Electric and Magnetic Evolutions in Composite Assemblies of Fe and Si Nano-Particles

Kenji Sumiyama1,*,1, Minoru Yamazaki1, Yuichiro Kurokawa2,*,2, Nobuyuki Shinhara2,*,3 and Takehiko Hihara2

1School of Science and Engineering, Tokyo Denki University, Hiki-gun, Saitama 350-0394, Japan
2Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

Temperature (T)-dependence of electrical resistivity (ρ) and magnetization curves have been observed for Fe and Si nano-particle (NP) composite assemblies prepared using a double-source-plasma-gas-condensation cluster deposition system. With increasing T, ρ monotonically decreases for the Fe composition, $c_{Fe} < 0.6$, where the Si NP networks are predominant (a semiconductor type conduction), while it monotonically increases for $c_{Fe} > 0.6$, where the Fe NP networks are formed (a metallic conduction). With increasing $c_{Fe}$, saturation magnetization monotonically increases, while magnetic coercivity increases for $c_{Fe} < 0.4$ and gradually decreases for $c_{Fe} > 0.6$. In these Fe and Si NP composite assemblies, magnetic dipole interactions between Fe NPs are reinforced by reductions in inter-particle distances though they are averaged by random configurations of Fe and Si NPs, and random orientations of magnetic moments of Fe NPs. Magnetic exchange interactions are also induced but not much enhanced with $c_{Fe}$ due to loose contacts between Fe NPs. [doi:10.2320/matertrans.M20144434]

(Rceived December 4, 2014; Accepted December 24, 2014; Published February 13, 2015)

Keywords: iron nanoparticle, silicon nanoparticle, conductivity, magnetic properties, transmission electron microscopy; nano-composite material, percolation

1. Introduction

It is promising to design and assemble elemental nanoparticles (NPs) whose sizes correspond to basic structural and functional units.1-5) NP sizes and configurations are controllable in NP assemblies, whereas precipitated particle-sizes and -distances cannot be independently controlled by post annealing and precipitation of rapidly solidified materials.6) A plasma-gas-condensation cluster deposition (PGCCD) system has been used to prepare clusters by a combination of plasma sputtering and inert gas condensation in high Ar gas atmospheres.4,7,8) Ferromagnetic metal (Co) clusters have been generated via many time collisions of vaporized metal and Ar atoms in a PGCCD system with a single cluster source. Their numbers increase with the deposition time and they contact with each other as continuously impinging on a substrate. Geometrical and electrical percolation phenomena and superparamagnetic-ferromagnetic transitions are observed at certain deposition thicknesses, $t_{c}$.4,9-14)

During these cluster deposition processes, an electric current (I) has been continuously detected between the two electrodes to which an electric voltage has been applied. I is negligibly small at first and suddenly starts to increase at a certain $t$ value. With a further increase in $t$, I nonlinearly increases and then linearly increases, suggesting fulfillment of a 2 dimensional percolation at around the critical percolation thickness ($t_{c}$) which is proportional to the critical cluster coverage.10)

Similar two step changes have been detected in the $T$-dependence of I when Fe and Si NPs have been formed and deposited on a substrate using the PGCCD system with double cluster sources (see Fig. 1).15) Electrical conductivity, $σ$ has been estimated for Fe and Si NP composite assemblies whose thicknesses have been well above $t_{c}$ and atomic compositions of Fe ($c_{Fe}$) have been varied. The $σ$ value in a logarithmic scale dramatically changes versus $c_{Fe}$ at around the critical Fe composition, $c_{Fe} = 0.6$ (47 vol% Fe).15,16) This result demonstrates that a 3 dimensional electrical percolation is fulfilled because $c_{Fe} < 0.6$ corresponds to the volume fraction of Fe NPs in 3 dimensional site percolation phenomena, $f_{Fe} = 0.15$, i.e., the packing density of NP assemblies is about 30% of bulk specimens, leading to $0.47 \times 0.3 = 0.14 \equiv f_{Fe} = 0.47$.14,17,18)

In this report, we describe experimental results on temperature dependence of electrical resistivity and magnetization as well as transmission electron micrographs for Fe and Si NP composite assemblies, and discuss how electrical and ferromagnetic characters evolve in these assemblies.

2. Experimental

Figure 1 shows the double source PGCCD system,15) which consists of two DC hollow cathode type glow discharge sources installed in two sputtering chambers, two nano-particle growth rooms, two intermediate rooms and a deposition room. In the PGCCD system, two Fe and two Si plates of 80 mm in diameters and 5 mm in thicknesses were set on the target holders, where Fe was 99.9% pure and Si was p-type doped of 9 ppm B for DC sputtering. These rooms were first evacuated down to $10^{-5}$ Pa by turbo molecular pumps, TMP, and composite molecular pumps, CMP. For glow discharge sputtering, TMPs were shut down and Ar gas (99.9999 vol%) was independently introduced through gas-inlets with adjusting mass flow controllers, while growth rooms were evacuated by a mechanical booster pump ($2.2 \times 10^{-7}$ m$^3$/s) to eject the Ar gas, sputtered atoms and formed NPs through small nozzles of growth ducts and
skimmers of the deposition room. Here, the Ar gas flow rates were $6.7 \times 10^{-6} \text{ m}^3/\text{s}$: the corresponding Ar gas pressure of the sputtering chambers 1 and 2 was 0.3 Pa by the evacuation using TMPs. The input electric powers for the glow discharge were as follows: the voltage was 300–350 V for the Fe targets, 400–450 V for the Si targets and the electric currents were about 1.0 A. The deposition rates and thus composition ratios of Fe and Si NPs were checked by a quartz oscillation type thickness monitor which was set-in and -out just before the substrate holder, and used as a sensitive microbalance. Thicknesses of deposited NP assemblies were also measured by a stylus instrument (SURFCM1-400D). In the present study we deposited Fe and Si NPs simultaneously on a substrate by operating the double glow discharge sources.

The morphology, size and structure of Fe, Si and Fe/Si NPs were observed using a transmission electron microscope (TEM; Hitachi Co., HF-2000) operating at 200 kV. TEM images were observed for specimens on TEM grids at the initial deposition stage and selected area electron diffraction patterns for those at the late deposition stage. Chemical composition ratios of Fe and Si NPs were determined by energy dispersive X-ray (EDX) analyzers installed in both TEM and a scanning electron microscope (SEM; Hitachi S-4700) operating at 5 kV, where the atomic composition of Fe is expressed as $c_{\text{Fe}}$. Using a four probe method with a digital multimeters (Keithley 2400-236), electrical resistivity, $\rho$, was measured between 5 and 300 K for Fe, Si, and Fe and Si NP composite assemblies deposited between two gold film electrodes, whose widths were 2 mm and separation distances 0.5 mm, on quartz glass substrates. Using a superconducting quantum interference device magnetometer (Quantum Design Co., MPMS-5) magnetization curves were measured between 4.2 and 300 K in magnetic fields up to 5 T for Fe and Fe and Si nano-particle composite assemblies deposited on quartz glass substrates.

3. Results

3.1 Morphologies and structures

Figures 2 and 3 show bright-field TEM images and electron diffraction (ED) patterns of the Fe and Si NP composite with $c_{\text{Fe}} = 0.41$ deposited on a TEM grid.
logarithmic scale for Fe/Si NP composite assemblies. Between \(c_{\text{Fe}} = 0.5\) and 0.7, \(\sigma\) varies more than six orders of magnitude at 5 K, while about three orders of magnitude at 300 K. These marked changes in \(\sigma\) are ascribed to the electrical percolation.\(^{15}\)

Figures 5(a) shows \(T\)-dependences of \(\rho\) in a logarithmic scale for Fe and Si NP composite assemblies. With increasing \(T\), \(\rho\) decreases for \(c_{\text{Fe}} < 0.6\), almost \(T\)-independent at \(c_{\text{Fe}} \geq 0.6\), while it increases at \(T > 50\) K for \(c_{\text{Fe}} > 0.6\) as shown in Fig. 5(c). The intrinsic energy gaps of Fe and Si NP composite assemblies are estimated to be about 117 meV for \(c_{\text{Fe}} = 0.53\) and 84 meV for \(c_{\text{Fe}} = 0.54\) from \(\log \rho^{-1}/T\) plots between 100 and 300 K (Fig. 5(b)). These values are smaller than 1.15 eV for bulk Si.\(^{21}\)

### 3.3 Magnetic properties

Figure 6 shows magnetization curves at room temperature for Fe and Si NP composite assemblies. In this figure a clear hysteresis is detected for all of the specimens. Saturation magnetization, \(M_S\), and magnetic coercivity, \(H_C\), are estimated from these results and shown in Figs. 7(a) and (b). In Figs. 7(a), \(M_S\) monotonically increases with \(c_{\text{Fe}}\) in Fe and Si NP composite assemblies. This result simply reflects the increase in the number of Fe atoms carrying magnetic moments, provided that the packing density of these nano-particle assemblies is about 30% of bulk counterparts\(^{17,18}\) and \(M_S = 2.13\) T for pure Fe.\(^{22}\) With increasing \(c_{\text{Fe}}\) in Fig. 7(b), on the other hand, \(H_C\) increases for \(c_{\text{Fe}} < 0.3\), reveals a maximum at around \(c_{\text{Fe}} = 0.5\), and gradually decreases for \(c_{\text{Fe}} > 0.6\), suggesting magnetic percolation of Fe NPs.

### 4. Discussion

Based on the composition- and temperature-dependences of electrical resistivity, we reconfirm that the threshold composition of the electrical percolation, \(c_{\text{Fe}}^* \approx 0.6\) in Fe and Si NP composite assemblies. In Fig. 5(c), however, \(\rho\) slightly increases with decreasing \(T\) at \(T < 50\) K for \(c_{\text{Fe}} = 0.70\)~0.75. This indicates a localization effect;\(^{23,24}\) conduction electrons are localized within pseudo-low dimensional networks of Fe NPs.\(^{25}\)

The composition dependence of \(H_C\) in Fe and Si NP composite assemblies resembles to the thickness dependence.
of \(H_C\) in ferromagnetic Co cluster assemblies\(^{11}\), whose \(H_C\) increases with \(t\) and becomes constant for \(t > t^*\), where the \(t^*\) value is lower than the two dimensional electrical percolation. In the latter, \(H_C\) is attributed to random magnetic anisotropy (RMA) which stems from magnetic dipole interactions between ferromagnetic NPs. In ferromagnetic NP assemblies, magnetizations of individual NPs are proportional to their volumes, while their magnetic dipole interaction is proportional to 4 powers of the magnetization and inversely proportional to 6 powers of the inter-NP distances.\(^{26}\) In Fe and Si NP assemblies, RMA is also reinforced and increased with \(c_{Fe}\) for \(c_{Fe} < c_{Fe}^*\), where fractal networks of ferromagnetic Fe NPs are extended.\(^{25,32}\) Once large networks of ferromagnetic Fe NPs dominate the whole Fe and Si NP composite assemblies, RMA is saturated and \(H_C\) becomes independent of \(c_{Fe}\) for \(c_{Fe} > c_{Fe}^*\).

However, \(H_C\) gradually decreases with \(c_{Fe}\) for \(c_{Fe} > c_{Fe}^*\) in Fig. 7(b). This feature should be compared with the following characteristic composition dependence of \(H_C\) in ferromagnetic metal and nonmagnetic oxide nano-granular materials.\(^{31,34}\) There, \(H_C\) markedly increases and shows the maximum just below the electrical percolation composition of ferromagnetic components being due to maximum growths of single domain particles and strain-induced magnetic anisotropy at their interfaces. Above the percolation composition it rapidly decreases, being ascribed to formation of both connecting network of ferromagnetic particles and multi-domain structures, where magnetization process is dominated by wall motions. The spatial magnetic correlation length estimated by small angle neutron scattering experiments on nanostructured Fe alloys were comparable to the magnetic exchange length, \(L_{ex}\) estimated by an extended random anisotropy model.\(^{35,36}\)

Assuming that such exchange-coupled assemblies of ferromagnetic particles behave like single domain particles,\(^{37,38}\) the magnetic coercivity is given by

\[
H_C = H_{c,0}[1 - (25k_BT/K_{eff}V)^{1/2}] = 2K_{eff}/M_S[1 - (25K_BT/K_{eff}V)^{1/2}],
\]

\[V = (L_{ex})^3,\]

where \(H_{c,0}\) is the magnetic coercivity at \(T = 0\) K, \(k_B\) the Boltzmann constant, \(K_{eff}\) the effective magnetic anisotropy constant and \(V\) the volume of a single domain particle.\(^{22,37,38}\)

As shown in Fig. 8(a), the \(H_C\) vs \(T^{1/2}\) plots for Fe and Si nano-particle composite assemblies obey eq. (1) and the \(L_{ex}\) values obtained from eq. (2) are shown as a function of \(c_{Fe}\) in Fig. 8(b). \(L_{ex}\) is slightly larger than the average Fe NP size (13 nm), gradually varies with \(c_{Fe}\) and becomes a maximum at around \(c_{Fe} = 0.5-0.6\). In the present Fe and Si NP composite assemblies, magnetic exchange interactions are reinforced within adjacent ferromagnetic Fe NPs (see Figs. 2 and 3).

In random assemblies of ferromagnetic NPs,\(^{29,32,39}\) frozen ferrofluids,\(^{40,41}\) granular magnetic materials,\(^{42}\) and amorphous ferromagnetic alloys,\(^{43}\) their magnetic properties, so-called super-ferromagnetism, are very complicated and sensitively depend on chemical compositions, temperature and preparation procedures due to the small ferromagnetic domains, their weak magnetic interactions and magnetic anisotropies originated from the surface (low symmetry) and intrinsic (crystalline anisotropy) effects in internally con-
nected small ferromagnetic NPs. Similar features are observed in the present Fe and Si NP composite assemblies. Their net magnetization and magnetic coercivity are ascribed to randomnesses in the orientations, spatial distributions and chemical configurations as well as the magnetic dipole and weak exchange couplings of ferromagnetic NPs.

5. Summary

We have prepared Fe and Si NP composite assemblies using the plasma-gas-condensation cluster deposition system with double cluster sources and measured their temperature (T) dependence of electrical resistivity, ρ, and magnetization curves. The ρ values dramatically change in several orders of magnitudes at around the 3 dimensional percolation composition, cFe = 0.6. ρ monotonically decreases with T for the Fe composition, cFe < 0.6, where the Si NP networks are predominant (the semiconductor regime), while monotonically increases with T for cFe > 0.6, where the Fe NP network are formed (the metallic regime). Saturation magnetization, $M_s$, monotonically increases, while magnetic coercivity, $H_C$, increases for $c_{Fe} < 0.4$ while gradually decreases for $c_{Fe} > 0.6$. These results indicate that magnetic dipole interactions between Fe NPs are reinforced with the reduction in inter-NP distances (the increase in the Fe NP density) and magnetic exchange interactions are also induced by loose contacts between Fe NPs. However, these magnetic interactions are averaged by random-orientations, -positions and -configurations of Fe and Si nano-particles, revealing super-ferromagnetic behaviors.

Acknowledgments

This work has been supported by a Grant-in-Aid for Scientific Research given by the Ministry of Education, Culture, Sports, Science and Technology, (MEXT), Japan. It was also partially supported by Nanotechnology Platform Program (Molecule and Material Synthesis of MEXT, Japan). One of the authors (KS) appreciates the supports from Research Institute of Science and Technology, Tokyo Denki University and Nagoya Industrial Science Research Institute.

REFERENCES