High Magnetization and High Electrical Resistivity in Dense Fe and Fe-Co Cluster Assemblies Prepared by Energetic Cluster Deposition

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Using a plasma-gas-condensation-type cluster deposition apparatus, positively charged Fe and Fe-Co alloy clusters have been deposited on a negatively biased substrate together with their neutral clusters. In these cluster assemblies the packing density and saturation magnetization per volume, \( M_s \), monotonically increase, while the magnetic coercivity, \( H_c \), rapidly decreases with increasing the bias voltage, \( V_b \). For the dense Fe and FeCo alloys, cluster assemblies prepared at \( V_b = -20 \) kV, \( M_s = 1.78 \) and 2.01 T, respectively and \( H_c < 80 \) A/m, whereas the electrical resistivity, \( \rho \), is 1 and 3 \( \mu \)\( \Omega \) m, respectively. These results indicate that the cluster assembling is a fascinating method to obtain excellent soft magnetic materials with high electrical resistivity because the magnetic exchange coupling between ferromagnetic clusters is so strong as to overcome the magnetic anisotropy of individual clusters and the conduction electrons are scattered by the cluster interfaces.

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1. Introduction

An isolated nanometer size magnetic particle is magnetically hard, having large magnetic coercivity as long as the size is larger than the onset size of superparamagnetism. When magnetic particles are connected to form a network and an assembly, the magnetic properties strongly depend on cluster sizes and magnetic interaction between adjacent clusters. Nanocrystalline (NC) materials have been prepared at first by mechanical compaction of ultrafine particles (UFPs) with nm in diameter produced by inert gas evaporation. The characteristic features have been discussed with the fact that a large amount of atoms are located at interfaces between UFPs. However the saturation magnetization of Fe-based NC materials was not so good as expected from their packing density because the cluster surfaces are easily oxidized. In a gas-deposition method, UFPs have been also generated by the inert gas evaporation, drawn out from the high inert gas evaporation room to a low pressure deposition room by a fast gas stream and directly deposited onto a substrate. With increasing the pressure difference between these two rooms, the packing density of NC materials were increased leading to rather high saturation magnetization.

NC materials have been also prepared by annealing of Fe-based amorphous alloys via substrate heating during deposition or post-annealing at around 700–1,000 K. Their excellent soft magnetic properties are attributed to the very fine grain size of nm and strong ferromagnetic exchange coupling between these ferromagnetic NC grains, where the magnetocrystalline anisotropy is averaged over the numerous number of grains. Such heat treatments are incompatible with serious device assembling processes even though precipitation has been a common and powerful technique in materials science and technology, and a low temperature fabrication process is desired.

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A present cluster-assembling method is similar to the compaction and gas-deposition of UFPs, and another alternative to fabricate nanoscale structure-controlled materials. By soft-landing of clusters on a substrate, sizes and shapes of deposited clusters are maintained, and the number of clusters increase with increasing the deposition time, however, cluster assemblies are porous stacks. Such a low density (about 30% of the bulk) cluster stack exhibits semi-hard magnetic properties: the magnetic coercivity, \( H_c \), ranges from a few hundreds to thousands of A/m. The saturation magnetization, \( M_s \), is less than the value calculated from the packing density because the surfaces of loosely packed Fe clusters are oxidized. Therefore, it is important to improve the density of cluster-assembled films by energetic cluster deposition for minimizing their oxidation and realizing soft magnetic materials. Simultaneously, high electrical resistivity is requisite for high frequency soft magnetic devices and sensors to minimize their eddy current loss.

This paper reports structure, magnetic and electrical properties of Fe and Fe-Co cluster-assemblies prepared by energetic deposition at room temperature and describes how the energetic cluster deposition is effective to obtain high-density Fe-based cluster-assemblies, which reveal a soft magnetic property, high saturation magnetization and high electrical resistivity.

2. Experimental Procedures

The samples were prepared by a plasma-gas-condensation (PGC)-type cluster beam deposition apparatus, whose schematic drawing is shown in Fig. 1. It is basically composed of plasma-glow-discharge vaporization (sputtering) and inert gas condensation techniques. The background pressure of all chambers (sputtering, cluster-forming and depositing chambers) was \(<5 \times 10^{-5} \) Pa. During cluster deposition, a large amount of 99.9999% pure Ar gas of 3.7 \( \times 10^{-4} \) mol/s were introduced continuously into the sputtering chamber and evacuated by a mechanical booster pump through a nozzle, making the sputtering chamber pressure maintain 2–7 \( \times 10^2 \) Pa. Fe and Co atoms of the target sputtered out in the inert gas space were decelerated by collisions with Ar gas atoms.
and collided with each other to form clusters. Fe and Fe-Co clusters were partially charged and no additional ionization process was necessary for ionizing clusters because they resided in the plasma region where the electron and ion densities were high. Clusters formed in the cluster growth room, were ejected from a small nozzle by differential pumping and a part of the cluster beam was intercepted by a skimmer, and then deposited onto a metallic sample holder which was able to be kept at a bias voltage \( V_a \) up to \( \pm 20 \text{kV} \) in the deposition chamber \( (7–10 \times 10^{-3} \text{ Pa}) \). Since the thickness monitor was installed behind the substrate in the deposition chamber, we employed the value detected by the thickness monitor as a quantitative measure of deposited clusters on a given area \( (\text{about 50 mm}^2) \) of a substrate. We also evaluated thicknesses of cluster-assembled films with an \( 3 \times 3 \text{ mm}^2 \) rectangle shape by a stylus instrument. The typical thickness of films used for magnetic and electrical resistivity measurements was about 1 \( \mu \text{m} \). Since the total weight was so small, we dissolved these films into a hydrochloric acid solution, analyzed the chemical composition of these solutions by atomic absorption spectroscopy and estimated the sample weights. We observed transmission electron microscope (TEM) images and electron diffraction patterns of Fe and Fe-Co clusters deposited on TEM microgrids and scanning electron microscope (SEM) images of those deposited on Si wafers. The chemical composition of Fe-Co cluster assembly was determined by an energy dispersive X-ray analyzer installed in TEM. For Fe and Fe-Co cluster assemblies deposited on quartz substrates magnetization curves were measured at room temperature with a superconducting quantum interference device magnetometer. Temperature dependence of electrical resistivity was measured between 5 and 300 K by a conventional four-point probe method in an He gas atmosphere of 100 kPa.

3. Results

The cluster assemblies prepared at \( V_a = 0 \text{ kV} \) had a sooty appearance, while those prepared at high \( V_a \) values were lustrous to eyes. Figures 2(a) and (b) show the SEM images of surface and cross-section of the Fe cluster-assemblies deposited at \( V_a = 0 \text{ and } \pm 20 \text{kV} \) with the mean cluster size \( d = 9 \text{ nm} \). As seen in this figure, the clusters with about 10–20 nm in diameter are randomly stacked. The packing density, \( P \), was estimated from weights and thicknesses of clusters assemblies deposited on a given area of the substrate. The relative \( P \) value against a bulk Fe specimen, for example, is about 35% for an Fe cluster assembly prepared at \( V_a = 0 \text{ kV} \), while it is about 85% for that prepared at \( V_a = \pm 20 \text{kV} \).

Figures 3(a) and (b) show cluster size distributions and transmission electron microscope images of Fe clusters deposited on a microgrid at room temperature with \( V_a = 0 \text{ and } \pm 20 \text{kV} \). Here, we estimated the cluster size distributions from digitized images recorded by a slow-scan charge-coupled device (CCD) camera for the area of \( 350 \times 350 \text{ nm}^2 \) using image-analysis software (Image-Pro PLUS: Media Cybernetics). \( d \) is about 9 nm and the standard deviation, \( \sigma \), is less than 10% of \( d \) for the Fe cluster assembly prepared at \( V_a = 0 \text{ kV} \). Comparing Figs. 3(a) and (b), \( d \) slightly increases to be about 9.7 nm and \( \sigma \) also increases for \( V_a = \pm 20 \text{kV} \).

Figures 4 shows electron diffraction patterns of Fe cluster assemblies prepared at \( V_a = 0 \text{ and } \pm 20 \text{kV} \). They display one set of diffraction rings of a body-centered-cubic (bcc) \( \alpha \)-Fe structure. In Fig. 4(a), moreover, there is also a ring corresponding to \( [311] \) of \( \text{Fe}_2\text{O}_3 \) or \( \gamma\text{-Fe}_2\text{O}_3 \) type phase where these two oxide phases cannot be distinguished by ED owing to their similar lattice parameters. Such surface oxidation of cluster assemblies occurred when they were exposed into ambient atmosphere. It progressed continuously in these cluster assemblies prepared at \( V_a = 0 \text{kV} \). It was also detectable by the magnetic measurement after 1 month: about 5% reduction in the magnetization due to the oxidation. In Fig. 4(b), on the other hand, the intensity of the ring \( [311] \) of \( \text{Fe}_2\text{O}_3 \) or \( \gamma\text{-Fe}_2\text{O}_3 \) type phase is very weak. The Fe cluster assembly prepared at \( V_a = \pm 20 \text{kV} \) was rather stable in ambient atmosphere, where the magnetization reduction was negligibly small even after 1 month.

Figures 5 and 6 show the in-plane magnetization curves at...
room temperature for the Fe cluster assembly with $d = 9 \text{ nm}$ and the Fe$_{70}$Co$_{30}$ cluster assembly with $d = 8 \text{ nm}$ prepared on room temperature substrates at several $V_a$ values. The application of $V_a$ leads to a magnetically soft behavior. At $V_a = 0 \text{ kV}$, the magnetization is saturated very slowly: magnetic coercivity, $H_c = 1.3 \times 10^4 \text{ A/m}$ for the Fe cluster assembly and $H_c = 7.6 \times 10^3 \text{ A/m}$ for the Fe$_{70}$Co$_{30}$ cluster assembly. With increasing $V_a$, on the contrary, the magnetization is saturated very rapidly: $H_c$ becomes less than $1 \times 10^2 \text{ A/m}$. It is important to mention that the saturation magnetization, $M_s$, for the Fe$_{70}$Co$_{30}$ cluster assembly is about 2.01 T, being much larger than 1.86 T for the Fe cluster assembly.

Figures 3 and 4 show the electrical resistivity, $\rho$, as a function of temperature, $T$, for the Fe cluster assembly and Fe$_{70}$Co$_{30}$ alloy cluster assembly prepared at $V_a = -20 \text{ kV}$. It roughly reveals ordinary metallic temperature dependence: the temperature coefficient of resistivity (TCR) is positive in this temperature range. Here, the marked irregularity in the medium temperature range is ascribed to the poor electric contact between the lead wire and specimen. The $\rho$ value at room temperature is about 0.9 $\mu\Omega\text{m}$ for of the Fe cluster assembly, while that is Fe$_{70}$Co$_{30}$ cluster assembly is about 3 $\mu\Omega\text{m}$, being much larger than that for the Fe cluster assembly.

4. Discussion

For the deposition of free clusters on substrates, a crucial parameter is a kinetic energy of clusters impinging on a substrate and discussed in terms of the impact energy per atom. We roughly distinguish three regimes depending on the impact energy value.$^{11,36}$ In a low energy regime corresponding to free clusters with an impact energy of about or lower than 0.1 eV per atom, one can expect the memory of the free cluster size without fragmentation and structural rearrangement during cluster-assemblying on the substrate, and the resulting assemblies are sooty and porous. In a medium energy regime of about 1 eV per atom, the clusters are deformed and/or partially destroyed, and the assemblies are lustrous with the better adhesion to the substrate. In a high energy regime (about or larger than 10 eV per atom), the clusters are fractured, becoming compact and smooth assemblies with the strong adhesion and mirror-like appearance.
As shown in Fig. 3, the cluster sizes of the specimen prepared at $-20 \text{kV}$ are not so much different from those of the specimen prepared at $0 \text{kV}$ though the cluster size and its distribution are slightly increased with applying $V_a = -20 \text{kV}$. It is reasonable to assume that clusters formed in the sputtering chamber are singly charged because multiply charged ones are very unstable. The kinetic energy of clusters can be determined by the bias voltage of $-20 \text{kV}$, because $9 \text{ nm}$ size clusters ejected from skimmer of the growth chamber have velocities ranging between 250 and $300 \text{ m/s}$ whose contribution to the kinetic energy is negligibly small. Since the impinging energy of $20 \text{kV}$ for a $9 \text{ nm}$ Fe cluster corresponds to $0.6 \text{ eV}$ per Fe atom, which is one order smaller than the cohesive energy of Fe ($4.3 \text{ keV}$), the $d$ value of clusters prepared at $V_a = -20 \text{kV}$ is not different from that of clusters prepared at $V_a = 0 \text{kV}$. Comparison between Figs. 2(a) and (b) and the weight and thickness measurements of clusters clearly indicate that $P$ is much improved from about $35$ to $85\%$ by applying $V_a = -20 \text{kV}$. Since the highest $P$ value of ideally spherical particles is about $74\%$ and expected in fcc or hcp packings, the present results suggest that the cluster shape is deformed by applying $V_a$.

With increasing $V_a$ the $H_c$ value decreases but the $M_s$ value increases, being consistent with the increase in $P$ in the Fe cluster\(^{13}\) and Fe\(_{70}\)Co\(_{30}\) cluster assemblies prepared by applying $V_a$ on room temperature substrates. The soft magnetic behaviors can be interpreted qualitatively by Herzer’s Random Anisotropy Model which basically stands on a single element system:\(^{10}\) the exchange coupling between Fe or Fe\(_{70}\)Co\(_{30}\) clusters are so strong and long-ranged as to overcome the magnetic anisotropy of individual ferromagnetic clusters and their magnetic dipole interaction.

In Fe cluster prepared at $V_a = 0 \text{kV}$ the $\rho$ value has been reported to be about $20\mu\Omega\text{cm.}^{13}$ This has been ascribed mainly to the porous stacking of Fe clusters and partly to the surface oxidation of Fe clusters. In Fe cluster and Fe\(_{70}\)Co\(_{30}\) cluster assemblies prepared at $V_a = -20 \text{kV}$, on the other hand, the $\rho$ values are much smaller, but still larger than Fe and Fe-Co alloy films. Therefore, it is mainly attributed to conduction electron scattering at the cluster surfaces and cluster interfaces which are clearly confirmed by SEM (Fig. 2) and TEM (Fig. 3) images.

Figure 8 shows the magnetization versus electrical resistivity plot of the Fe cluster and Fe\(_{70}\)Co\(_{30}\) cluster assemblies together the results of typical soft magnetic materials.\(^{18}\) These two physical properties cannot be maximized independently and their optimum limits are inversely correlated as described empirically by a broken line. However, this figure demonstrates that the energetic cluster deposition can
provide a possible way to surpass the limit and produce novel soft magnetic materials for high frequency uses.

Finally it is worth to mention that the progressive oxidation in porous cluster assemblies can be much suppressed in dense cluster assemblies. Figure 9 shows the packing fraction, $P$, and saturation magnetization per weight, $\sigma_s$, as a function of $V_s$ for Fe cluster assemblies.

5. Summary

We have employed a plasma gas condensation technique and an energetic cluster deposition method to produce high density Fe and Fe$_70$Co$_{30}$ cluster assemblies with soft magnetic properties. The accelerating voltage plays important roles on increasing the density of the cluster-assembled films. We reconfirm the high magnetic flux density, very low magnetic coercivity and the high electrical resistivity in these cluster assemblies. The characteristic features are attributable to the random but very dense stacking of Fe metal clusters and Fe$_70$Co$_{30}$ alloy clusters, i.e., their ferromagnetic exchange coupling and weak metallic contact.

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