# Effect of substitutionally dissolved Ce in Si on the magnetic and electric properties of magnetic semiconductor $Si_{1-x}Ce_x$ films

T. Yokota, N. Fujimura,[a] and T. Ito
*Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan*

(Received 30 April 2002; accepted 4 October 2002)

A magnetic semiconductor Si:Ce thin film was prepared using a vacuum evaporation system with electron-beam guns. The as-deposited thin film was amorphous and exhibited $n$-type conduction. It showed temperature dependence of resistivity ($\rho-T$), as in a normal semiconductor, and a diamagnetic property. By annealing at 973 K, however, the film epitaxially crystallizes and the conduction changes to the $p$-type. The resistivity of the film abruptly decreases by three orders of magnitude below 30 K, unlike that of the as-deposited film. The magnetic susceptibility measured at a low magnetic field (750 Oe) also decreases around the same temperature in $\rho-T$ curves. These magnetic and carrier transport phenomena are responsible for the substitutionally dissolved Ce in Si.
 [DOI: 10.1063/1.1524030]

Semiconductors doped with a magnetic element [diluted magnetic semiconductors (DMS)] have been widely studied, especially for the III–V (e.g., Mn-doped GaAs) and II–VI (e.g., Mn-doped CdTe, etc.) compound semiconductors.[1–3] We have also been interested in Si-based DMS, which is a promising material, especially for microelectronics applications. In bulk Si:Ce samples, various phenomena, such as antiferromagnetism, heavy fermion type transport behavior, and ferromagnetic ordering, have been observed.[4] In the case of a polycrystalline bulk sample, the inhomogeneous microstructure and compositional distribution make the investigation of its real magnetic and electrical properties difficult. To study the fundamental magnetic and carrier transport properties of dilutely Ce-doped Si and to explore its utility for microelectronics applications, we must first eliminate its inhomogeneous microstructure, grain boundaries, and precipitates.

In the present letter, we describe the fabrication of single phase Si:Ce films and their magnetic and transport properties. We also examine the annealing effects, which vary the crystallographic state of the host Si and the coordination of Ce.

The Si:Ce thin films were deposited by vacuum evaporation using electron-beam (EB) guns on (100)Si substrates. The deposition rates of Si and Ce were measured using a thickness monitor. The composition of the films was evaluated by Rutherford backscattering. The structure of the films was evaluated by x-ray diffraction (XRD) and a transmission electron microscope (TEM), and we also determined the diffraction (TED). The temperature dependences of resistivity and the Hall effect were measured from 2 to 300 K. The magnetic properties were evaluated using a superconducting quantum interface device magnetometer.

Compared with the III–V or II–VI semiconductors, the solubility of magnetic elements in Si is relatively low. We anticipated that a nonequilibrium growth technique was required to dissolve a large amount of Ce into Si. The $Si_{1-x}Ce_x$ films were prepared at the relatively low temperature of 400 °C. The thickness of the samples was fixed at 1200 nm to avoid the effect of the substrate in measuring the electric properties. Figure 1 shows the XRD and TED patterns of the as-deposited Si:0.3 at. % Ce film. The XRD pattern shows only a 004 diffraction of the Si substrate. A very broad diffraction of 111 was observed at around 28° and indicated that the film was amorphous. The TED pattern also suggests that the film was amorphous without any precipitation of silicides and other component in the crystalline phase.

Although the trivalent state of Ce makes an acceptor level in the Si matrix, the conduction of the film measured at 300 K was $n$-type, probably due to its amorphous nature. The carrier density was calculated to be $1.2\times10^{16}$ cm$^{-3}$. The temperature dependence of resistivity was measured in the temperature range from 4.2 to 300 K. Figure 2 shows the resistivity change against the inverse temperature. The resistivity increases with decreasing temperature according to $\rho=\rho_0\exp(E_a/kT)$, as is usually found for thermally activated conduction processes having an activation energy of $E_a$. The acceptor level was determined to be 50.6 meV in the temperature range from 100 to 160 K. The magnetization curve against the applied magnetic field ($M-H$ curve) at 2 K shows diamagnetic behavior due to the existence of the amorphous Si film and Si substrate. The Ce may be tetravalent without a $4f$ electron which has the electronic structure $4f^0 5d^o 6s^2$. In the case of Ce, $4f^1 5d^1 6s^2$ is the most stable state, but the state of an empty, half full, or completely full $f$

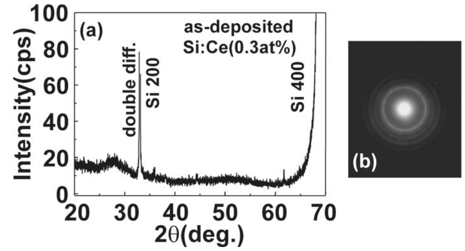


FIG. 1. X-ray diffraction pattern (a) and transmission electron diffraction (b) of an as-deposited Si:0.3 at. % Ce film.

[a]Electronic mail: fujim@ams.osakafu-u.ac.jp

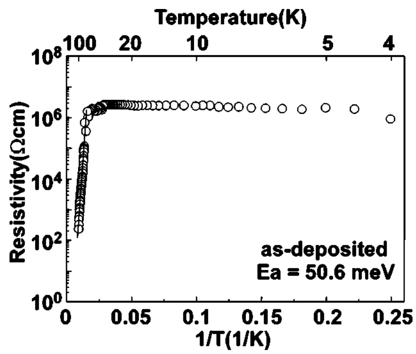


FIG. 2. Temperature dependence of resistivity for as-deposited Si:Ce.

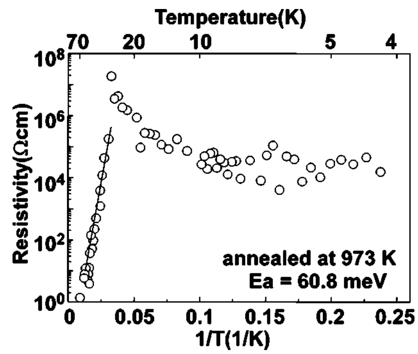


FIG. 4. Temperature dependence of resistivity for annealed Si:Ce.

level ($Ce^{4+}f$ shell empty, $Eu^{2+}f$ shell half full, $Tb^{4+}f$ shell half full, and $Yb^{2+}f$ shell half full)[5] is also stable for rare earth elements.

In order to crystallize the film, samples were annealed at 773–1273 K for 15 h in a vacuum ($\sim 10^{-7}$ Torr). Figure 3 shows the annealing temperature dependence of the XRD patterns. The film is still amorphous after annealing at 773 K and crystallizes above 873 K. By annealing at 973 K, a polycrystalline diffraction pattern is clearly observed. However, there is a shoulder at the lower angle side of 400 Si substrate diffraction (inset in Fig. 3). The diffraction intensity of the shoulder, which was identified as that of the film, is hundreds of times as large as the expected diffraction intensity of a polycrystalline film, leading us to conclude that, the film consists of epitaxially grown Si and a small amount of poly-Si. A detailed structural analysis[6] has revealed that polycrystalline Si exists near the surface of the film. Since the polycrystalline region could be removed by chemical etching, all the experiments subsequently discussed were performed using the sample etched off the surface layer. No silicide precipitation has been recognized in the annealed sample, even by TED observation.

Although the as-deposited sample was of the $n$-type, the conduction type of the sample annealed above 873 K exhibited $p$-type behavior, and the carrier density increases as the annealing temperature increases. The Ce may become trivalent, which is the most stable electronic structure: $4f^15d^16s^2$. The sample annealed at 973 K had the highest

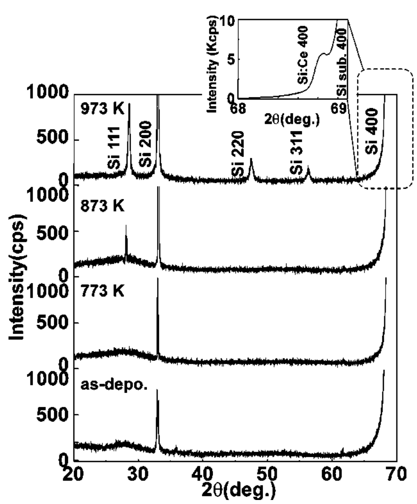


FIG. 3. Annealing temperature dependence of x-ray diffraction patterns of Si:Ce film; inset shows the narrow scan around Si 400.

hole density ($2.9\times10^{16}$ cm$^{-3}$). Figure 4 shows the resistivity change versus the inverse temperature of the sample annealed at 973 K. The acceptor level was determined to be 60.8 meV in the temperature range from 60 to 80 K. The resistivity exponentially increases until 33 K with a decreasing temperature, and immediately decreases by three orders of magnitude below 33 K.

Figure 5 shows the temperature dependence of magnetic susceptibility ($\chi - T$). It also has a cusp at about 38 K. This anomalous magnetic susceptibility change seems to be related to the anomalous temperature dependence of resistivity below 33 K, as shown in Figure 4. Figure 6 shows $M-H$ curves at 100 and 2 K, which are higher and lower temperatures, respectively, than the cusp temperature. The $M-H$ curve at 100 K has a steep slope below 0.1 T, and this behavior disappears at least at 2 K. These magnetic properties suggest that a spin-glass-like interaction[7] occurs in Si:0.3 at. % Ce film. The existence of the cusp in the $\chi - T$ curve can be attributed to the frozen state (spin-glass state) of the magnetic moment of the Ce spin. Just below the transition temperature ($T_g$), the critical scattering originating from the spin ordering occurs, and the resistivity and $\chi$ become larger. The spins then begin to interact as a frozen state (spin-glass) just at $T_g$, which is thought to be responsible for the drastic drop in resistivity and magnetic susceptibility.[8]

Blocking phenomena observed in the sample, including dispersed ferromagnetic particles, should be considered as an alternative solution.[9] In any case, although the magnetic moment decreases below the cusp temperature, such a particle was not observed in TEM. Detailed TED and XRD analyses reveal that no silicide[10–12] has been contributed to these phenomena. The annealing effects using an identical sample also suggest that these phenomena do not originate from an impurity effect in the Si:Ce.

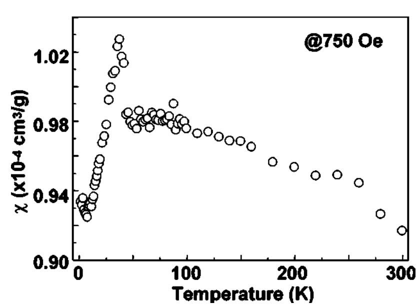


FIG. 5. Temperature dependence of magnetic susceptibility measured at 750 Oe.

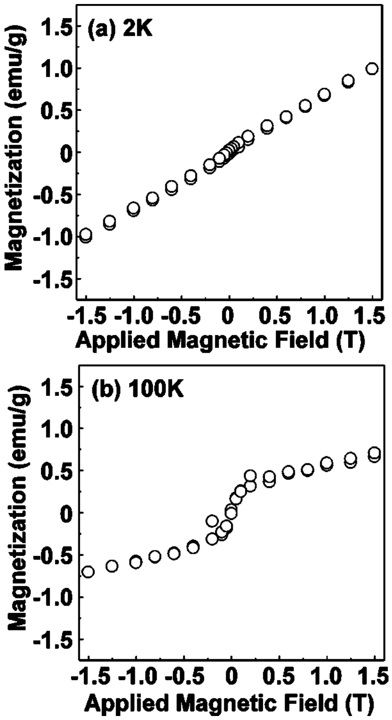


FIG. 6. Magnetization curves of annealed Si:Ce at (a) 2 K and (b) 100 K.

Judging from the consequences of lattice expansion in the Si:Ce epitaxial layer and the change in carrier type by annealing, substitutionally dissolved Ce in Si is considered to be responsible for these magnetic properties.

Magnetic element, Ce, doped Si films were fabricated by vacuum evaporation using EB guns. Since the Si:Ce film was grown at a low temperature to achieve the high solubility of Ce in the Si host, the film was amorphous. In the amorphous host, Ce exists as a tetravalent structure without $4f$ electron, which should be responsible for the $n$-type conduction and diamagnetism. However, the crystallized films by annealing have a larger lattice constant compared with that of Si and a positive magnetic behavior up to 100 K, which indicates the existence of a $4f$ electron. $\rho - T$ and $\chi - T$ measurements reveal that the spin-glass interaction may occur in the films. Based on these results, coordination of Ce in Si is considered to play a very important role for these magnetic and transport phenomena.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (A), Spin Controlled Semiconductor Nanostructures (No. 10138218) from the Ministry of Education, Science, Sports and Culture, a Grant-in-Aid for Scientific Research, No.13875009, Grant-in-Aid Exploratory Research, No. 13875009, Grant-in-Aid for Scientific Research (S), No.14102021, Grant-in-Aid for JSPS Fellows, No. 00000652, from the Japan Society for the Promotion of Science, and The Murata Science Foundation.

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