Electric and Magnetic Evolution in Sputter-Deposited $\text{Fe}_x\text{Si}_{1-x}$ Alloy Films

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$\text{Fe}_x\text{Si}_{1-x}$ alloy films have been prepared by an rf sputter-deposition method. X-ray diffraction patterns indicate that an amorphous phase is formed for $x < 0.8$. Temperature dependence of electrical resistivity indicates the following electric evolution. Carrier-excitation from the impurity- to the conduction (or valence) bands is dominant for $x < 0.2$ (the semiconductor regime), the band conduction is affected by strong impurity- and random-scatterings for $x > 0.4$ (the metallic regime), and the carrier-excitation between the impurity band and the mobility edge is retained due to the electron-localization effect in the amorphous structure for $0.2 < x < 0.4$ (the transition region). The thermomagnetic- and magnetization-curves indicate the following magnetic evolution. The ferromagnetic phase appears at $x \cong 0.3$ and the Curie temperature rapidly increases with increasing x . The magnetic (spin- or cluster-) glass region is very narrow ($x = 0.3 \sim 0.55$) at low temperature. These magnetic behaviors are ascribed to the instability of Fe magnetic moments and the depression of RKKY interactions in the low x range.

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1. Introduction

Component mixing is a basic procedure to control material functions which depend on their compositions, sizes, structures, contact modes and cohesive characters. We have prepared composite assemblies of Fe and Si nano-particles (NPs) using the plasma-gas-condensation cluster deposition system with double cluster sources^{1,2)}. In their composition dependence of electrical resistivity, ρ , the ρ value changes in several orders of magnitude at around the 3 dimensional percolation composition of Fe atoms, $c_{\text{Fe}} = 0.6$ ¹⁾. With increasing temperature, T , ρ monotonically decreases for $c_{\text{Fe}} < 0.6$, where a Si NPs network is predominant (the semiconductor regime), while slightly increases for $c_{\text{Fe}} > 0.6$, where an Fe NPs network is fulfilled (the metallic regime). Magnetic moments of Fe atoms are stable and the saturation magnetization, M_s , monotonically increases with c_{Fe} ²⁾. Magnetic coercivity, H_c , increases with c_{Fe} for $c_{\text{Fe}} < 0.4$ because magnetic dipole interactions between Fe NPs are reinforced by the reduction in the inter-nano-particle distance (the increase in the Fe nano-particle density), while it gradually decreases for $c_{\text{Fe}} > 0.6$ because magnetic exchange interactions are slightly induced. However, the exchange interaction is not intensified due to the loose contacts between Fe NPs and averaged by randomness in the orientations, positions and configurations of Fe and Si NPs^{1,2)}.

In contrast with these results, we made $\text{Fe}_x\text{Si}_{1-x}$ alloy films and observed temperature dependence of electrical resistivity, and thermomagnetic and magnetization curves, to discuss how metallic and magnetic characters evolve with x .

2. Experimentals

About 0.2 μm thin $\text{Fe}_x\text{Si}_{1-x}$ alloy films were prepared by a conventional rf-sputtering equipment whose input electric power was 150 W. The back-ground pressure of the sputtering chamber was about 0.2 mPa, while the Ar gas pressure of 3 Pa was kept during the film-deposition period of 3600×4 s. An Fe disc (56 mm in diameter and 2 mm in thickness), on which rectangle Si plates (5 mm in width and 0.4 mm in thickness) were placed, was used as a composite target. Chemical compositions of films were adjusted by changing the number and configuration of Si plates. Substrates were conventional glass plates for X-ray diffraction and electrical resistivity measurement, quartz glass plates for magnetic measurement and polyimide films for chemical analyses.

Thicknesses of deposited films were measured by a stylus instrument (SUFCOM-1400D). The chemical compositions of deposited films were determined by an energy dispersive X-ray (EDX) analyzer installed in a scanning electron microscope (SEM; JSM-5310LVA). X-ray diffraction patterns were observed in the standard Bragg-Brentano geometry using an X-ray diffractometer with a Cu target (RINT-2200H). Electrical resistivity, ρ , was measured in a four probe mode between 5 and 300 K using a physical properties measuring system (PPMS, Quantum Design) where $\text{Fe}_x\text{Si}_{1-x}$ alloy films were deposited between four Au gold stripe electrodes whose separation distances were 1 mm on quartz glass substrates. Thermomagnetic curves in a low field of 24 kA/m between 2 and 300 K and magnetization curves up to 4 MA/m between 5 and 300 K were observed using a superconducting quantum interface device magnetometer (MPMS-5, Quantum Design). The thermomagnetic and magnetization curves of an weight-

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ed quartz substrate were also observed and subtracted from the above data.

3. Results

3.1 Structures

Figure 1 shows X-ray diffraction patterns of $\text{Fe}_x\text{Si}_{1-x}$ alloy films. No clear peak nor broad hallow are detected for $x < 0.8$, while a few Bragg peaks allotted to a bcc phase are detected for $x > 0.8$. These results agree with the reported ones³⁻⁶, indicating that $\text{Fe}_x\text{Si}_{1-x}$ alloy films with $x < 0.8$ are amorphous.

3.2 Electrical properties

Figure 2 shows electrical resistivity, ρ in a logarithmic-scale of $\text{Fe}_x\text{Si}_{1-x}$ alloy films as a function of temperature, T . The ρ

Fig. 1 X-ray diffraction patterns of $\text{Fe}_x\text{Si}_{1-x}$ alloy films. ▼: Bragg angles of bcc Fe phases

Fig. 2 Electrical resistivity, ρ in a logarithmic-scale of $\text{Fe}_x\text{Si}_{1-x}$ alloy films as a function of temperature, T .

values are larger than those of $\text{Fe}_x\text{Si}_{1-x}$ alloy films prepared by an electron-beam deposition method in a vacuum condition of $6.7 \mu\text{Pa}$ ⁴. The electrical conductivity, $\sigma = (1/\rho)$ at 5, 21 and 300 K are collected from the data in Fig. 2, and shown in a logarithmic-scale as a function of x in Fig. 3. With increasing x , σ at first rapidly increases and then gradually increases, where σ is roughly independent of T for $x > 0.5$ and the inflection composition, $x_C \cong 0.42$ at 5 and 21 K, while $x_C \cong 0.22$ at 300 K.

In Fig. 4(a) (the ρ in a logarithmic-scale versus $1/T$ plots for $x < 0.5$), the ρ values are large and increase with increasing $1/T$, indicating a semiconducting character. Table 1 shows the average energy gaps, E_g , which are estimated by fitting the following equation

$$\rho \propto \exp\left(\frac{E_g}{k_B T}\right) \quad (1)$$

to the experimental results for $1/T < 10^{-2} \text{ K}^{-1}$ ⁷. These values are much smaller than that of bulk Si, 1.11 eV (at 300 K)⁸. In Fig. 4(b) (the ρ in a logarithmic-scale versus T plots for $x > 0.4$), the ρ values for $x > 0.6$ are smaller than those for $x < 0.5$ and slightly increase with T , indicating a metallic character suffered from heavy impurity scattering.

3.3 Magnetic properties

Figures 5 shows magnetization curves (magnetization, M versus magnetic field, H) at 5 K for $\text{Fe}_x\text{Si}_{1-x}$ alloy films, revealing a saturation behavior for $x > 0.4$. Figure 6 shows the x dependence of spontaneous magnetization, M_0 at 5 K, which were estimated by linearly extrapolating the high field portions of M versus H curves to $H = 0 \text{ A/m}$ in Fig. 5. As shown in Fig. 6, the present results are well consistent with the reported ones^{3,5,6}. M_0 is 0 Wb/m^2 at $x \leq 0.4$ and monotonically increases with x for $x > 0.4$.

Figure 7 shows thermomagnetic curves observed in $H = 24 \text{ kA/m}$ for zero-field cooled (ZFC) and field cooled (FC) $\text{Fe}_x\text{Si}_{1-x}$ alloy films. In these figures, bifurcations between ZFC and FC curves are detected at low temperatures for $0.36 < x < 0.53$, while no bifurcation down to 2 K for $x < 0.35$ and $x > 0.55$. We define the magnetic (spin or cluster) glass temperature, T_g as a bifurcation starting temperature.

The Curie temperature, T_C is determined by the Curie-Weiss law,

Fig. 3 Composition (x) dependence of electrical conductivity, $\sigma = 1/\rho$ at 5, 21 and 300 K of $\text{Fe}_x\text{Si}_{1-x}$ alloy films.

Fig. 4 (a) Electrical resistivity, ρ in a logarithmic-scale versus $1/T$ plots of Fe_xSi_{1-x} alloy films with $x < 0.5$. (b) ρ versus T plots of Fe_xSi_{1-x} alloy films with $x > 0.4$.

Table 1 Energy gap, E_g estimated from fitting eq. (1) to electrical resistivity, ρ in the logarithmic scale versus inverse temperature, $1/T$ for Fe_xSi_{1-x} alloy films with $x < 0.5$.

c_{Fe}	E_g [meV]
0.46	3.25
0.41	4.37
0.35	19.6
0.31	35.4
0.25	54.9

$$\chi = \frac{C}{T - T_C}, \quad C: \text{the Curie-Weiss constant} \quad (2)$$

and plotting the inverse magnetic susceptibility, χ^{-1} versus T in Fig. 8, and by the Arrott plots of magnetization curves observed at several temperatures. T_C is also estimated as a temperature at which linear extrapolations of low temperature and high temperature portions of ZF curves cross. Figure 9 shows T_C and T_g as a function of x , i.e., the magnetic phase diagram of Fe_xSi_{1-x} alloy films. As shown in Fig. 9, the present results of T_C are consistent with the reported ones⁶⁾.

Fig. 5 Magnetization curves (magnetization, M versus magnetic field, H) at 5 K for Fe_xSi_{1-x} alloy films.

Fig. 6 Composition (x) dependence of spontaneous magnetization, M_0 at 5 K for Fe_xSi_{1-x} alloy films.

4. Discussion

4.1 Electrical properties

In the present Fe_xSi_{1-x} alloy films, ρ values are much larger than those of Fe_xSi_{1-x} alloy films prepared by an electron-beam deposition method in the better vacuum condition⁴⁾. Such difference is attributable to oxygen contamination. However, no oxide Bragg peak is detected in their X-ray diffraction patterns and their M_0 values agree with each other. Usually films sputter-deposited in high Ar gas atmosphere consist of columnar grains which result in low density grain boundaries⁹⁾. Since the background vacuum condition is worse to maintain high Ar atmosphere, grain boundaries are prefer to be oxidized¹⁰⁾. Therefore, the high ρ values are as-

Fig. 7 Thermomagnetic curves observed in $H = 24$ kA/m for zero-field cooled (ZFC) and field cooled (FC) $\text{Fe}_x\text{Si}_{1-x}$ alloy films. (a) $x = 0.36$, (b) $x = 0.40$, (c) $x = 0.44$, (d) $x = 0.48$, (e) $x = 0.53$ and (f) $x = 0.56$.

cribed to preferred oxidation of grain boundaries.

In amorphous $\text{Fe}_x\text{Si}_{1-x}$ and $\text{Au}_x\text{Si}_{1-x}$ alloy films prepared by an electron-beam deposition method in the better vacuum condition, the σ values at 77 K for $x > 0.4$ are linearly extrapolated to $0 \Omega \cdot \text{m}$ at around $x \approx 0.4^{4,11)}$, being consistent with $x_C \approx 0.42$ at 5 and 21 K in the present $\text{Fe}_x\text{Si}_{1-x}$ alloy films, while the σ value gradually decreases to be $0 \Omega \cdot \text{m}$ at around $x \approx 0.2$ due to the change in their amorphous structures, i.e., a continuous random network to a dense random packing of hard sphere, or a covalent bond type to a metallic bond type. For $x < 0.2$ impurity levels form a narrow impurity band which is separated from the conduction (or valence) band,

and thermal excitation of carriers (electrons or holes) is the main conduction channel. With increasing x from 0.22 to 0.42, they overlap to form a band tail, but carriers are localized in the amorphous (random) structure to retain a mobility gap between them. As long as the Fermi level is lower than the mobility edge, an activation type conductivity is predominant at finite temperature. For $x > 0.42$, the mobility gap diminishes, but σ is heavily suppressed by the structure-randomness and impurity scattering^{7,12)}.

The detailed experiment and systematic analyses of electrical resistivity data indicate the semiconductor to metal transition threshold $x_C = 0.24$ for $\text{Ni}_x\text{Si}_{1-x}$ alloy films^{13,14)} and $x_C =$

Fig. 8 Inverse magnetic susceptibility, χ^{-1} of zero-field cooled $\text{Fe}_x\text{Si}_{1-x}$ alloy films as a function of temperature, T . (a) $x = 0.36, 0.40, 0.44, 0.48$, (b) $x = 0.53, 0.56$.

0.14 for $\text{Cr}_x\text{Si}_{1-x}$ alloy films^{15,16)} where an electron-localization effect and an electron-electron interaction are predominant at low temperature. These value are roughly consistent with $x_c \approx 0.22$ at 300 K (high temperature) in the present $\text{Fe}_x\text{Si}_{1-x}$ alloy films. Taking into account of the weight density of Fe is $7.87 \times 10^3 \text{ kg/m}^3$ and that of Si $2.33 \times 10^3 \text{ kg/m}^3$, we convert x into the volume fraction, v . Then, $x_c \approx 0.22$ corresponds to the critical (percolation volume fraction, $v_c \approx 0.14$, which is roughly consistent with $v_c \approx 0.16$ for the 3 dimensional percolation^{17,18)}. In the percolation theory, moreover, σ is correlated with v and v_c as follows¹⁹⁾:

$$\sigma \propto (v - v_c)^t, \quad (3)$$

Here, t is the critical exponent which theoretically depends only on the system dimension. As shown in Fig. 10, the slope of $\log \sigma$ at 300 K versus $\log(v - v_c)$ gives $t \approx 1.80$, being comparable with $t = 1.9 \sim 2.1$ for 3 dimensional percolation (cf. $t = 1.1 \sim 1.3$ for the 2 dimensional percolation).

It is worthwhile to mention that the σ value in a logarithmic

Fig. 9 The magnetic phase diagram of $\text{Fe}_x\text{Si}_{1-x}$ alloy films. T_c : Curie temperature and T_g : magnetic (spin- or cluster-glass) temperature obtained by the present results. T_c' and T_c'' : Curie temperature reported by Mangin and Marchal⁶⁾. P: the paramagnetic region, F: the ferromagnetic region and MG: the magnetic glass region.

Fig. 10 Logarithmic electric conductivity, $\log \sigma$ at 300 K versus logarithmic Fe composition, $\log(v - v_c)$ plot in $\text{Fe}_x\text{Si}_{1-x}$ alloy films, where v is the volume fraction of Si and $v_c = 0.14$ the critical (percolation) volume fraction corresponding to the critical composition, $x_c = 0.22$ estimated from Fig. 3.

mic scale versus the Fe concentration c_{Fe} plot dramatically changes at around $c_{\text{Fe}} \approx 0.6$ in Fe/Si nano-particle composites^{1,2)}. Since the packing densities of these nano-particle assemblies are about 30% of bulk specimens, $v_c \approx 0.6 \times 0.3 = 0.18$, which also roughly agree with $v_c = 0.16$ ¹⁷⁻¹⁹⁾.

4.2 Magnetic properties

Owing to random distribution of individual atoms and superposition of ferromagnetic (FM) and antiferromagnetic (AM) exchange interactions, the alignment of magnetic-mo-

ments is directionally and spatially random. When FM interactions surmount AM interactions, they compete with thermal fluctuation at high temperatures, determining the Curie temperature, T_C . However, FM interactions only compete with AM interactions at low temperatures, revealing the magnetic (spin or cluster) glass phase and magnetic glass temperature, T_g^{20} .

We have to emphasize that the magnetic glass region in Fig. 9 is very narrow in comparison with those in $\text{Fe}_x\text{Au}_{1-x}$ alloys and $\text{Fe}_x\text{Al}_{1-x}$ alloy films. In $\text{Fe}_x\text{Au}_{1-x}$ alloys^{21–23}, isolated Fe atoms carry magnetic moments and they are magnetically coupled via strong direct- and indirect- (RKKY) exchange interactions with increasing x . Moreover, since a magnetic moment of Fe atom is enlarged by lattice expansion of Fe atoms embedded in a matrix of larger Au atoms, the ferromagnetic state is stable for $x > 0.16$, the triple temperature is rather high and the magnetic glass region extends down to $x = 0$. In bcc $\text{Fe}_x\text{Al}_{1-x}$ alloys, magnetic moments of Fe atoms decrease with the number of nearest neighbor Al atoms²⁴ and antiferromagnetically coupled with each other²⁵, while vanish in the B2 type ordered phase where all Fe atoms are surrounded by Al atoms in their nearest neighbor sites. Since magnetic moments of Fe atoms are also suppressed with decreasing x in the amorphous and disordered phase²⁶, the ferromagnetic state is stable only for $x > 0.5$ and the magnetic glass region extends down to $x \approx 0.3$.

In $\text{Fe}_x\text{Si}_{1-x}$ alloys, magnetic moments of Fe atoms also rapidly decrease with increasing the number of Si atoms in their nearest neighbor sites owing to chemical bonding between 4s + 3d electrons of Fe atoms and 2s + 2p electrons of Si atoms. Moreover, the conduction electron density is not so high as those in $\text{Fe}_x\text{Au}_{1-x}$ and $\text{Fe}_x\text{Al}_{1-x}$ alloys, RKKY type long range magnetic interactions are not so strong for $x < 0.4$. Indeed, the intermetallic-compound, B20 type FeSi, is a narrow gap semiconductor and paramagnetic at the ground state, whereas magnetic moments are induced by thermal fluctuation, revealing a Curie-Weiss type magnetic susceptibility^{27–29}. In this context, the ferromagnetic state and the magnetic glass region simultaneously disappear at around $x = 0.3$.

5. Summary

Amorphous $\text{Fe}_x\text{Si}_{1-x}$ alloy films were prepared by rf sputter-deposition. Impurity-semiconductor-type conduction is observed for $x < 0.2$, metallic conduction, which is strongly affected by impurity-scattering, is observed for $x > 0.4$, and complicate conduction influenced by structure randomness and electron localization are observed for $0.2 < x < 0.4$. In the magnetic phase diagram of $\text{Fe}_x\text{Si}_{1-x}$ alloy films, the magnetic (spin- or cluster) glass region is very narrow, whereas ferromagnetic and magnetic glass phases simultaneously disappear at $x \approx 0.3$. These characteristic behaviors are ascribed to the instability of Fe magnetic moments and the depression of RKKY type interactions in the low x alloy films.

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