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Preparation of Nanocrystalline Fe Films by Low Energy Cluster Deposition Using a Sputter Cluster Source

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Nanocrystalline Fe films were obtained by the deposition of Fe clusters. Clusters were created by a hollow cathode sputtering at a high pressure in the range of hundreds of Pa, and were directly deposited on the substrate. In this experiment, Fe clusters with mean diameters of 2 nm, 4 nm and 6 nm were deposited on a glass substrate, and the structures and magnetic properties of resultant films with thicknesses of 100 nm to 300 nm were investigated. Although the films were found to be composed of small crystallites, the crystallite size determined from XRD peak-width was not proportional to the cluster size. The crystallite sizes of the films obtained by deposition of clusters of 2 nm, 4 nm and 6 nm in diameter were 12 nm, 8 nm and 6 nm, respectively. Such nanocrystalline Fe films had a large coercive force of about 250 Oe.

Key words: iron film, cluster deposition, sputtering, sputtered film, gas flow sputtering

1. INTRODUCTION

Nanocrystalline soft magnetic materials are derived from crystallizing amorphous ribbons of specific chemistries of (Fe,B)-based alloys [1]. The soft magnetic behavior in these materials arises from a spatial averaging of the magnetic anisotropy of the aggregate of randomly oriented nanosized particles, and smaller grains are thought to result in softer magnetic properties [2], [3]. Material selection and size control are often haunted by the problems of miscibility and post-processing. The usual dimensions of the grains or granules are in the range of a few nm to 10 nm. Particles of these sizes can be produced reproducibly by a gas aggregation process. Thus, deposition of Fe clusters could be used as a method of *in-situ* production of nanocrystalline soft magnetic materials. Various cluster depositions have been studied in recent years [4]-[6], but soft magnetic materials have never been prepared.

Several types of gas aggregation sources utilizing thermal evaporation [7], electrical arc erosion [6], sputtering [8], and laser vaporization [9] have been developed for the purpose of low-energy deposition of small particles. Sputtering, as a cluster source, is very versatile, allowing various alloys and compounds to be applied and small clusters with a sharp size distribution to be obtained. However, deposition rates using sputtering are low compared with those by other methods such as thermal evaporation or arc erosion. A low deposition rate often leads to severe oxidation of the deposits and difficulty in varying deposition parameters. The use of gas flow sputtering (GFS) using a hollow cathode discharge enables a deposition rate much higher than the rate that is possible by conventional sputtering to be obtained [10].

In this work, we deposited Fe clusters on a substrate by using GFS, and we investigated the structures and magnetic properties of resultant films in order to explore the possibility of using this process for the production of nanocrystalline Fe films with soft magnetic properties.

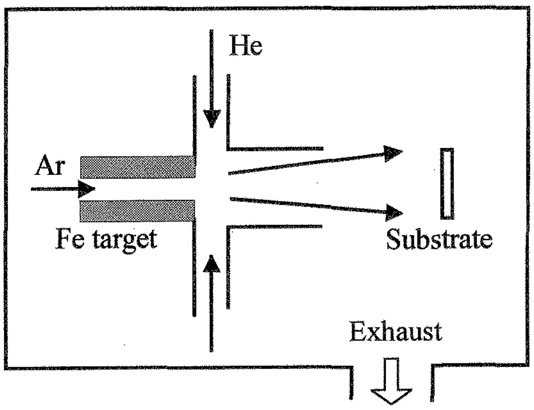

Fig. 1. Schematic diagram of the set-up for the cluster deposition with low energy.

2. EXPERIMENT

Figure 1 shows a schematic illustration of the set-up used for the Fe-cluster deposition. The cluster source has been described in detail elsewhere [10]. This source operates on the principle of GFS, i.e., GFS is a process of sputtering conducted at around 100 Pa using a hollow cathode (target). Since the mean free path of sputtered atoms is less than 0.1 mm in such an atmosphere, they are thermalized by collisions with sputtering gas (Ar) near the target. As a consequence, thermalized vapor whose kinetic energy is equal to thermal energy of atmospheric Ar gas is created. The thermalized vapor is transported by the forced Ar flow that is streaming through the target and sprayed onto the substrate. When the vapor is supersaturated, which is generally the case for metals and semiconductors, the vapor atoms condense into clusters in Ar gas, and resultant clusters can be deposited on the substrate. The deposition of vapor or clusters can be controlled by changing the sputtering conditions. This is a unique advantage of GFS compared with conventional techniques.

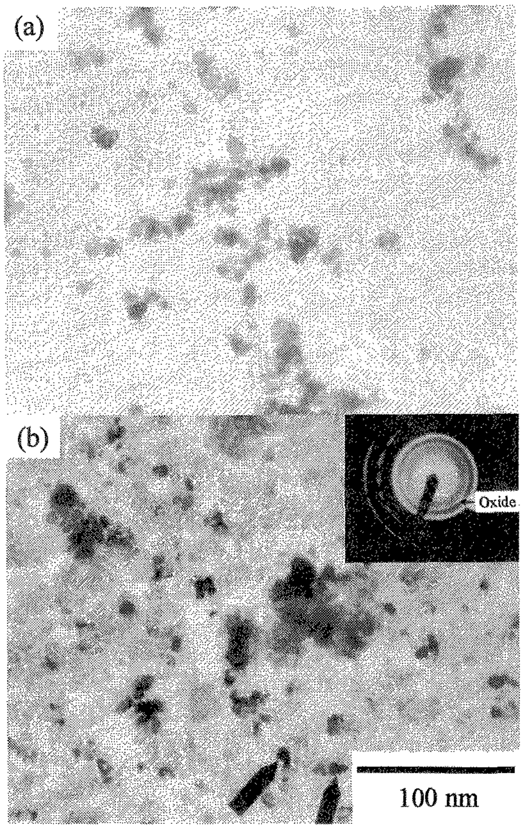

Fig. 2. Typical TEM images of Fe clusters of 6 nm in diameter deposited on an amorphous carbon coated grid; (a) the deposition time was 10 s, (b) the deposition time was 3 min.

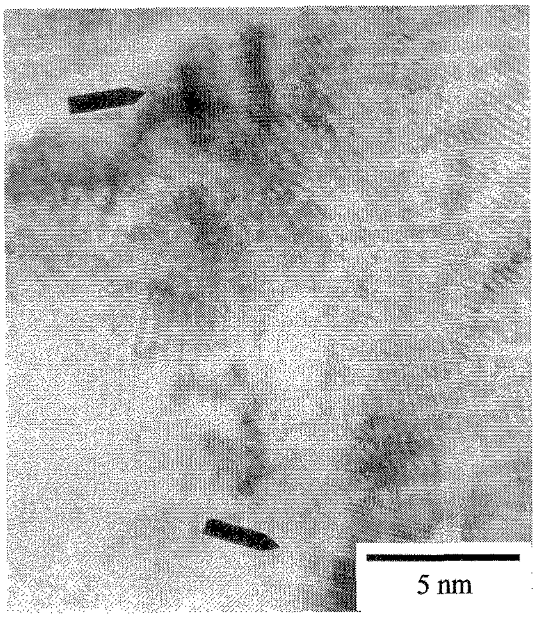

Fig. 3. High-resolution image of Fig. 2(b). The arrows indicate the grains whose lattice image corresponds to the (110) lattice of α-Fe.

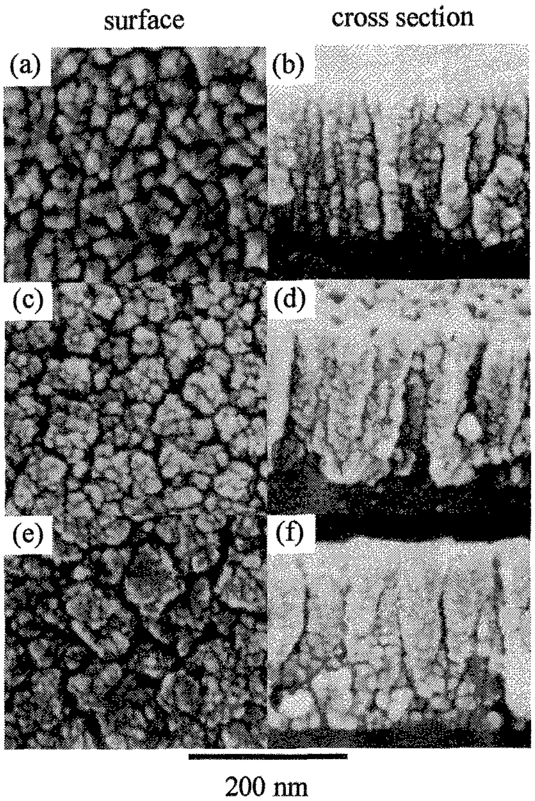

Fig. 4. SEM images of surfaces and cross sections of thick Fe films obtained by deposition of clusters of, (a) and (b) 2 nm, (c) and (d) 4 nm, (e) and (f) 6 nm, in diameter.

A small Fe pipe with the inner diameter of 6 mm and length of 60 mm was used as the target, and He gas was injected through many small holes arranged with the same separation around the target holder, while Ar gas was used for sputtering (Fig.1). The flow rates of Ar and He were 500 sccm and 750 sccm, respectively. The total pressure in the chamber was 300 Pa during sputtering, while the base pressure was $6.5x10^{-5}$ Pa. The discharge current was fixed at 1.5 A. The sizes of supported clusters, measured under a transmission electron microscope (TEM), depended on the operating conditions of the source [10] and also on the distance from the target. Small clusters with a mean diameter of ≈2 nm were obtained at 7 cm from the target, and clusters with a mean diameter of 4 nm were obtained at 11 cm from the target. The cluster size increased with increase in distance from the target but did not exceed 6 nm at the distance over 15 cm. The glass substrates were placed at positions 7 cm, 11 cm and 16 cm from the target, and the deposition of clusters of three different sizes was investigated. The temperature of the substrate increased to a higher value near the target. At 7 cm from the target, it increased to about 80 ℃ during the deposition.

The structures of the samples were examined under a TEM and a scanning electron microscope (SEM). The crystal structure was studied by x-ray diffraction (XRD), and the magnetic properties were measured using a vibrating sample magnetometer (VSM).

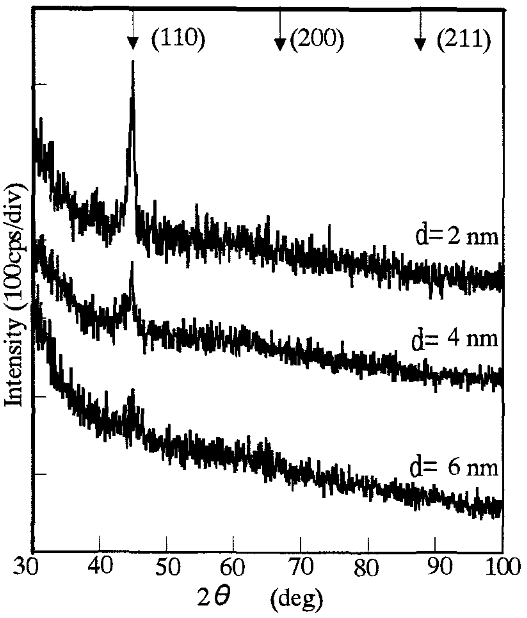

Fig. 5. XRD patterns of the films shown in Fig. 4.

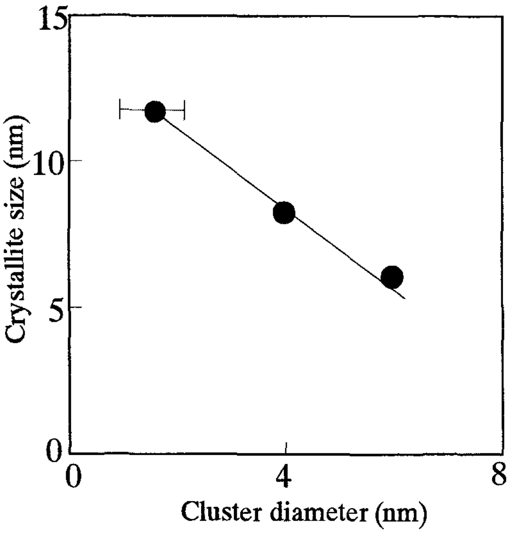

Fig. 6. The crystallite size derived from the peak-width of (110) reflection in XRD as the function of mean diameter of depositing clusters.

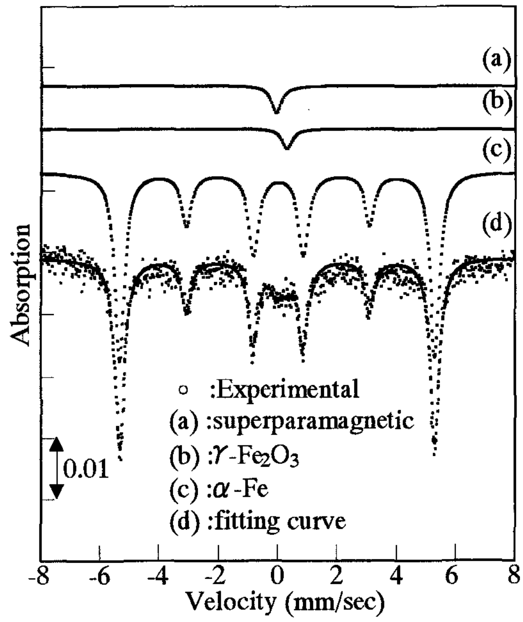

Fig. 7. Mössbauer spectra obtained on an Fe cluster deposited film at 300 K. The size of depositing cluster was 6 nm.

3. RESULTS AND DISCUSSION

First, we deposited Fe clusters and investigated the sintering of clusters. Figure 2 shows TEM images of Fe clusters of 6 nm in diameter deposited over different periods on TEM grids coated with a carbon film. It can be seen that some of clusters aggregated in the sample shown in Fig. 2(a), which was deposited over a period of 10 s. On the other hand, a continuous film is formed in the sample shown in Fig. 2 (b), which was deposited over a period of 3 min, corresponding to a thickness of about 10 nm. Figure 3 shows a high-resolution image of the image shown in Fig. 2 (b). Well-sintered small crystal grains can be seen, and its diffraction pattern indicates bcc Debye rings of α-Fe. Several grains of about 6-8 nm in diameter, the lattice image of which corresponds to the (110) lattice of α-Fe, can be seen in the photograph. Since this grain size does not differ greatly from that of the source clusters, it is thought that a few clusters coalesce into a large grain through the deposition accompanying sintering but that most of them do not. These observations revealed that Fe clusters of these sizes can be sintered well at temperatures below 100 °C.

Next, we deposited Fe clusters on glass substrates over a long period to produce thick films. Figure 4 shows SEM images of surfaces and cross sections of films obtained by the deposition of clusters of 2 nm, 4 nm and 6 nm in diameter. These thick films had a metallic luster and strong adhesion. However, a columnar structure with distinct boundaries was formed, and the size of columns increased as the cluster size increased, as can be seen in Fig. 4. The XRD patterns of the films shown in Fig. 4 are shown in Fig. 5. Only a peak corresponding to the (110) reflection of α-Fe was observed for all films, and the intensity of the diffraction peak became stronger as the size of the depositing cluster decreased. We obtained the crystallite size (the out-of-plane coherence length of crystallites) from the FWHM of (110) peak. We have used the program PROFIT [11] to obtain the FWHM of the diffraction peak, because the peak profile was not so clear. The results are shown in Fig. 6. The results indicate that the size of crystal grains formed increases as the size of clusters deposited decreases. However, it is noteworthy that the size of Fe clusters of 6 nm in diameter does not change throughout process, a finding is consistent with TEM observation. In a particle system, as the particle size is reduced, the melting point generally decreases to a lower temperature than that of the bulk, promoting the coalescence of particles [12]. Furthermore, in this case,

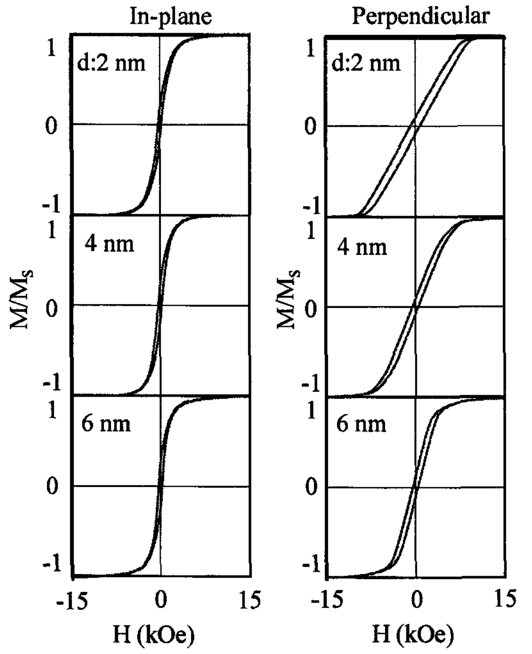

Fig. 8. In-plane and perpendicular magnetization curves of Fe films obtained by deposition of clusters of 2 nm, 4 nm and 6 nm in diameter.

the substrate temperature near the target increased; this must be one of the causes for the coalescence of small clusters (clusters of 2 nm and 4 nm in diameter) to large grains.

Figure 7 shows Mössbauer spectra measured on a Fe cluster deposited film at room temperature without magnetic field. As the sample, clusters of 6 nm in diameter was deposited on polyimide film over a period of 2 hours (corresponding to 450 nm in thickness) and over-coated with an Ag film (70 nm in thickness) to prevent the oxidation during the measurement. The spectra revealed the presence of the sextet of α -Fe with a hyperfine field around 332 KOe, representing 92% of the signal with 3% of ferric oxide and 5% of superparamagnetic iron. Although the γ -Fe_2O_3 phase was identified as ferric oxide in this study, there has been considerable ambiguity because the intensities of signals for components other than α -Fe were too weak to be clearly identified. It is noteworthy that by using a conventional vacuum chamber and 99.9999% processing gases, such low-oxidized films can be obtained by cluster deposition. We have little knowledge about the oxide phase and superparamagnetic component so far, but the superparamagnetic component may be related to the columnar boundaries that accompany cracks with many surface atoms.

The value of the saturation magnetization was small (about 90%) compared with that of α -Fe for all thick films. However, since these films were considerably porous (Fig. 4), this magnetization reduction was attributed to the oxidation after the deposition. The magnetization curves obtained at room temperature are shown in Fig. 8. Their overall features were similar to those generally observed for ferromagnetic continuous films with a perpendicular magnetic anisotropy. One of characteristic features is a low residual magnetization in in-plane curves. Another one is that in the perpendicular curves the magnetization saturates at a lower field as the cluster size increases. For the case of clusters of 6 nm in diameter, the in-plane curve and the perpendicular curve have nearly the same saturation fields. In addition, the residual magnetizations in both curves are small. These features are generally observed in a particle system rather than in a continuous film. In this Fe-cluster deposition, TEM observation revealed that the sintering among the clusters takes place very well and that crystal grains are closely packed, but it was also observed that secondary grains related to the columnar structure are formed and that the films become considerably porous. The particle-like structure constructed by the secondary grains of large size (20-50 nm, see Fig. 4) may dominate the magnetization properties. We had expected these nanocrystalline Fe films to have soft magnetic properties, but the values of the coercive field were high (about 250 Oe) for in-plane curves. The films obtained were considerably porous, and we assumed that the high coercivity is due to the morphology. The magnetic poles that appeared on the surface of secondary grains generate a field to prevent the magnetization. Soft magnetic properties are not obtained in such a porous film.

4. CONCLUSION

A cluster source utilizing GFS was shown to be useful for depositing nanosized Fe clusters. Fe films obtained by this cluster deposition were composed of very small crystal grains (estimated to be 6 nm to 12 nm in diameter) but had a high coercivity. The main cause for high coercivity was assumed to be the formation of secondary grains related to the columnar structures.

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