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<tr>
<td>Citation</td>
<td>Science Journal of Kanagawa University, 26: 7-12</td>
</tr>
<tr>
<td>Date</td>
<td>2015-06-30</td>
</tr>
<tr>
<td>Type</td>
<td>Departmental Bulletin Paper</td>
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<tr>
<td>Rights</td>
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Silicide Synthesis by Fe$^+$ Implantation in Si Substrates

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Abstract: We performed Fe ion implantation in Si(001) substrates at room temperature with fluences of $1 \times 10^{16}$, $2 \times 10^{16}$, $5 \times 10^{16}$, and $1 \times 10^{17} \text{cm}^{-2}$ followed by annealing treatments at 900, 950 and 1000˚C for 1 h, aiming at the characterization and optimization of the process to synthesize $\beta$-FeSi$_2$. The elemental depth profiles and reaction products were quantitatively investigated by Rutherford backscattering (RBS) and Raman spectroscopy. It was clarified by RBS analysis of as-implanted samples that the implanted Fe atoms are mostly located around the depth predicted by Monte Carlo simulation. We could not observe $\beta$-FeSi$_2$-derived components in the Raman spectra. After annealed at 900˚C, Fe silicide compounds are segregated on the surface. The elemental composition depends on ion fluences and the atomic concentration of Fe for the highest-dosed sample with $1 \times 10^{17} \text{cm}^{-2}$ is found to reach $\sim$ 25%. Strong Raman peaks corresponding to $\beta$-FeSi$_2$ are observed in all prepared samples. The depth profile of Fe is markedly changed for the samples postannealed above 950˚C. Raman signals become much weaker with increasing ion fluences and postannealing temperatures. Under the present experimental conditions, using Raman analysis low-dose implantation around $2 \times 10^{16} \text{cm}^{-2}$ followed by annealing at low temperatures was suggested to be effective for the synthesis of $\beta$-FeSi$_2$ crystals.

Keywords: ion implantation, iron silicide, semiconductor, light-emitting devices

Introduction

As miniaturization and high integration of electronic devices are progressing, delay of electronic signals in wiring metals cannot be negligible, causing that the performance is gradually deviated from the “scaling law”. One of the methods to overcome the issue is to replace a means of communication from electron to light. If high-performance light-emitting devices are fabricated on integrated circuits (IC), the problem could be significantly solved and then the opto-electronic IC should be realized. So far, many researchers made great efforts for fabricating optical devices directly on a Si substrate$^{11}$. In the process, however, harmful and rare elements are usually necessary. At present, enough emission has not been realized yet.

It is recently expected that $\beta$-FeSi$_2$ is one of the candidates for realizing new opto-electronic devices. It is well known that $\beta$-FeSi$_2$ has semiconducting properties with a bandgap of $\sim$ 0.85 eV$^3$. A particular structure of $\beta$-FeSi$_2$ shows a direct optical transition at 1.5 µm band, which is expected to be light-emitting devices for glass fiber$^{2,3}$. Indeed, the composition elements of Si and Fe exist a lot in the earth and can be safely treated; therefore $\beta$-FeSi$_2$ is called as environmental semiconductor. In spite of a lot of works, the optimum condition to form single crystalline $\beta$-FeSi$_2$ with low defect densities, which is thought to be necessary for realizing high-quality light emitting devices, has not been found yet. In order to realize reliable devices, we have to understand the physical and chemical properties of Fe-silicides. Although there are a lot of reports so far, it is not clearly understood that the formation process of Fe-silicides depending on
various parameters of implantation temperature, fluence, and postannealing temperature.

In the present work, we aim at formation of high-quality $\beta$-FeSi$_2$ crystals grown by Fe implantation in the Si substrate followed by thermal annealing and ion beam irradiation. The elemental depth profiles of Fe-silicide were quantitatively analyzed by Rutherford backscattering spectroscopy (RBS). The stoichiometry and crystal type of products are determined by micro Raman spectroscopy (MRS) analysis. In this paper, we show the results and discuss the optimum condition to obtain effectively $\beta$-FeSi$_2$ crystals in a silicon substrate.

**Methods**

We performed Fe$^+$ ion implantation at an energy of 50 keV in Si(001) substrates at room temperature (RT). The ion-fluences were $1\times10^{16}$, $2\times10^{16}$, $5\times10^{16}$, and $1\times10^{17}$ ions/cm$^2$. Some of the samples were postannealed at 900, 950 and 1000ºC for 1 h. The details of the condition are summarized in table 1.

<table>
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<th>Incident ion</th>
<th>Fe$^+$</th>
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<tbody>
<tr>
<td>Energy</td>
<td>50 keV</td>
</tr>
<tr>
<td>Substrate temp.</td>
<td>Room Temp.</td>
</tr>
<tr>
<td>Ion fluence ($\times10^{16}$ ions/cm$^2$)</td>
<td>1.0, 2.0, 5.0, 10.0</td>
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It is well known that depth profiles of ions implanted in materials are readily calculated by Monte Carlo simulation based on binary collision approximation. The simulation code called as TRIM (Trajectory and Ranges of Ions in Matter) now prevails all over the world by Ziegler et al.\textsuperscript{4).

Figure 1 shows calculated depth-distributions of Fe ions introduced in Si at an incident energy of 50 keV. Surface sputtering effect by ion-bombardment is taken into account for this profile. As a result, the Fe concentration is slightly raised near the surface region as increasing ion-fluence.

Here, the atomic density of $\beta$-FeSi$_2$ crystal is known as $4\times10^{22}$ atoms/cm$^3$. The Fe concentration in FeSi$_2$ compound therefore should be $1.3\times10^{22}$ atoms/cm$^3$. The stoichiometric FeSi$_2$ can be obtained by Fe-implantation at fluence of between $5\times10^{16}$ and $1\times10^{17}$ ions/cm$^2$ as shown in Fig.1. The depth giving the maximum concentration is estimated to be 30-40 nm. Here, it must be noted that dynamical effects of thermal diffusion and aggregation processes are not considered in the TRIM simulation; therefore it is necessary to optimize the condition to form iron silicides for various conditions of ion implantation and postannealing.

<table>
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The existence of $\beta$-FeSi$_2$ was confirmed by MRS exited by LASER with a wave length of 532 nm. It has been previously reported that typical Raman signals of $\beta$-FeSi$_2$ are observed at Raman shifts of around 190 and 250 cm$^{-1}$. These components are assigned to be Ag phonon mode of $\beta$-FeSi$_2$\textsuperscript{5).

**Results**

**RBS analysis**

Figure 2 shows RBS spectra measured by 1988 keV Li$^{2+}$ incidence for the Fe-implanted Si(001) substrates prepared at various ion-fluences of (a) $1\times10^{16}$ cm$^{-2}$, (b) $2\times10^{16}$ cm$^{-2}$, (c) $5\times10^{16}$ cm$^{-2}$ and (d) $1\times10^{17}$ cm$^{-2}$. Black, red, green and blue dots correspond to the spectra recorded for the samples as-implanted and postannealed at 900, 950 and 1000ºC, respectively. We show depth profiles of the elemental composition of Fe obtained by analyzing the RBS spectra using computer
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Simulation code in Fig. 2 (6,7,8). Implanted Fe ions for as-implanted sample at ion fluences of $1 \times 10^{16}$, $2 \times 10^{16}$ cm$^{-2}$ and $5 \times 10^{16}$ cm$^{-2}$ are distributed around the depth expected in the TRIM simulation (shown by black curves in Fig. 1). On the other hand, Fe component for the $1 \times 10^{17}$ cm$^{-2}$-dosed sample appears at the surface position. It is responsible for surface sputtering of Si during the high-dosed ion irradiation.

After postannealed at 900°C (red curves), some of the implanted Fe atoms are found on the surface, indicating that surface segregation occurred significantly. The elemental composition of Fe-embedded layers strongly depends on ion-fluences; the atomic fraction of Fe for the $1 \times 10^{17}$ cm$^{-2}$-dosed sample reaches to ~25%.

Postannealing above 950°C dramatically changes the elemental depth profiles as shown with green and blue dots in Fig. 2. The shift of surface position of Fe should be due to surface oxidation by residual oxygen-containing species such as water vapor, carbon oxides and oxygen molecule in the furnace. It should be interestingly noted that any Fe atoms are located in the silicon oxide layer. Here, Fe has segregation coefficient value of $k = 1 \times 10^{-7}$ at 1000°C, where $k = N_{Si}/N_{SiO_2}$; therefore Fe atom exhibits a strong tendency to preferentially segregate to the SiO$_2$/Si interface. That seemingly impedes the diffusion of Fe from SiO$_2$ into the Si bulk (9,10,11). The fact is indeed contradictory to our experimental result.

The atomic fraction of Fe is found to be considerably decreased to ~10% for the highest-dosed specimen. The depth profile is also diffused in deeper layers. The diffusion rate for the highly-dosed samples seems to be faster. The reason is now under consideration.

**Raman analysis**

Figure 4 shows Raman spectra observed for the as-implanted sample at ion-fluence of $5 \times 10^{16}$ cm$^{-2}$ typically. Each spectrum was measured at five different positions on the sample.

We cannot clearly confirm the signals derived from β-FeS)$_2$ and Si, indicating that the crystallinity disappears due to high-dose ion irradiation. Other samples with different ion-fluences also showed similar tendency.
Fig. 4. Raman spectra recorded for the as-implanted

Figure 5. Raman spectra observed for the 900˚C-annealed samples depending on ion-fluences of (a) 1×10^{16}, (b) 5×10^{16} cm² and (c)1×10^{17} cm².

Figure 5 shows Raman spectra observed for the 900˚C-annealed samples depending on ion-fluences of (a) 1×10^{16}, (b) 2×10^{16}, (c) 5×10^{16} and (d) 1×10^{17} cm². We observe strong β-FeSi₂-derived components (around 190 and 250 cm⁻¹) at any positions regardless of the ion fluences. The FWHM of the Raman components for the sample with 1×10^{17} dose is found to be slightly wider, indicating that the quality of β-FeSi₂ compound should be worse. The peak intensity is getting higher with respect to the ion fluence. Considerable increase of the Si component appearing at 520 cm⁻¹ indicates that the crystallinity is quite recovered by high-temperature annealing.

After annealing at 950 and 1000˚C shown in Figs. 6 and 7, respectively, Raman peaks corresponding to β-FeSi₂ are found to be weaker with increasing ion doses. The signals are rarely observed for the highly-dosed samples above 1×10^{17} and 5×10^{16} cm² followed by annealing at 950˚C and 1000˚C, respectively.

Fig. 6. Raman spectra recorded for the samples postannealed at 950˚C with different ion-fluences of (a) 2×10^{16}, (b) 5×10^{16} cm² and (c)1×10^{17} cm².
**Discussion**

It is found in the Raman analysis that low dose implantation around $2 \times 10^{16}$ cm$^{-2}$ followed by ~900°C annealing should be effective for synthesizing $\beta$-FeSi$_2$ crystal. On the other hand, the elemental depth profile of Fe embedded in Si with areal density of $2 \times 10^{16}$ cm$^{-2}$ obtained by RBS analysis shows much lower than 33%, which corresponds to the atomic fraction of Fe in FeSi$_2$. It is indicated that the $\beta$-FeSi$_2$ crystal is not uniformly formed with layered structure.

According to the phase diagram of Si and Fe, $\beta$-FeSi$_2$ is thermodynamically stable below 937°C. In addition, $\beta$-FeSi$_2$ is dissolved into $\alpha$-FeSi$_2$ or Fe-rich FeSi phases above temperatures of about 950°C. Omae et al. found that the as-implanted sample at high fluence of $4 \times 10^{17}$ cm$^{-2}$ showed a layered $\varepsilon$-FeSi and $\beta$-FeSi$_2$ structures. Postannealing at 600°C transformed the $\varepsilon$-FeSi into the $\beta$-FeSi$_2$ structure. It is consistent with our result that higher dosed samples seem to form $\beta$-FeSi$_2$ structure by low temperatures annealing. Rajaesh et al. previously reported the $\beta$-FeSi$_2$ formation by ion beam synthesis at RT followed by annealing at 900°C. They found that a fluence of $1 \times 10^{16}$ cm$^{-2}$ was enough to form $\beta$-FeSi$_2$ in Si and the annealing temperature should have been 900°C or below. They also mentioned that higher dosages increased defect concentrations and alpha phase structure.

We have clearly found high-quality $\beta$-FeSi$_2$ in Raman spectra even at high temperatures annealing (~1000°C) for low dosed samples. It should be noted that high-dose implantation of Fe produces a lot of defects near the surface. The induced defects could promote diffusion of Fe and structural transition from $\beta$-FeSi$_2$ to $\alpha$-FeSi$_2$ even at low temperatures annealing.

**Conclusions**

In this paper, we clarified the relation between ion-fluence and postannealing temperatures in synthesizing the $\beta$-FeSi$_2$ structure. The specimen were prepared by Fe ion implantation at 50 keV energy into Si(001) substrate at various fluences of 1, 2, 5 and $10 \times 10^{16}$ ions/cm$^2$ at RT, followed by annealing at 900, 950 and 1000°C for 1 h in Ar atmosphere. The depth profiles of each element and the crystal structure of products were quantitatively analyzed by RBS and MRS. According to the RBS results for as-implanted samples, Fe atoms are found around the depth expected in TRIM simulation. Raman peaks derived from $\beta$-FeSi$_2$ structure are not clearly observed. The implanted Fe atoms are diffused to the surface area after annealed at 900°C for 1 h. Remarkable Raman peaks are observed in all samples with different fluences. The elemental compositions of Fe after annealed at 950 and 1000°C are dramatically changed and most Fe atoms are diffused in deeper layers of the Si substrate. Raman signals for $\beta$-FeSi$_2$ are found to be much weaker as increasing ion fluences and postannealing temperatures. We finally conclude that low dose implantation around $2 \times 10^{16}$ cm$^{-2}$ followed by annealing at low temperatures of around 900°C should be effective for forming $\beta$-FeSi$_2$ crystal.

**Acknowledgement**

The authors would like to express his thanks to Mr. Saito Y. for his help on maintenance of experimental apparatuses and many supports of experiments. We also would like to acknowledge Prof. Mizuno T. for his corporation in using Raman spectroscopy. This research was supported by a grant from...
Reserch Institute for Integrated Science, Kanagawa University (RIIS201410).

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