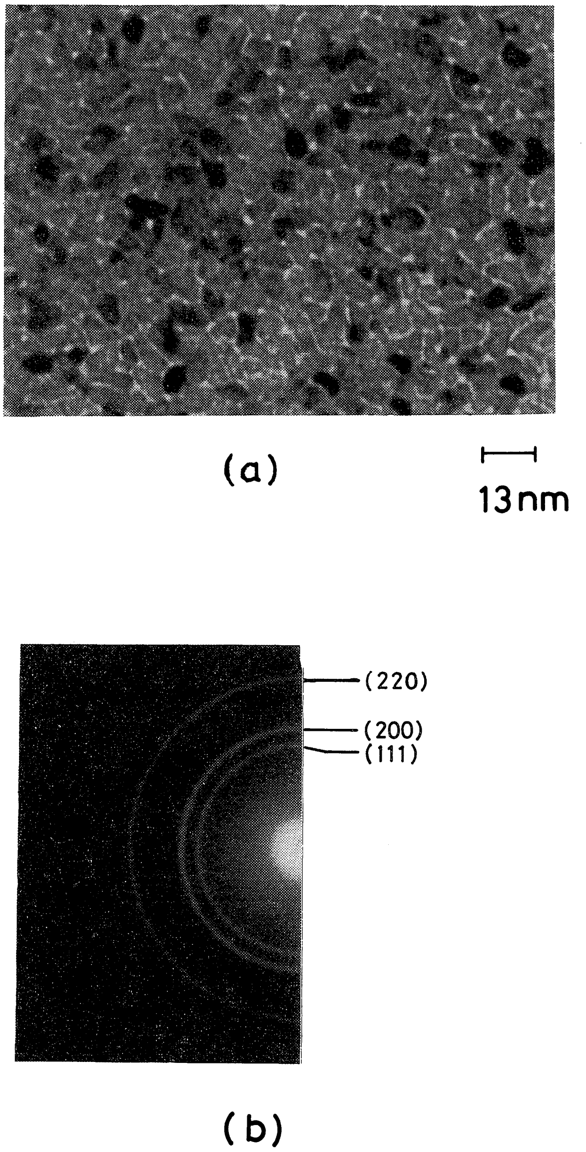

Fig. 5. (a) TEM image of the as-deposited [SiO(10 nm)-CoO(10 nm)-SiO(3 nm)]. (b) Transmission electron diffraction pattern of the same sample.

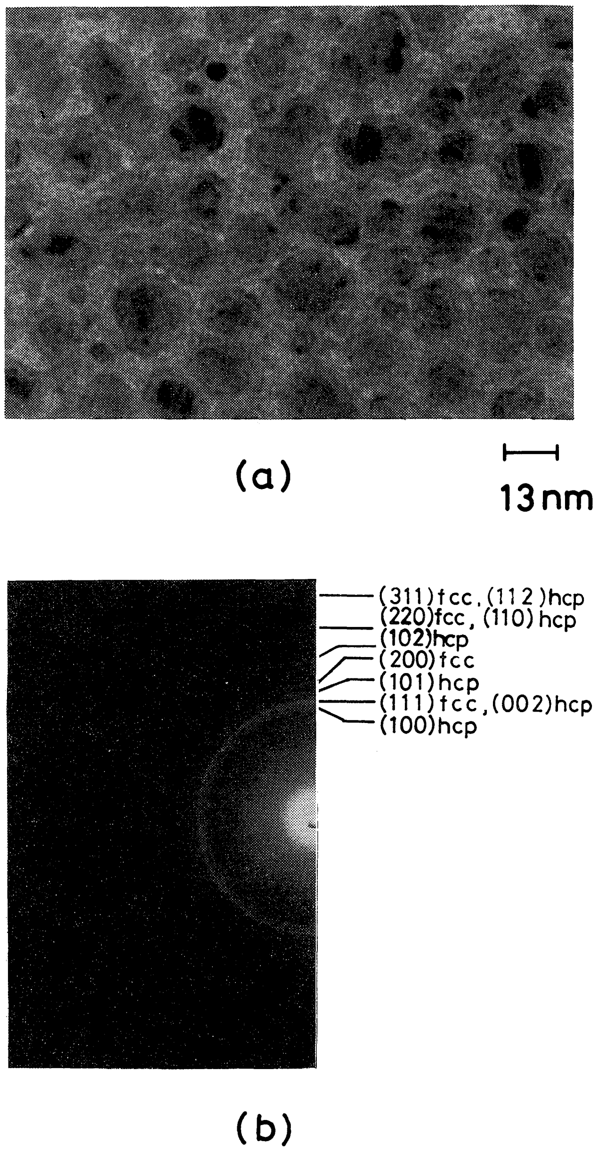

Fig. 6. (a) TEM image of [SiO(10 nm)-Co(10 nm)-SiO(3 nm)]. (b) Transmission electron diffraction pattern of the same sample.

films is reduced, some portions of the layer would remain as CoO and maintain the original SiO-SiO interlayer distance. When the remaining CoO is successively reduced, the Co particles already formed would maintain the interlayer distance. When CoO changes into Co, the volume reduces to about a half; this comes from the release of oxygen and an increase of the density from 6.3×10^3 kg m^{-3} for CoO to 8.9×10^3 kg m^{-3} for Co.

The formation of the highly dispersed ultrafine particles is caused by both of the constant SiO-SiO interlayer distance before and after reduction and of the volume decrease from CoO to Co. If the Co particles have the shape of columns with a diameter and a height equal to CoO layer thickness d and arrayed in a regular triangular lattice, as shown in Fig. 9, the distance between the nearest neighbor columns is calculated to be 1.35 d, showing formation of isolated particles.

The Co ultrafine particles less than 20 nm constitute a single magnetic domain. For an assembly of single domain particles with the easy axes oriented at random, in a non-ferromagnetic matrix, the value of Hc is expressed as follows:[8]

$$Hc = 0.48 \times 2\,K/Is \qquad (1)$$

where K is the magnetic anisotropy energy constant and Is is the saturation magnetization. Using $Is=1.79$ T[9] and $K=4.6\times10^5$ Jm^{-3}[10] for hcp Co, Hc would be about 247 kAm^{-1}. In Fig. 3, maximum coercivity of 63 kAm^{-1} is considerably lower compared with the calculated value. K value for fcc Co is considered to be as large as 2×10^4 Jm^{-3},[11] and Hc would be about 11 kAm^{-1}.

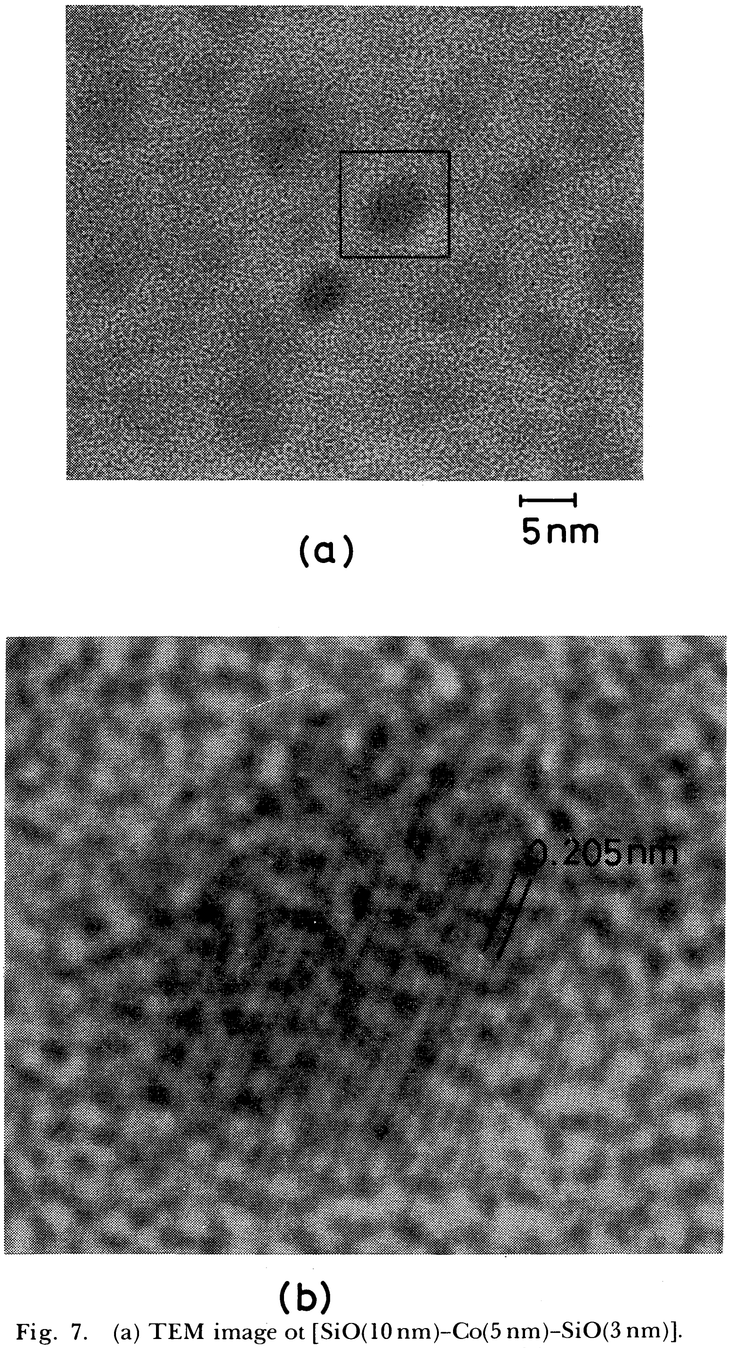

Fig. 7. (a) TEM image ot [SiO(10 nm)-Co(5 nm)-SiO(3 nm)]. (b) The lattice image of the particle indicated in (a).

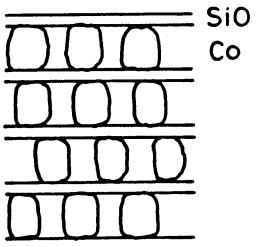

Fig. 8. Schematical illustration of the multilayered structure containing Co particles supported by continuous SiO layers.

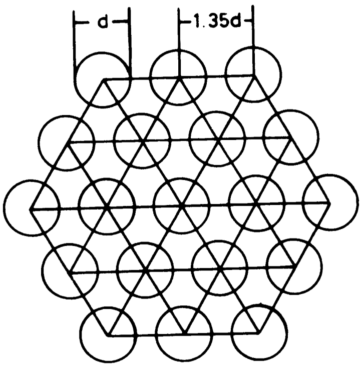

Fig. 9. Schematical illustration of the location and size of the reduced Co particles in film plane.

If the assembly of Co particles consists of both the fcc and the hcp particles, the low value of Hc obtained suggests that the amount of the fcc phase particles should be more than that of the hcp particles. However, the results of X-ray and electron diffraction measurements indicated only a small amount of the fcc phase. As the difference between the free energies of fcc and hcp in Co metal is small, a particle may frequently contain both phases; the fcc stacking may be regarded as stacking faults in the hcp phase.

Therefore, individual particles obtained may contain both phases. The existence of the fcc phase in the hcp Co may decrease the large uniaxial magnetic anisotropy energy due to hexagonal symmetry.

Using Is=1.79 T and Hc=63 kAm^{-1} of the experimental value, K would be 1.2×10^5 Jm^{-3}. Using this K value, we can calculate the critical size for superparamagnetism at room temperature by the expression,[11]

$$\tau = \tau_0 \times \exp(KV/kT) \qquad (2)$$

where τ is the superparamagnetic relaxation time, τ_0 is the frequency factor, V is the magnetic volume of the particles, k is Boltzman's constant and T is the temperature. When the coercivity is zero for a static magnetic measurement, τ is of the order of 10^2 s. The blocking temperature T_B is defined as the temperature below which the particles show ferromagnetism, i.e., the temperature at which τ is of the order of 10^2 s. The critical size for superparamagnetism at room temperature is calculated by the relation $KV/kT=25$, assuming $\tau_0=10^{-9}$ s and $\tau=10^2$ s. The diameter calculated for column particles is 10.3 nm. In Fig. 6, the average size is 9 nm, but the sizes are distributed from 20 nm to 4 nm. The decrease in Hc for particle diameters below 1.6 nm in Fig. 3 is attributed to the presence of the superparamagnetic particles. With decreasing thickness, the ratio of the superparamagnetic particles increases and the value of Hc drops abruptly. It is reasonable that the particles with an average size of 9 nm have half the value of the maximum coercivity. At 77 K, the value of the anisotropy would be estimated to be 3.0×10^5 Jm^{-3} from maximum Hc=160 kAm^{-1}. The critical size for superparamagnetism is 4.8 nm; this is reasonable in consideration of the value of the coercivity of the Co particles with an average size of 5 nm.

So far, we have discussed the K value and the critical size for superparamagnetism on the assumption that the fcc phase exists within the hcp Co particles. The calculated values are in good agreement with the observed ones, which indicates that our assumption is reasonable.

The values of Is and Hc in the reduced films persisted over 1 year or longer. Therefore, SiO is a good protector to oxidation of Co ultrafine particles. On the other hand, SiO-coated CoO is readily reduced to Co at 200°C; accordingly oxygen atoms should be able to pass through SiO layer. Furthermore, it is clear that SiO has a function to support the original shape of the starting material such as the multilayered structure during reduction. It is concluded that these characteristics of SiO as a coating make it suitable for use in the preparation of metallic or oxide ultrafine particles for magnetic recording media and catalyst.

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