Uneven Distribution of Silicon Crystalline Grains in RF-Sputtered $\beta$-FeSi$_2$ Films Deposited on Off-Oriented Silicon Substrate

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Applications in high-efficiency Si/$\beta$-FeSi$_2$ heterojunction solar cells require the preparation of crack-free $\beta$-FeSi$_2$ films on silicon. In a previous study, we obtained crack-free $\beta$-FeSi$_2$ films on silicon(100) just substrate by substrate heating during RF-sputtering even though we annealed the films at temperatures as high as 900°C after deposition. However, these films contained a numerous silicon crystalline grains because of substrate heating. Moreover, this process required more energy for substrate heating during deposition.

In this study, FeSi$_x$ films were deposited on silicon(100) substrate 4° off the [110] direction at room temperature through the RF sputtering method using an FeSi$_3$ target. The film annealed at 900°C also contained a large amount of silicon. Different from the films on silicon(100) just substrate, however, the film developed cracks on its surface.

1. Introduction

Iron silicides have many phases, such as $\alpha$, $\beta$, $\gamma$, and $\varepsilon$ phases. Among these phases, only the $\beta$ phase can be used for solar cells because it has semiconducting properties. $\beta$-FeSi$_2$ has attracted attention because it is a good candidate for silicon-based optoelectronic materials. Furthermore, from an ecological point of view, FeSi$_2$ consists of Fe and Si, the resources of which are abundant, and it is harmless to the environment and to humans [1]. $\beta$-FeSi$_2$ is a promising material for thin solar cells because its absorption coefficients are larger than those of silicon by two orders of magnitude [2]. In addition, it can absorb infrared light because its band gap is ~0.85 eV [3]. Its reported conversion efficiency of 22.4% was calculated by computer simulation using a p-Si/n-FeSi$_2$ heterojunction solar cell; this value is higher than that of a p-Si/n-Si homojunction solar cell [4].

Preparation of $\beta$-FeSi$_2$ through molecular beam epitaxy and metal–organic vapor-phase epitaxy is difficult because Fe and Si have high melting points. Therefore, reactive deposition epitaxy [5], ion beam synthesis [6], and RF sputtering [7–9] are generally used to prepare $\beta$-FeSi$_2$. RF sputtering, in particular, is among the simplest of these methods.

In a previous study conducted in our laboratory, we prepared crack-free $\beta$-FeSi$_2$ films that had been heated during deposition on a silicon(100) just substrate [10]. Substrate heating during deposition effectively reduced cracks on the surfaces of the $\beta$-FeSi$_2$ films. However, the intensity of the X-ray diffraction (XRD) peak for $\beta$-FeSi$_2$ (202/220) weakened because of the decrease in the amount of $\beta$-FeSi$_2$ in the films due to formation of silicon crystals.

With did not perform fabrication of $\beta$-FeSi$_2$ films on other substrates in our laboratory. A wide variety of conditions for $\beta$-FeSi$_2$ fabrication need to be investigated to meet its challenges.

In this study, FeSi$_x$ films were deposited on silicon(100) substrate 4° off the [110] direction at room temperature through the RF sputtering method using an FeSi$_3$ target. After deposition, FeSi$_x$ films were annealed at 400–900°C. After annealing, the crystallinity of the films was analyzed by XRD measurements. Film surfaces were observed under an optical microscope, and film thicknesses were measured by scanning electron microscopy.

2. Experiments

FeSi$_x$ films were deposited on silicon(100) substrate 4° off the [110] direction at room-temperature through the RF sputtering method using an FeSi$_3$ target (99.9% purity). The RF power during sputtering was 100 W. The distance between the substrate and target was set at 30 mm. Post-annealing in Ar gas at 400–900°C for 10 min was carried out in a quartz furnace.

The crystallinity of the films was analyzed by XRD measurement using CuK$\alpha$ radiation. Measurement was performed at an incident angle of 3°, and the sample holder was rotated during measurements. The incident X-ray angle was kept small because only the diffraction signal from the film and not from the substrate needed to be detected. This technique is known as grazing-incidence XRD method. The film surface was observed under an optical microscope (VF-7510: Keyence).
3. Results and Discussions

Figure 1 (a) shows XRD patterns of the films deposited at 300°C on the just substrate. Figure 1 (b) shows XRD patterns of the films deposited at room temperature on the off substrate. As shown in Figure 1, in both condition, the films annealed at temperature over 500°C completely transformed to β-FeSi₂, and other phases such as ε-FeSi did not form on the surface.

Figure 2 presents results of peak decomposition of β-FeSi₂(202/220) at around 29° for the films annealed at 900°C. For both films, a Si(111) peak at 28.4° was superimposed against the β-FeSi₂(202/220) peak.

Figure 3 depicts the deposition-time dependence of the intensity ratio between β-FeSi₂(202/220) and Si(111) peaks. In both conditions, the ratio increased when deposition time was short. This indicates that a layer containing silicon crystals formed near the substrate under both conditions.

Figure 4 shows the film surfaces observed by optical microscopy. Figure 4 (a) shows the surface of the film deposited on the just substrate at 300°C and annealed at 700–900°C for 10 min in Ar gas. As shown in Fig. 4 (a), no cracks formed on the surface of the film annealed at 900°C. Figure 4 (b) displays the film surface that was deposited on the off substrate at room temperature and annealed at 700–900°C for 10 min in Ar gas. Cracks were observed on the surface of the film annealed at 900°C, as marked by bold lines in Fig. 4 (b).
In our previous study [10], we compared the β-FeSi$_2$ films deposited on the just substrate at room temperature and at 300°C. The film deposited at 300°C and annealed at 900°C had no cracks on the surface, whereas, the film deposited at room temperature and annealed at 900°C had cracks. It was considered that the film deposited at 300°C had a layer containing silicon crystals near the substrate and that the layer acted as a buffer which was effective to reduce cracks.

In this study, the β-FeSi$_2$ films deposited on the just substrate at 300°C and on the off substrate at room temperature were compared. In both cases, silicon crystals were formed near the substrate which was revealed by the results of XRD measurements, as shown in Fig. 3. However, cracks were appeared on the surface of the films deposited on the off substrate which was contrary to our expectations. Many cracks were generated during cooling. This may be primarily due to the difference in expansion coefficients between silicon and β-FeSi$_2$, which are $2.6 \times 10^{-6}/°C$ and $6.7 \times 10^{-6}/°C$ respectively [11]. No cracks were observed on the surface of the β-FeSi$_2$ film deposited on the just substrate and annealed at 900°C because of randomly distributed silicon crystalline grains near the β-FeSi$_2$/Si interface.

The β-FeSi$_2$ film deposited on the 4° off silicon substrate and annealed at 900°C had many cracks on the surface although it contained silicon crystalline grains near the substrate. This may be due to selective accumulation of silicon crystalline grains at steps of the substrate, which did not effectively reduce cracks.
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Figure 5 shows a schematic of the deposition process on the just substrate at 300°C and on the off substrate at room temperature. As previously reported [12], the ratio of Fe and Si atoms in the films deposited at room temperature is almost 1:2 because of the difference in sputtering yield between Fe and Si in Ar when FeSi3 is used as sputtering target. On the other hand, Si atoms of the films deposited on the just substrate at 300°C tended to bond to Si substrates at the initial stage of deposition because of substrate heating. Films deposited on the off substrate at room temperature were the same as those deposited on the just substrate at 300°C in that a layer contained more silicon atoms near the substrate.

Figure 6 presents a schematic of the annealing process for the films deposited on the just substrate at 300°C for 30 min and annealed at 900°C. A layer containing silicon crystals might have formed near the Si substrates, as suggested by the XRD results. However, this formation was not effective to reduce surface cracks on the films deposited on the off substrate at room temperature. This may be due to the selective accumulation of silicon crystalline grains at steps of the off substrate.

![Deposition Schematic](image)

**Fig. 5** Schematic of the deposition process for the films deposited on the just substrate at 300°C and on the off substrate at room temperature.

![Annealing Schematic](image)

**Fig. 6** Schematic of the annealing process for the films deposited on the just substrate at 300°C for 30 min and annealed at 900°C.

4. **Summary**

FeSi films were deposited on silicon(100) substrate 4° off the [110] direction at room temperature through the RF sputtering method using an FeSi3 target. Post-annealing was carried out at 400–900°C. All films completely transformed to β-FeSi2 after annealing at >500°C. In this condition, a layer containing silicon crystals formed near the substrate. This result is similar to that for β-FeSi2 film deposited on silicon(100) just substrate that had been heated during deposition. No cracks formed on the film surface on the just substrate annealed at 900°C. In contrast, cracks formed on the film surface on the off substrate annealed at 900°C. These cracks may be due to the difference in the distribution of crystalline silicon grains.

**References**


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