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Formation and magnetic properties of the fcc-FeN compound clusters prepared by plasma-gas-condensation

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Abstract

The compound FeN clusters with cluster sizes of $d = 8$–25 nm were synthesized using a plasma-gas-condensation (PGC) cluster deposition apparatus with changing the nitrogen gas flow rate R_{N_2}, and their crystal structures and magnetic properties were investigated. The fcc single-phase FeN clusters which have a tetrahedron shape are obtained, and their lattice parameter is $a = 0.428$ nm, being close to that ($a = 0.433$ nm) of ZnS-type FeN films but clearly different from that ($a = 0.457$ nm) of NaCl-type FeN films. The magnetic measurement results indicate that the present ZnS-type FeN clusters are non-magnetic. The characteristic cusp at $T_f = 8$ K on the zero field cooling (ZFC) thermomagnetic curve is attributed to superparamagnetic behavior of Fe-oxide layer crystallites formed on the FeN cluster surfaces.

Keywords: fcc-FeN cluster; Tetrahedron structure; Magnetic properties; Plasma-gas-condensation

1. Introduction

Recently there has been growing interest in obtaining various nanostructured materials by using different preparation methods and understanding their novel physical properties, being significantly different from those for the corresponding bulk counterparts [1–3]. Many kinds of metal nanoparticles or nanoclusters have been fabricated by various techniques including colloidal chemistry [4,5], inert gas condensation [6–8], laser deposition [9], mechanical attrition [10], and electrodeposition methods [11]. Besides the metal clusters, compound (nitride or oxide) clusters are also interesting because of their excellent oxidation- and corrosion-resistance in comparison with their pure metal clusters. In particular, Fe-nitrides are attractive because some of them are of excellent magnetic properties, for example, high magnetic flux density of α''-$Fe_{16}N_2$ and γ'-Fe_4N. There have been a few reports on the study of Fe-nitride particles in which γ'-Fe_4N particles were prepared by heating acicular Fe particles in NH_3–H_2 gas mixture [12,13] and by a reactive gas evaporation method in ammonia gas atmosphere [14,15].

In the present study, an fcc single-phase FeN clusters with a tetrahedral habit were obtained by using a combination of reactive sputtering in $Ar + N_2$ gas atmosphere and gas-condensation cluster deposition technique. Here, we report formation and magnetic properties of Fe–N clusters obtained by this method and discuss structural characteristics of the obtained FeN clusters and effect of Fe-oxide layer of cluster surface on the magnetic behavior.

2. Experiment

The Fe–N clusters were prepared by the plasma-gas-condensation-type cluster beam deposition apparatus, whose detail was described elsewhere [8,16]. The apparatus is composed of the three main parts: sputtering, cluster growth and deposition chambers. The metal vapors were generated from a Fe target by dc sputtering. A continuous Ar gas stream up to 300 sccm (standard cubic centimeter per minute) was injected into the sputtering chamber through a nozzle. A N_2 gas stream up to 1.5 sccm was also introduced into the sputtering chamber from a gas inlet. The vaporized atoms in the sputtering chamber are decelerated by collisions with a large amount of Ar gas, and are swept into the cluster growth room, which is cooled by liquid nitrogen. The Fe–N clusters formed by reactive process

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are ejected from a small nozzle by differential pumping and a part of the cluster beam is intercepted by a skimmer, and then deposited onto a sample holder in the deposition chamber.

The deposition rate of Fe–N clusters was measured by a quartz oscillator-type thickness monitor installed behind the substrate. The microgrid, which was covered by a carbon-coated colodion film and supported by a Cu grid, was used as a substrate for transmission electron microscope (TEM) observation. The size of clusters deposited on the microgrids was estimated by TEM and the crystal structure was analyzed by electron diffraction (ED) patterns. The samples were exposed in air for transportation and observed with the Hitachi HF-2000 TEM operating at 200 kV. Magnetic measurement was performed using a superconducting quantum interference device magnetometer between 5 and 300 K with the maximum field of 50 kOe.

3. Results

Fig. 1 shows (a) typical bright-field (BF) TEM images and (b) ED patterns of the Fe–N clusters obtained at R_{N_2} = 0, 0.5, and 1.5 sccm, respectively. The experimental parameters were as follows: Ar gas flow rate: R_{Ar} = 300 sccm and sputtering power: P_W = 400 W. At R_{N_2} = 0 sccm, we obtained almost spherical or cubic shape Fe clusters whose mean diameter is about d = 13 nm. The ED pattern of these Fe clusters displays one set of diffraction rings of a bcc structure. At $R_{N_2} > 0.5$ sccm, almost all Fe–N clusters are of a tetrahedron shape with cluster sizes of d = 8–25 nm. The corresponding ED patterns reveal one set of diffraction rings of an fcc structure. The estimated lattice constants (a) from the ED patterns are shown in Fig. 2. The a value of Fe–N clusters with an fcc structure is independent of R_{N_2}, being about 0.428 nm and close to the experimental value (0.433 nm) of ZnS-type FeN compound films [17]. It is clearly different from that (0.457 nm) of NaCl-type FeN compound films [18,19]. In addition, as seen in Fig. 1(b), for all samples there is another ring corresponding to {3 1 1} of Fe_3O_4 or γ-Fe_2O_3 phase, where it is not possible to differentiate between these two phases by ED because their lattice parameters are very similar. This is due to partial oxidation of the cluster assembly only by exposing it to the ambient atmosphere.

Fig. 3 shows the saturation magnetization, M_s, of the Fe–N clusters as a function of R_{N_2}. As seen here, the M_s value decreases drastically when introducing the Ar gas into the sputtering chamber: form 85 emu/g at R_{N_2} = 0 sccm to 2 emu/g at R_{N_2} = 0.3 sccm. As shown in the inset of Fig. 3, M_s decreases gradually with further increasing R_{N_2} and becomes to 0.05 emu/g at R_{N_2} = 1.5 sccm. In order to examine the magnetic state of obtained Fe–N clusters, we measured temperature dependence of magnetization at low magnetic field. Fig. 4 shows the thermomagnetic curves,

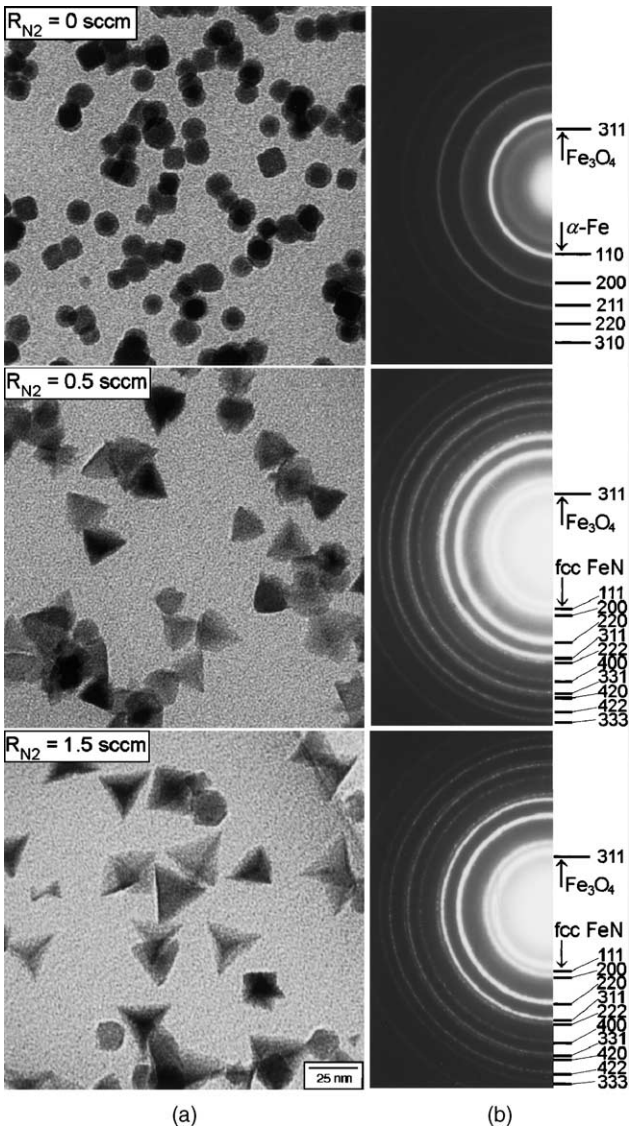

Fig. 1. Bright-field TEM images and electron diffraction patterns of the Fe–N clusters obtained at different N_2 gas flow rates, R_{N_2}: (a) R_{N_2} = 0; (b) 0.5; and (c) 1.5 sccm.

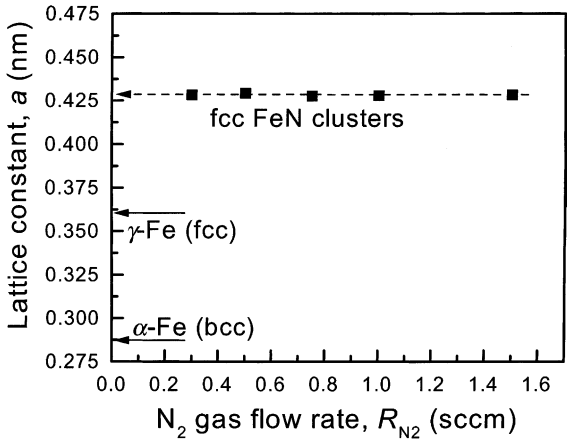

Fig. 2. The estimated lattice constants, a, from the ED patterns for the fcc-FeN compound clusters as a function of N_2 gas flow rate, R_{N_2}.

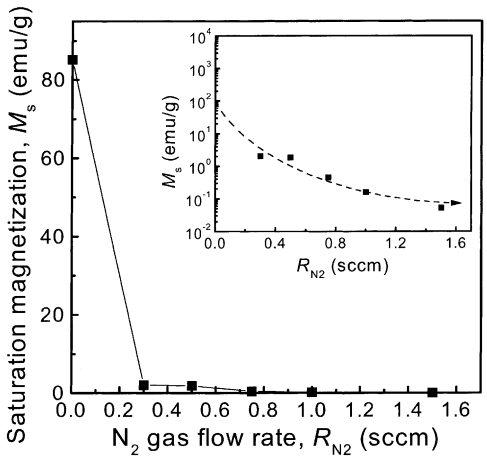

Fig. 3. Saturation magnetization, M_s, for the fcc-FeN compound cluster assemblies as a function of N_2 gas flow rate, R_{N_2}. The inset shows log M_s vs. R_{N_2}. The dash line with a arrow is guide to the eye.

M_{ZFC}–T and M_{FC}–T, for the zero field cooled (ZFC) and field cooled (FC) stages of the Fe–N cluster assemblies prepared at $R_{N_2} = 1.5$ sccm. For the zero field cooled measurement, the sample was cooled in the absence of an external magnetic field from $T = 300$ to 5 K. Then $H = 10$ Oe was applied and the magnetization was measured with increasing temperature. For the field cooled measurement, the sample was cooled in the presence of $H = 10$ Oe from $T = 300$ to 5 K, and then the magnetization was measured with increasing temperature at $H = 10$ Oe. As seen from Fig. 4, a magnetic cooling effect is observed at low temperatures. At sufficient high temperatures (above 150 K) a typical paramagnetic behavior is observed: there is no difference between ZFC and FC magnetization. Below 150 K, the ZFC magnetization starts to deviate from the FC magnetization, and below $T_f = 8$ K, this irreversibility is more marked (see the inset of Fig. 4). The ZFC curve exhibits a characteristic cusplike maximum at T_f, while the FC curve shows a continuous increase with decreasing the temperature.

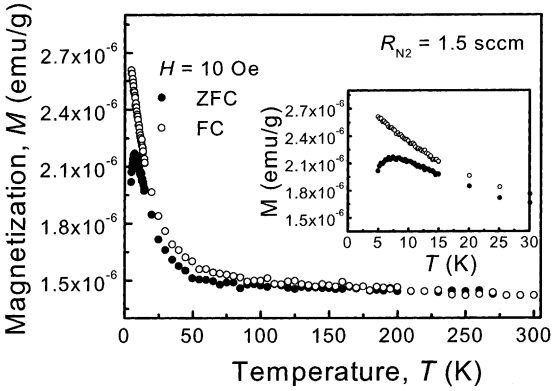

Fig. 4. Low field thermomagnetic curves measured with increasing temperature after zero field cooling and field cooling the samples from 300 to 5 K for the fcc-FeN compound cluster assemblies prepared at $R_{N_2} = 1.5$ sccm.

4. Discussion

We have demonstrated that the FeN compound clusters with the fcc single-phase were formed using the combination of reactive sputtering in $Ar + N_2$ gas atmosphere and gas-condensation cluster deposition technique. Moreover, almost all FeN clusters have a tetrahedral habit. Here, we simply discuss the structural characteristics of the obtained FeN clusters. In general, the minimum energy shape for a given volume is determined by the Wulff construction. This construction gives the equilibrium shape of a free-floating small particle, and is mathematically equivalent to stating that the normal distance from a common center to any given surface facet is proportional to the surface free energy of the facet. However, in many cases (especially for very small particles) the experimental structure is not the Wulff shape, but clearly determined in a large part by growth conditions such as non-free space, a substrate effect, a non-equilibrium state, etc. A typical example is called multiply-twinned particles (MTPs) for metals with an fcc structure. They are first discovered by Ino [20], and Ino and Ogawa [21]. Ino's original approach to modeling these particles was in terms of arrangements of twin-related tetrahedrons packed along (1 1 1) faces. The five units can be arranged to form a pentagonal bipyramid (namely decahedron), and the twenty an icosahedron. From Ino's calculation [20] on critical sizes for stable and quasi-stable states of the icosahedral and decahedral particles, an icosahedral particle is essentially stable for $r \leq r_{iw}$ in comparison with an equilibrium Wulff shape, while a decahedral particle is not essentially stable but quasi-stable for $r \leq r_{dt}$, where r is an edge length of the particles, and r_{iw} and r_{dt} are the critical edge lengths. The calculated critical values are in good agreement with experimental results. For single tetrahedral particle, because of its largest total surface area compared with those of the icosahedral and decahedral particles, it becomes quasi-stable only when $r > r_{dt}$. The quasi-stable size $2r_{dt}$ of fcc γ-Fe decahedral particles, for instance, is about 170 nm, being larger by an order of magnitude than the size of the FeN clusters. All FeN clusters reveal a tetrahedron habit, indicating that their sizes are larger than quasi-stable size $2r_{dt}$ of the decahedral particle. As seen in Fig. 1, the size of the FeN tetrahedral clusters is about $d = 8$–25 nm, which is much lower than quasi-stable size $2r_{dt}$ of pure metal with fcc structure [20]. This implies that the fcc-FeN compound cluster has a low (1 1 1) surface energy and/or high elastic strain energy and twin boundary energy compared with pure metal clusters with fcc structure.

In Fe–N compounds, the fcc-FeN phase whose nitrogen concentration is nearly 50% was reported recently in comparison with other nitride phases. With regard to the magnetic properties of the fcc-FeN phase, there are also many different reports. From Mössbauer spectroscopy measurements performed by Nakagawa et al. [18] and Hinomura and Nasu [17], it has been suggested that NaCl-type FeN is an antiferromagnet. Recently, it has been reported that the NaCl-type FeN film shows no magnetic order down to 4.5 K.

Theoretically, however, it has been suggested that if a purely bulk sample of the NaCl-type FeN is synthesized, it will be a ferromagnet [22,23]. For ZnS-type FeN, on the other hand, no hyperfine field has been observed at the Fe site by Nakagawa et al. [18] and Hinomura and Nasu [17]. Suzuki et al. [24] also synthesized the ZnS-type FeN film and the lattice constant observed by them was in agreement with that of Refs. [17,18]. Their sample exhibits a mictomagnet character and a shift of its magnetic hysteresis loop after magnetic field cooling at low temperatures, which was considered to be related to the antiferromagnetism of the ZnS-type FeN compound. For the present fcc-FeN compound clusters, their crytal structure should be the ZnS-type fcc structure by comparing the lattice constant value ($a = 0.428$ nm) with those (ZnS-type: $a = 0.433$ nm; NaCl-type: 0.457 nm) of other experimental works [17–19,24]. According to our magnetic measurement results, the ZnS-type FeN clusters can be considered as a paramagnetism, being in agreement on the observation result of Mössbauer spectroscopy in the ZnS-type FeN film [17,18]. Because of partial surface oxidation of the clusters by exposing them to the ambient atmosphere, Fe oxide layers were easily formed on the Fe cluster surfaces and thus cause a shift of hysteresis loop after magnetic field cooling at low temperatures [25]. In the case of the present ZnS-type FeN clusters, the cluster surface oxidation also takes place although their oxidation-resistance should be better than the pure metal clusters. Therefore, the characteristic cusp at $T_f = 8$ K on the ZFC curve (Fig. 4) is attributed to superparamagnetic behavior of small Fe-oxide layer crystallites on the FeN cluster surfaces.

5. Conclusion

We have studied the crystal structure and magnetic properties of the Fe–N clusters produced by the PGC-type cluster deposition apparatus. The ZnS-type fcc single-phase FeN clusters have been obtained and their lattice parameter is $a = 0.428$ nm. The shape of the FeN clusters depends on the nitrogen gas flow rate R_{N_2}. When $R_{N_2} \geq 1$ sccm, almost all clusters are of a tetrahedral habit and their sizes are about $d = 8$–25 nm which are smaller by an order of magnitude than the critical size of the pure γ-Fe decahedral particles. The magnetic measurement results suggested that the present ZnS-type FeN clusters are non-magnetic. The characteristic cusp at low temperature on the zero field cooling thermomagnetic curve is ascribed to superparamagnetic behavior of Fe-oxide layer crystallites on the FeN cluster surfaces.

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