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Sputter Etching of Si Substrate to Synthesize Highly Oriented β-$FeSi_2$ Films

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Ion beam sputter deposition (IBSD) under ultra-high vacuum conditions has been employed to synthesize β-$FeSi_2$ films on Si (100) substrates. We have investigated the effect of sputter etching (SE), followed by annealing of Si substrate on the crystal structure of β-$FeSi_2$ film, which was evaluated by X-ray diffraction (XRD) and reflection high energy electron diffraction (RHEED). The results revealed that surface amorphous layer of the substrate obstructs formation of highly orientated β-$FeSi_2$ films. The substrate annealing after the etching improves the crystallinity of the films formed on it.

Key words: ion beam sputter deposition, iron silicide, X-ray diffraction, surface treatment, film growth

1. INTRODUCTION

Widely used compound semiconductors contain harmful or quantity-limited elements, such as As, Cd, In, Ge, etc. From the viewpoint of ecological and environmental safety, we should avoid the employment of these elements for device fabrication.

β-$FeSi_2$ is one of the ecologically friendly semiconductors with an excellent property for optoelectronic devices. Its direct band gap of about 0.87 eV [1] is valuable for the fabrication of infrared emitters and detectors, and matches the transmission window of SiO_2 fibers at 1.55 μm [2]. Thus the β-$FeSi_2$ film growth on Si substrate attracts attention as the candidate for all Si integrated circuit with optical interconnection. However, the fabrication process of highly oriented β-$FeSi_2$ film has not been optimized.

We have prepared β-$FeSi_2$ films on Si (100) substrate by means of ion beam sputter deposition (IBSD) [3-5]. It was clarified that the surface treatment of Si substrate has a great influence on the crystal structure of the film formed on it, and that the sputter etching (SE) is a suitable treatment to synthesize highly oriented β-$FeSi_2$ films [5].

The SE is an effective method to remove the native oxide layer of Si substrates, but it makes the substrate surface amorphous with a lot of defects. Indeed, the interdiffusion of Fe and Si atoms might be enhanced at the amorphous layer of the surface. The film growth study by solid phase epitaxy revealed that the β-$FeSi_2$ on amorphous silicon was formed at lower temperature than that on crystalline silicon [6].

In this study, we have investigated the effect of amorphous surface layer of Si substrates on the crystal structure of β-$FeSi_2$ films. The surface of Si (100) substrate was cleaned and amorphized by Ne^+ SE. After the SE, Fe was deposited on the heated substrate. Some of the films were formed after SE with post-irradiation annealing. In order to characterize the crystal structure of these films, X-ray diffraction (XRD) and reflection high energy electron diffraction (RHEED) were performed.

2. EXPERIMENTAL

The IBSD apparatus has been described elsewhere [3, 4]. The substrate was 10×10×0.5 mm^3 slab, which was cut from n-type Czochralski grown Si (100) wafer. After the ultrasonic cleaning with an organic solvent, the substrate was installed into the IBSD chamber.

ion energy [keV]	flux [$m^{-2}s^{-1}$]	irradiation time [min]	fluence [m^{-2}]	peak depth of Ne^+ [nm]	displacement per atom
1	$2.1x10^{16}$	140	$3.0x10^{20}$	3.6	0.73
3	$2.5x10^{17}$	20	$3.0x10^{20}$	7.7	2.2
10	$5.0x10^{17}$	10	$3.0x10^{20}$	20	6.8

Table 1 Ne^+ SE condition of each ion energy.

Two types of surface treatment were employed: (i) only the SE and (ii) the SE with the post-irradiation annealing. The Ne^+ SE was performed with the incident energy of 1, 3, or 10 keV at an angle of 30° to the surface normal. The depth distributions of implanted Ne^+ and primary displaced Si atoms are calculated using TRIM-98 simulation code [7]. The calculated results are shown in Fig. 1. The conditions of irradiation are listed in details in Table. 1. After the SE, some of the substrates were annealed at the temperature of 1073 K for 30 minutes in order to recrystallize by removing defects of the substrate and implanted Ne atoms.

The Ar^+ was produced by RF gas discharge and accelerated to bombard the Fe target (purity; 99.998 %). The sputtered Fe atoms were deposited on heated Si substrate at the temperature of 973 K. The Ar^+ energy is 35 keV and the deposition rate is 5×10^{-3} nm/s. The thickness of deposited Fe is 31 nm, which is monitored by Ar^+ fluence and a quartz crystal microbalance. The thickness of a β-$FeSi_2$ film is determined to 100 nm from the bulk densities of Si and β-$FeSi_2$. The base pressure of the deposition chamber was less than 8×10^{-8} Pa. The residual gas pressure during etching and deposition was about 1×10^{-6} Pa and 1×10^{-5} Pa, respectively. The structural analysis of the deposited films was performed with a θ-2θ XRD (MAC Science, MXP3T) and RHEED (Omegatron, OME-0050LSv).

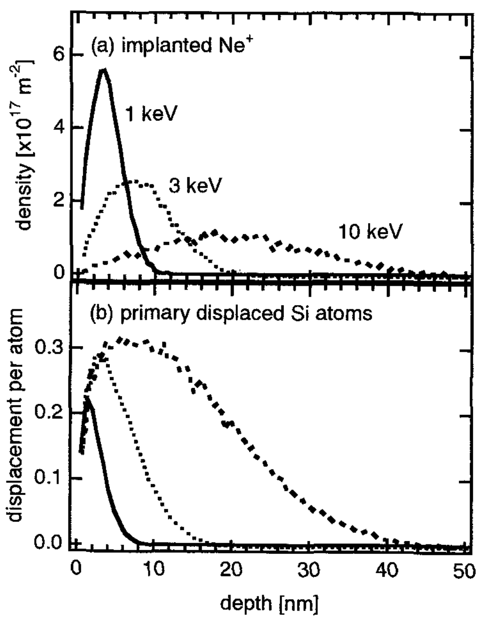

Fig. 1 Calculated depth distribution of (a) implanted Ne^+ and (b) primary dipsplaced Si atoms. Incident ion energies are 1 keV (solid line), 3 keV (dotted line), and 10 keV (dashed line).

3. RESULTS AND DISCUSSION

3. 1 "SE only" case

XRD spectra of the films formed at 973 K after each SE are shown in Fig. 2 (a) - (c). The intensities of all XRD spectra are normalized with the peak height of Si 400 reflection. Various peaks of β-$FeSi_2$ and α-$FeSi_2$ are observed in Fig. 2 (a) - (c). It shows that the formed films are polycrystalline. The peak heights of β-$FeSi_2$ 400, 600, and 800 reflections are much weaker than that of β-$FeSi_2$ 202, 220 and β-$FeSi_2$ 204 reflections. It indicates that surface amorphous layer of the substrate obstructs formation of highly oriented β-$FeSi_2$ film with an epitaxial orientation of β-$FeSi_2$ (100) // Si (100) Although the temperature of bulk phase transition from β-$FeSi_2$ to α-$FeSi_2$ is 1210 K [8], we observed α-$FeSi_2$ at 973 K. The amount of α-$FeSi_2$ increases with the ion energy of SE. The appearance of stoichiometrically Si-rich phase, α-$FeSi_2$, shows that surface amorphous layer enhance the interdiffusion of Fe and Si. The formation of α-$FeSi_2$ at low temperature (873 K) is observed for IBSD films using an Fe-Si target [3].

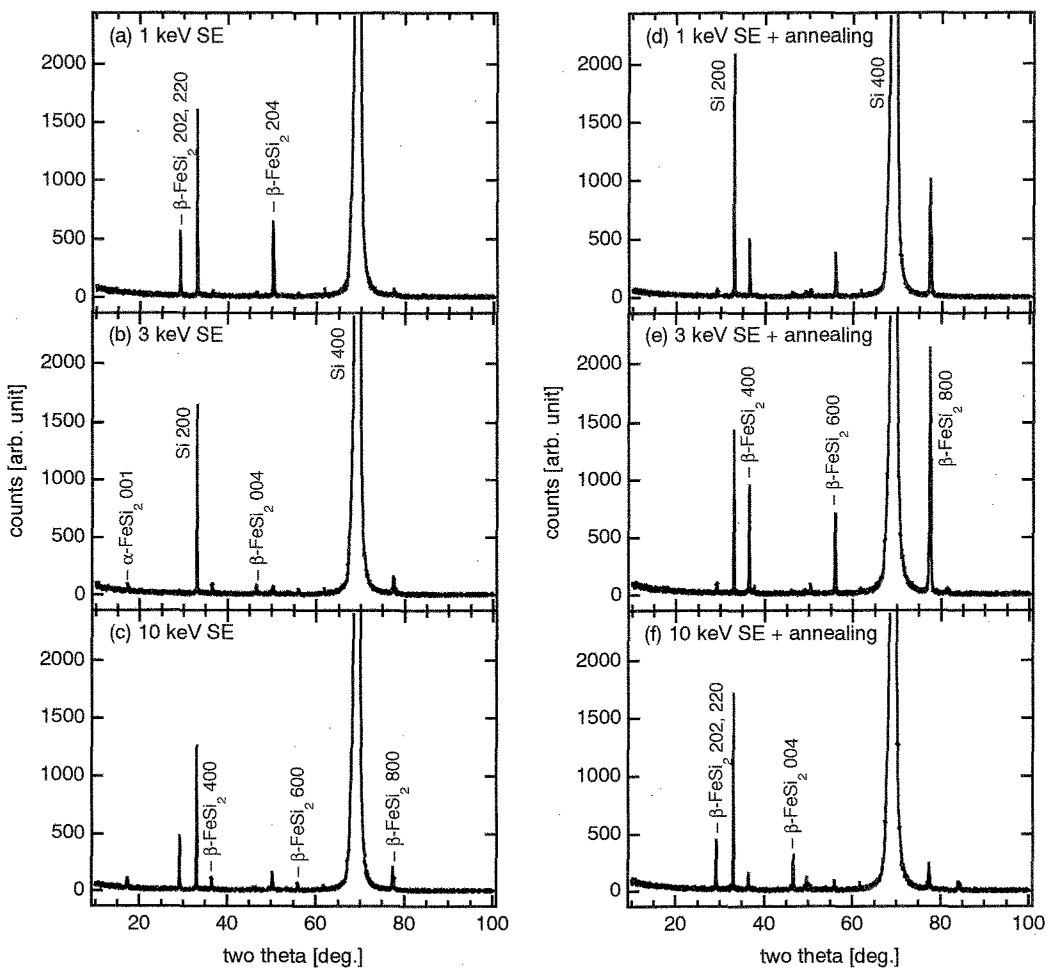

Fig. 2 The XRD spectra of $FeSi_2$ films formed with various surface treatments. (a) - (c): SE only and (d) – (f): SE, followed by annealing at 1073 K for 30 minutes.

RHEED patterns of these films are shown in Fig 4 (a) - (c). The spot-like patterns are observed. It shows that the surface is atomically rough.

3. 2 "SE with post-irradiation annealing" case

XRD spectra of the films formed at 973 K after SE, followed by annealing are shown in Fig. 2 (d) – (f). The formation of the highly oriented β-$FeSi_2$ films were observed in Fig. 2 (d) and (e), whereas the spectrum of Fig. 2 (f) indicates the formation of a polycrystalline film.

The peak height of β-$FeSi_2$ 800 reflection in all XRD spectra is shown in Fig. 3. For ion energies of 1 and 3 keV, the peak height increased by an annealing at 1073 K for 30 minute. It shows that the amount of epitaxially oriented β-$FeSi_2$ in the formed film increased by the annealing. We have not yet revealed the reason why the highest oriented β-$FeSi_2$ film was formed with intermediate etching energy of 3 keV.

RHEED patterns of these films are shown in Fig 4 (d) - (f). The streak-like patterns are observed in Fig 4 (d) and (e). It shows that the surface is atomically flat. However, clear pattern is not observed in Fig. 4 (f). The surface crystallinity of the film is poorer than that of the other films.

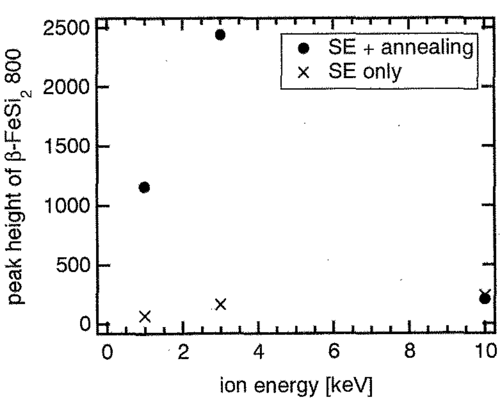

Fig. 3 The peak height of β-$FeSi_2$ 800 reflection in all XRD spectra shown in Fig. 2.

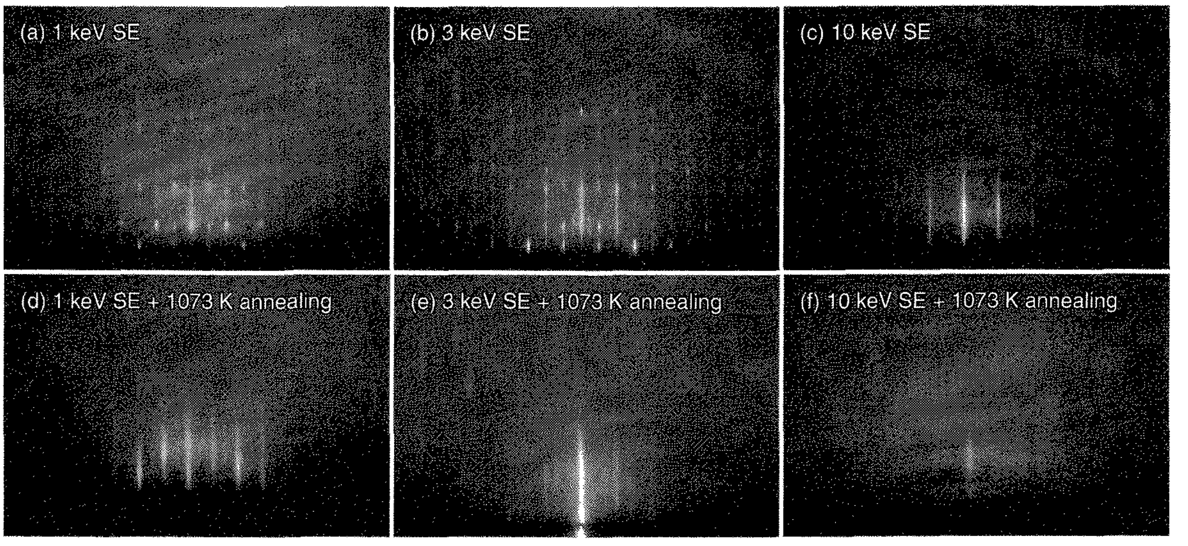

Fig. 4 RHEED patterns of the β-$FeSi_2$ films formed on Si (100) substrate.

In order to evaluate the surface recrystallization by the annealing, we observed the RHEED patterns of the substrate surface after SE and annealing, as shown in Fig. 5. The streaks, which indicate the crystallized surface, are shown in both patterns. The improved orientation of the film is independent whether the substrate surface is still amorphous or recrystallized. For 10 keV SE, defects are produced deep in the substrate (several tens of nanometer), as shown in Fig. 1. It is considered that a lot of defects still remain after the annealing at 1073 K for 30 minutes. These defects obstruct the formation of highly orientated β-$FeSi_2$ films.

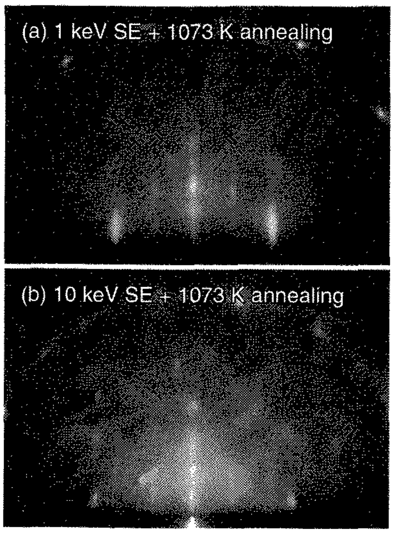

Fig. 5 RHEED patterns of Si (100) substrate after (a) 1keV SE and post-irradiation annealing and (b) 10keV SE and post-irradiation annealing. Similar pattern was observed for 3keV SE and post-irradiation annealing.

4. SUMMARY

We have investigated the effect of sputter etching and post-irradiation annealing of Si substrate on the crystal structure of β-$FeSi_2$ film. The results revealed that surface amorphous layer of the substrate obstructs formation of highly orientated β-$FeSi_2$ films. The substrate annealing after the etching improves the crystalinity of the films formed on it.

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