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

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Fe$_x$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 $x = 0.3$ and the Curie temperature rapidly increases with increasing $x$. The magnetic (spin- or cluster-) glass region is very narrow ($x = 0.3 ~ 0.55$) 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.

[Received February 5, 2016; Accepted March 16, 2016; Published April 15, 2016]

Keywords: iron-silicon alloy films, semiconductor to metal transition, magnetic phase diagram, sputter-deposition, electrical resistivity, thermomagnetic curve, magnetization

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, $\rho$, the $\rho$ value changes in several orders of magnitude at around the 3 dimensional percolation composition of Fe atoms, $c_{Fe} = 0.6^{11}$. With increasing temperature, $T$, $\rho$ monotonically decreases for $c_{Fe} < 0.6$, where a Si NPs network is predominant (the semiconductor regime), while slightly increases for $c_{Fe} > 0.6$, 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 $c_{Fe}^{2,3}$. Magnetic coercivity, $H_C$, increases with $c_{Fe}$ for $c_{Fe} < 0.4$ 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 $c_{Fe} > 0.6$ 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 Fe$_x$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. Experiments

About 0.2 $\mu$m thin Fe$_x$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 $\times$ 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-5310LV). 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, $\rho$, was measured in a four probe mode between 5 and 300 K using a physical properties measuring system (PPMS, Quantum Design) where Fe$_x$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-
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 Fe$_x$Si$_{1-x}$ alloy films. No clear peak nor broad hollow 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 ones$^{3-6}$, indicating that Fe$_x$Si$_{1-x}$ alloy films with $x < 0.8$ are amorphous.

3.2 Electrical properties

Figure 2 shows electrical resistivity, $\rho$ in a logarithmic-scale of Fe$_x$Si$_{1-x}$ alloy films as a function of temperature, $T$. The $\rho$ values are larger than those of Fe$_x$Si$_{1-x}$ alloy films prepared by an electron-beam deposition method in a vacuum condition of 6.7 $\mu$Pa$^9$. 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 $x$, $\sigma$ at first rapidly increases and then gradually increases, where $\sigma$ 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 $\rho$ in a logarithmic-scale versus $1/T$ plots for $x < 0.5$), the $\rho$ 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

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

(1)

to the experimental results for $1/T < 10^{-2}$ 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 $\rho$ in a logarithmic-scale versus $T$ plots for $x > 0.4$), the $\rho$ 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 Fe$_x$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 $H = 0$ 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 $H = 24$ kA/m for zero-field cooled (ZFC) and field cooled (FC) Fe$_x$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,
χ = \frac{C}{T - T_c}, \quad C: the Curie-Weiβ constant \hspace{1cm} \text{(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 \(T_p\) as a function of \(x\), i.e., the magnetic phase diagram of Fe\(_{1-x}\)Si\(_x\) alloy films. As shown in Fig. 9, the present results of \(T_C\) are consistent with the reported ones\(^6\).

### Table 1

<table>
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<tr>
<th>(c_{Fe})</th>
<th>(E_g) [meV]</th>
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<tr>
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<td>3.25</td>
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<td>35.4</td>
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### Discussion

#### 4.1 Electrical properties

In the present Fe\(_{1-x}\)Si\(_x\) alloy films, \(\rho\) values are much larger than those of Fe\(_{1-x}\)Si\(_x\) alloy films prepared by an electron-beam deposition method in the better vacuum condition\(^5\). 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 boundaries\(^9\). Since the background vacuum condition is worse to maintain high Ar atmosphere, grain boundaries are prefer to be oxidized\(^10\). Therefore, the high \(\rho\) values are as-
cribed to preferred oxidation of grain boundaries.

In amorphous Fe$_x$Si$_{1-x}$ and Au$_x$Si$_{1-x}$ alloy films prepared by an electron-beam deposition method in the better vacuum condition, the $\sigma$ values at 77 K for $x > 0.4$ are linearly extrapolated to 0 $\Omega \cdot$ m at around $x \approx 0.44$, being consistent with $x_C \approx 0.42$ at 5 and 21 K in the present Fe$_x$Si$_{1-x}$ alloy films, while the $\sigma$ value gradually decreases to be 0 $\Omega \cdot$ 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 $\sigma$ is heavily suppressed by the structure-randomness and impurity scattering.

The detailed experiment and systematic analyses of electrical resistivity data indicate the semiconductor to metal transition threshold $x_C = 0.24$ for Ni$_x$Si$_{1-x}$ alloy films and $x_C =$.
0.14 for CrSi$_{1-x}$ 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 Fe$_x$Si$_{1-x}$ alloy films. Taking into account of the weight density of Fe is $7.87 \times 10^3$ kg/m$^3$ and that of Si $2.33 \times 10^3$ 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, $\sigma$ is correlated with $v$ and $v_c$ as follows$^{19}$:

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

(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 $\sigma$ value in a logarithmic scale versus the Fe concentration $c_{Fe}$ plot dramatically changes at around $c_{Fe} \approx 0.6$ in Fe/Si nano-particle composites$^{12}$. 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-

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

Fig. 9 The magnetic phase diagram of Fe$_x$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 $T_C^{\alpha}$: Curie temperature reported by Mangin and Marchal$^6$. 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 Fe$_x$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.
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, $T_g$.

We have to emphasize that the magnetic glass region in Fig. 9 is very narrow in comparison with those in Fe$_x$Au$_{1-x}$ alloys and Fe$_x$Al$_{1-x}$ alloy films. In Fe$_x$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 Fe$_x$Al$_{1-x}$ alloys, magnetic moments of Fe atoms decrease with the number of nearest neighbor Al atoms$^{24}$ and antiferromagnetically coupled with each other$^{25}$, 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 phase$^{26}$, the ferromagnetic state is stable only for $x > 0.5$ and the magnetic glass region extends down to $x \approx 0.3$.

In Fe$_x$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 Fe$_x$Au$_{1-x}$ and Fe$_x$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 Fe$_x$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 conductions influenced by structure randomness and electron localization are observed for $0.2 < x < 0.4$. In the magnetic phase diagram of Fe$_x$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.

Acknowledgments

We appreciate Mr. T.Toya in the Frontier Research Collaboration Center of Tokyo Denki University for his guidance for chemical analyses. This work was supported by Nanotechnology Platform Program (Molecule and Material Synthesis), the Ministry of Education, Science, Culture and Sports, Japan. One of the authors (K.S.) was indebted to Research Institute of Science and Technology, Tokyo Denki University and Nagoya Industrial Science Research Institute for their supports.

REFERENCES