Ce concentration dependence on the magnetic and transport properties of Ce doped Si epitaxial films prepared by molecular beam epitaxy

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Diluted magnetic semiconductors, Si:Ce thin films with the Ce concentration below 1.5 at. %, were prepared by solid source molecular beam epitaxy. Magnetization curves (*M-H*) for all the samples show superparamagnetic behaviors at least up to 300 K. Temperature dependence of the magnetic susceptibility (χ-T) has a cusp, which is ascribed to the spin glass. Temperature dependence of resistivity (ρ-T) also has a cusp at around the cusp temperature in χ-T curves. As the amount of substituted Ce in Si estimated from the lattice constant increases, the cusp temperature also increases. The amount of substituted Ce in Si is considered to play an important role for the anomalous magnetic and transport properties.
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I. INTRODUCTION

Semiconductors doped with magnetic elements [diluted magnetic semiconductors (DMS)] have been widely studied, especially for the group III–V (for example, Mn doped GaAs) and the group II–VI compound semiconductors.[1,2] On the other hand, we have been interested in Si based DMS. Si:Ce bulk samples and vacuum evaporated films were prepared, and various phenomena such as ferromagnetic ordering, anomalous ρ-T behavior, spin glasslike behavior, and giant magnetoresistance have been observed.[3–5] To study the origin of these anomalous behaviors, the inhomogeneous microstructure, grain boundaries, defects, and precipitates should be eliminated and highly Ce doped Si films are required.[6]

In this article, the effects of substituted Ce concentration on the magnetic and transport properties of the molecular beam epitaxy (MBE) deposited Si:Ce films with excellent crystallinity are discussed.

II. EXPERIMENT

Si:Ce epitaxial films were deposited on (001) Si substrate by a solid source MBE system. Simultaneous evaporation of Si and Ce was carried out by using high-temperature Knudsen cells. The evaporation temperature of Si was fixed as 1450 °C. The cell temperature of the Ce source was varied from 1050 to 1150 °C to change the Ce concentration of the film that yields the Si:Ce films with the Ce concentration from 0.5 to 1.5 at. %. Surface and cross sectional morphologies were evaluated by field emission type scanning electron microscope. The structural analysis of the films was performed with *in situ* reflection high energy electron diffraction, conventional x-ray diffraction (XRD: operated at 30 kV, 40 mA), rotation target type x-ray diffraction (RT-XRD: operated at 50 kV, 200 mA), transmission electron microscope and transmission electron diffraction (TED). Superconducting quantum interference device was used for evaluating the magnetic properties. Resistivity and the Hall effect were measured using the van der Pauw method in the temperature range from 4 to 270 K.

III. RESULTS AND DISCUSSION

The Si films with the Ce content below 1.5 at. % were prepared at the fixed substrate temperature of 500 °C. The composition of the film is estimated from the deposition rate of each material. The thickness of all the samples was fixed at 480 nm. The XRD and TED measurements reveal that all the films were grown epitaxially on the (001) Si substrate. The precipitation of fine-grained CeSi with antiferromagnetic nature was observed only in the sample with the Ce concentration of 1.5 at. %. In other samples, no silicide precipitation was recognized even by RT-XRD and TED. To estimate the amount of substitutionally dissolved Ce in Si lattice, *d* spacing along the ⟨001⟩ direction was measured using XRD. Figure 1 shows the change in the lattice constant along the growth direction against the Ce concentration. All the films have expanded lattice due to the substitution of Ce ions with a larger ionic radius than that of Si. As the Si:0.5 at. % Ce film has the largest lattice constant, it should contain the largest amount of substituted Ce. In the Si:1.5 at. % Ce film, silicide formation should be responsible for the smaller lattice constant. Based on these crystallo-

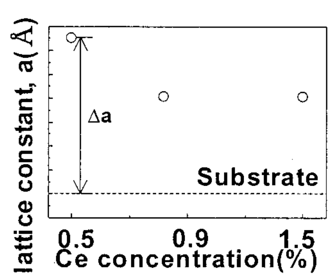

FIG. 1. Change in the lattice constant, *a*, along the growth direction against the Ce concentration estimated from XRD patterns. Δa indicates the strain along the growth direction.

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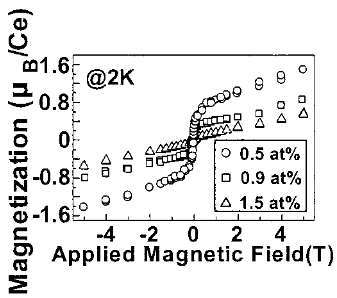

FIG. 2. Magnetization curves of Si:Ce thin films with various Ce concentrations measured at 2 K.

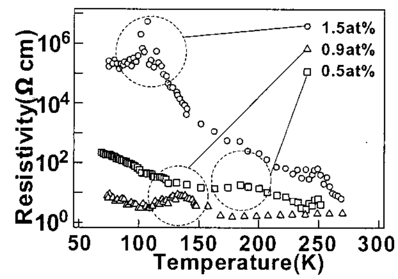

FIG. 4. Temperature dependence of resistivity of SiCe thin films in the temperature range from 70 to 270 K.

graphic evaluations, the lattice constant seems to represent the amount of substitutionally dissolved Ce (effective Ce content).

Figure 2 shows the *M-H* curves of these samples measured at 2 K. All the samples exhibit positive magnetization. Si:0.5 at. % Ce with the largest lattice constant has the largest magnetization. The smallest saturated magnetization of Si:Ce 1.5 at. % implies that silicide formation does not affect the positive magnetization. The magnetic susceptibility of all the samples at the applied magnetic field below 0.05 T is larger than the paramagnetic moment of the Ce^{3+} free ion calculated using the Brillouin function. So as to examine the magnetic behavior more carefully, the temperature dependence of the magnetic susceptibility (χ-T) at the magnetic field of 0.05 T was examined as in Fig. 3. The difference between the experimental and theoretically calculated paramagnetic susceptibility as mentioned just above becomes larger with increasing the measurement temperature. It indicates that films have a superparamagnetic nature. All the χ-T curves have a cusp above 70 K. Although the cusp temperature decreases with increasing the Ce concentration, there is a positive relationship between them if we use the lattice strain (Δa, see Fig. 1) instead of the Ce concentration, which indicates substituted Ce content (effective Ce content). Since the cusp temperature of previously reported Si:0.5 at. % Ce film fabricated by conventional vapor deposition was 30 K,[5] well substituted Ce in Si and the elimination of defects should be effective for increasing the cusp temperature. Figure 4 shows the temperature dependence of the electrical resistivity (ρ-T) of these samples. Resistivity of Si:Ce 1.5 at. % exponentially increases and is well fitted to the ρ-T curve calculated with the experimentally measured carrier concentration at room temperature. On the other hand, others exhibit degenerated semiconductor like ρ-T behaviors. Furthermore, all of the ρ-T curves feature a cusp near the cusp temperature in the χ-T curves. By increasing the effective Ce content, and thereby increasing the carrier concentration, the shape of the cusps observed in χ-T and ρ-T curves become indistinct. The magnetic properties suggest that a spin glasslike interaction occur in all of the samples.[7] Then the cusp in the χ-T curves could be attributed to the frozen state of the dispersed spin. The cusp in the ρ-T curves originates from the spin fluctuations just above the spin-freezing temperature. An alternative explanation to the spin-glass is a blocking phenomena like that observed in dispersed ferromagnetic particulate material.[8] In any case, the magnetic moment decreases below the cusp temperature, which increases with the effective Ce content. Silicide formation does not seem to play a role in the magnetic properties. To reveal the relationship between the magnetic property and the transport properties, magnetoresistance (MR) was measured in Fig. 5. In all samples, distinct magnetoresistance is not observed above the cusp temperature. However, positive MR is observed below cusp temperature and the largest MR ratio was obtained in the 0.5 at. % Ce sample. The positive MR ratio exceeding 20% was recognized at the magnetic field within 0.1 T, which corre-

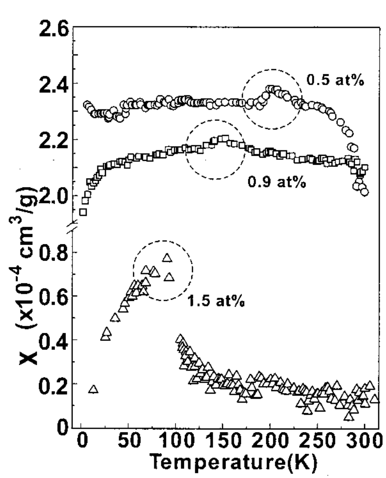

FIG. 3. Temperature dependence of the magnetic susceptibility of Si:Ce thin films measured at 0.05 T.

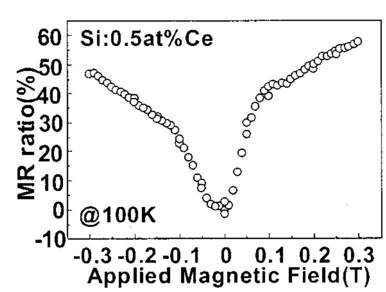

FIG. 5. Magnetoresistance of Si:0.5 at. % Ce, which exhibits the largest magnetization. Measurement was performed at 100 K.

sponds to an abrupt increase of magnetization in the *M*-*H* curve.

Based on these results, we can conclude that there is a strong positive relationship among the effective Ce concentration cusp temperatures in the χ-T and ρ-T curves. However, the increase in effective Ce concentration produces an increase in the carrier concentration, which may deteriorate the spin glasslike interaction. We need to emphasize that silicide formation does not contribute to these magnetic behaviors.

IV. CONCLUSIONS

The effects of Ce concentration in the MBE deposited Si:Ce films on the magnetic and transport properties were discussed. As the amount of substituted Ce for Si increases, the magnetic moment increases, and the cusp temperatures in the ρ-T and χ-T curves also increase. The MR behavior drastically changes at the cusp temperature. On the other hands, silicide formation does not affect these magnetic behaviors.

ACKNOWLEDGMENTS

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