β-FeSi₂ thin film grown on a Si(111) surface with ferromagnetic interface

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Abstract.
Thin iron silicide films were grown by solid phase epitaxy method on Si(111) surface. Silicide structure and magnetic properties at 40 K were observed with reflection high-energy electron diffraction and surface magneto-optic Kerr effect in-situ. The bcc-Fe film was grown at 40 K and transformed to polycrystals at 670 K annealing. The SMOKE revealed ferromagnetic property of the polycrystals at 40 K. After 820 K annealing, a β-FeSi₂ film was formed. This sample was ferromagnetic at 40 K. We suggest a multilayer structure including a ferromagnetic interface between the β-FeSi₂ film and the Si(111) substrate.

1. Introduction
The β-FeSi₂ structure with a semiconducting band gap (∼0.87 eV [1]) has received considerable attention as a very attractive material for optoelectronic devices and is also focused on as an environmentally friendly semiconductor (Kankyo semiconductor). For β-FeSi₂ formation, interdiffusion and silicidation are key processes, and their structure and the electronic properties have been widely studied. Iron-silicide alloys are well known as excellent soft magnetic materials, and their alloying method and magnetic properties have been studied extensively [2–8]. These physical properties of the alloys are different from single-crystals or polycrystal materials [9, 10]. A lot of studies have been performed to understand the mechanism of Fe/Si multilayered films, where strong antiferromagnetic coupling is discovered, [11]. This understanding is also very important for possible applications in microelectronics, since it can allow the integration of magnetic devices in silicon technology.

Some previous calculations showed that β-FeSi₂ has 0.3 μₜₜ ferromagnetic moment with distortion by the Jahn-Teller effect [12]. Until now, the magnetic properties of β-FeSi₂ single crystals have been studied [13–19]. The diamagnetic behavior for pure β-FeSi₂ polycrystals [13] and the ferromagnetic behavior for β-FeSi₂ polycrystalline films [14] were reported below 100 K. Evidence of a ferromagnetic phase was detected in neither β-FeSi₂ single crystal [15–18] nor thin films [19].

In this paper, we present the relation between the structure and magnetism of bcc-Fe, FeₓSi polycrystals and β-FeSi₂ thin film grown on Si(111) surface, using reflection high-energy electron diffraction (RHEED) and surface magneto-optic Kerr effect (SMOKE) in-situ. We found the ferromagnetic property in the β-FeSi₂ system.
2. Experiment

All experiments were performed in an ultra-high vacuum (UHV) system consisting of an air-lock chamber, a gas chamber, and a main chamber equipped with alumina crucible evaporators, a thickness monitor, a RHEED gun and a screen, and electric magnets and optics for SMOKE measurements. The sample position is controlled by a four-axis (X, tilt-Y, Z, and azimuth $\phi$) manipulator with a He refrigerator; the sample stage can be cooled at 40 K. The base pressures of the gas and the main chambers were less than $7 \times 10^{-9}$ Pa. Si(111) mirror-polished wafers (0.5 mm in thickness, n-type, Sb-doped 0.02 $\Omega$ cm), cut in sizes of $4 \times 26$ mm$^2$, were degassed in UHV over 1 h and flashed at 1520 K several times below $2-3 \times 10^{-8}$ Pa in the gas chamber. After the transferring to the stage in the main chamber at 40 K, the samples were flashed again below $7 \times 10^{-9}$ Pa. Clean 7$\times$7 reconstructed patterns were confirmed with RHEED.

We prepared various Fe silicides by the solid phase epitaxy method (annealing after deposition). Fe (99.999%) was deposited at $\Theta_{Fe} = 54$ monolayer (ML) on Si(111)-7$\times$7 clean surfaces at 40 K below $3 \times 10^{-8}$ Pa. The typical deposition rates were about 0.2 Å/min. The film thickness was calibrated by a quartz crystal monitor; unity ML is defined as a thickness of 0.92 Å (= $7.83 \times 10^{14}$ atoms/cm$^2$). Subsequently, the samples were annealed at $T_a$ between 470 to 820 K for five min below $7 \times 10^{-9}$ Pa. After cooling to 40 K of the samples both RHEED and SMOKE measurements were carried out. For the magnetic measurements using SMOKE, hysteresis loops of Kerr signals were recorded in in-plane (longitudinal) and out-of-plane (polar) magnetic field geometries. The light source was a He-Ne laser (632.8 nm, 7 mW) with linear polarization (ellipticity $\leq 10^{-5}$, s-polarization : p-polarization = 1 : 1) at 80° incidence, and was intensity-modulated (50 kHz). The intensity of the reflected light through a polarizer was monitored by a photodiode, and input to a Lock’in amplifier. Maximum magnetic field applied was about 600 Oe in both in-plane and out-of-plane directions. The field at the sample position was calibrated using Hall sensors on a holder. To study the magnetic anisotropy in in-plane direction, we rotated the sample in the azimuth and carried out SMOKE measurements for four directions, [110]$_{Si}$, [101]$_{Si}$, [211]$_{Si}$ and [112]$_{Si}$.

3. Results and discussion

After the deposition at 40 K, RHEED patterns showed transmission diffraction spots of bcc-Fe(111) (figure 1 (a)). Hysteresis curves were observed in both in-plane and out-of-plane directions, as shown in figures 1 (b) and (c), respectively. For the in-plane, the hysteresis curves in [101]$_{Si}$ and [211]$_{Si}$ (not shown) were similar to those in [110]$_{Si}$ and [112]$_{Si}$ (figure 1 (b)), respectively. Since there was no significant difference for the hysteresis loops, [110]$_{Si}$ and [112]$_{Si}$ (figure 1 (b)), there is no magnetic anisotropy in these in-plane directions. We can confirm that the magnetic easy axis lies in the in-plane direction because of square shapes in the hysteresis loop.

For the surface at $T_a = 670$ K, RHEED patterns showed Debye rings, indicating polycrystals. Hysteresis loops were also observed both in-plane and out-of-plane directions. The shape of the hysteresis loops was not square for either direction and seemed to be a minor loop.

We should note that the origin of the hysteresis curve in our system would be different from that in the bulk. For the surface, the effects of surface anisotropy, morphology, shapes and size etc. on magnetic property are more complicated. The interaction effect in fine particle systems strongly depends on the combination of the magnetic state and the physical microstructure. For instance, the calculations of the magnetic properties of a nanosized Co fine particle system by Monte Carlo method showed that the interparticle interactions lead a significant reduction in the saturation remanence which is enhanced by the physical microstructure [21]. Fine particles with surface modification also exhibit some unique phenomena: enhancing the coercivity [22–29]. To account for these phenomena, the underlying mechanism has been proposed for the coercivity as a function of the surface anisotropy [26–28]. In particular, when surface anisotropy energy
is positive, which tends to align the surface magnetization to be tangential to the surface, the coercivity is enhanced [29].

In Si(111)-Fe systems, the magnetic interaction between Fe and Si atoms may have an effect on the hysteresis behavior. Our applied magnetic field maximums (±600 Oe) were not enough to saturate the magnetization completely. In this case, the observed hysteresis loops become so-called "minor loop". Therefore, non-square hysteresis loops can appear even at easy axis directions.

One of the possible phases for the polycrystal is $\epsilon$-FeSi (B20 structure), suggested for the sample preparing by Fe and Si co-deposition method; the presence of heavily twinned $\epsilon$-FeSi has been reported using transmission electron microscopy (TEM) analysis [32]. The B20 $\epsilon$-FeSi has been well known as "strongly correlated" or "Kondo insulator" and its anomalous thermal magnetic properties have been studied experimentally [33] and theoretically [34]. The $\epsilon$-FeSi thin films, however, exhibiting a strong antiferromagnetic coupling was reported by magneto-optical spectroscopies [35]. First principle density-functional calculations showed B20 structure is the most stable structure with component of FeSi, and non-ferromagnetic [36], or nonmagnetic [20]. Therefore, we consider that this polycrystal phase is not B20 $\epsilon$-FeSi structure, but Fe-rich silicide, Fe$_x$Si ($x \geq 2$).

For the surface at $T_a = 820$ K annealing, the RHEED patterns displayed characteristic 1/4 and 3/4 diffraction streaky spots, as shown in figure 2 (a). This complex RHEED pattern has been attributed to the epitaxial phase of the semiconducting orthorhombic $\beta$-FeSi$_2$ in SPE growth [30]. In this region, we also observed "minor" hysteresis loops, indicating ferromagnetic property, both in in-plane and out-of-plane directions (figures 2 (b) and (c), respectively). We also obtained similar results at both $[110]_{Si}$ and $[101]_{Si}$ $([211]_{Si}$and $[112]_{Si}$) directions. Since we observed the minor loops at the all directions, we can not determine the easy/hard axis from the shapes of the hysteresis loops. Single crystal of $\beta$-FeSi$_2$ is paramagnetic, and RHEED patterns showed no spots due to the other silicides. Thus, we suggest that Fe-rich silicide layers, Fe$_x$Si ($x \geq$
Figure 2. (a) An RHEED pattern of $\beta$-FeSi$_2$ film on Si(111) surface ($T_a = 820$ K), the RHEED pattern displaying characteristic 1/4 and 3/4 diffraction streaky spots (arrows) at 40 K with the incidence of $[1\overline{1}0]_{Si}$ direction. SMOKE hysteresis loops recorded at 40 K, for $\beta$-FeSi$_2$ film on Si(111), with the magnetic field applied along (b) in-plane ($[1\overline{1}0]_{Si}$ (solid) and $[11\overline{2}]_{Si}$ (dashed)), and (c) out-of-plane.

2) remained at the interface, beneath the $\beta$-FeSi$_2$ top layers. Actually, in a $\beta$-FeSi$_2$ film system obtained by reactive deposition epitaxy, a multilayer structure was reported [31]: $\beta$-FeSi$_2$/Fe-rich dilicide FeSi$_{1+x}$/Si studied with RHEED, Auger electron spectroscopy, and cross-section TEM.

4. Summary
The bcc-Fe, polycrystals and $\beta$-FeSi$_2$ films were formed on Si(111) grown by SPE method. In-situ RHEED and SMOKE at 40 K revealed that the ferromagnetic bcc-Fe(111) film with easy axis lying in-plane direction is formed after the deposition. It transformed to an Fe-rich polycrystal film after 670 K annealing. A $\beta$-FeSi$_2$ film with ferromagnetic interface layers was grown after 820 K annealing.

This ferromagnetic interface between the $\beta$-FeSi$_2$ film and the Si(111) substrate, that is, ferromagnetic heterojunctions, could open up the possibility to inject spin-polarized carriers from ferromagnetic metals into a semiconductor. In particular, a combined system of $\beta$-FeSi$_2$ epitaxial phase and ferromagnetic interface may achieve additional attributes leading to the development of novel integrated optoelectronic devices with spin-polarized luminescence.

5. References
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