A couple of ion-induced processes are applied to fabricate a highly crystalline film of semiconducting silicide, $\beta$-FeSi$_2$ on a Si substrate. One is the sputter deposition process, in which 35 keV Ar$^+$ ions are utilized to deposit sputtered iron (Fe) on Si substrate to form $\beta$-FeSi$_2$ in the temperature range around 973 K by means of ion beam sputter deposition (IBSD) method. The other is the sputter etching (SE) of the substrate surface prior to deposition, which plays a critical role in determining the crystalline properties of $\beta$-FeSi$_2$ films. Authors have shown that when the SE conditions are properly chosen, continuous and relatively homogeneous $\beta$-FeSi$_2$ thin films with high crystal orientation are fabricated with IBSD method in the temperature range of 873-973 K, with the film thickness of 50-100 nm. In addition, the interface is fairly smooth, where the transition layer at the interface is limited to a few atomic layers. Although care was taken to minimize the defect concentration in the obtained films, even the most highly-oriented $\beta$-FeSi$_2$ films contain a small amount of defects. To make the defect concentration as low as possible, SE treatment was performed at lower incident energies. It was found that for Ne$^+$ ions the incident energy could be lowered to 0.8 keV to obtain highly-oriented $\beta$-FeSi$_2$ films.

Key words: sputter etching, ion irradiation, semiconducting silicides, thin film, surface properties

1. INTRODUCTION

“Semiconducting silicides” [1], such as $\beta$-FeSi$_2$, BaSi$_2$, Mg$_2$Si, etc., are composed of elements which are non or less toxic and are naturally abundant, so that they are called “ecologically-friendly”, or “Kankyo” semiconductors in Japan. These materials have been investigated for various applications, such as optoelectronics, photovoltaics, photonics, thermoelectrics, and so on [2].

As is often the case with Si-based semiconductor devices, preparation of Si substrate surface prior to film fabrication is critically important. In order to obtain clean surfaces and eliminate defects at interfaces, high temperature thermal etching (TE) at about 1473 K has been employed. Whereas TE method requires high temperature treatment to remove oxide and carbide, in particular, wet etching (WE) methods based on chemical treatment and low temperature cleaning (below 1073 K) were successfully applied to molecular beam epitaxy (MBE) growth of Si [3]. Both TE and WE treatments were employed by the present authors to treat Si substrate prior to fabrication of $\beta$-FeSi$_2$ films. In the case of TE treatment, transmission electron microscopy (TEM) observation revealed that the films were composed of coalesced $\beta$-FeSi$_2$ with various crystal orientations [4, 5]. In the case of WE method, although highly-oriented $\beta$-FeSi$_2$ films are often obtained, the film / substrate interface appeared to be wavy [6].

On the other hand, when sputter-etching (SE) and the subsequent thermal annealing of the substrate are applied, it was shown that a highly-oriented $\beta$-FeSi$_2$ (100) film with sharp interface can be grown on Si (100) substrate by means of ion beam sputter deposition (IBSD) method [4].

Above-mentioned success with SE treatment led authors to further investigate the possibility of this method to fabricate $\beta$-FeSi$_2$ films with excellent crystalline properties. In other words, authors’ main goal is to fabricate $\beta$-FeSi$_2$ thin films which are continuous, single-phased, and have high crystal orientation, by applying ion-induced processes and nano-characterization techniques.

2. EXPERIMENTAL

2.1 Basic principles of IBSD method and apparatus

The method employed to fabricate $\beta$-FeSi$_2$ thin films in the present study is so-called the ion beam sputter deposition (IBSD) method, where in the present study mass-separated Ar$^+$ ions were produced by RF discharge and accelerated to 30-35 keV to sputter solid iron (Fe) or iron-silicon (Fe-Si) compound target onto Si substrate. Some advantages of this method are as follows:

(i) Transport of ion beams (including mass-separation) can be controlled electromagnetically so that various irradiation conditions can be applied.

(ii) Deposition can be performed under high vacuum conditions, if the ion beam transport sections can be differentially-pumped.

(iii) Essentially no irradiation damages are induced through deposition of sputtered species which are typically in the range of 10’s eV.

The basic features of the experimental device are as follows. The deposition chamber is evacuated by two...
Application of sputter etching treatment to the formation of semiconducting silicide film on Si substrate

turbomolecular pumps (STP-451, Seiko Seiki, and TMU 071P, Pfeiffer Vacuum GmbH) and Ti sublimation pump (PGT-6F, ULVAC Inc.). The ultimate pressure in the vessel is below $1 \times 10^{-8}$ Pa, as measured by ionization gauge (GI-N5, ULVAC Inc.). In addition, there are two ion beam irradiation systems connected to the deposition chamber. One of them is evacuated by a diffusion pump (Diffstak 160/700, Edwards, Ltd.) and a turbomolecular pump (V250, Varian) to generate and transport mass-separated Ar$^+$ ion beam for sputter deposition described above. The other line, which is evacuated by two turbomolecular pumps (V250, Varian) is used for sputter etching of the substrate surface using inert gas ions, such as Ne$^+$, Ar$^+$, etc., which are produced in a duoplasmatron ion source. Typical conditions of Ne$^+$ irradiation are as follows: incident energies; 1-3 keV, corresponding ion current densities; 1-10 $\mu$A/cm$^2$, residual gas pressure during irradiation; $< 2 \times 10^{-6}$ Pa.

For in-situ monitoring of the film thickness, a quartz crystal microbalance (QCM, CRTM-1000, ULVAC, Inc.) is located near the substrate. For in-situ analysis of surface structure and residual gas compositions, a reflection high energy electron diffraction (RHEED; OME-0050LSv, Omegatron) and a quadrupole mass spectrometer (QMS; QMS-400, ULVAC, Inc.) are equipped, respectively. The substrate is heated by tungsten (W) heater in the range of RT and 1173 K. The temperature was measured by a pyrometer (TR-630, Konica Minolta, Inc.).

2.2 Experimental procedures

A Si wafer (n-type, purity; 99.999 %, The Nilaco Corporation) is cut into a size of $10 \times 10 \times 0.5$ mm$^3$ and used as substrate. It was ultrasonically rinsed in acetone before being installed in the deposition chamber. After degassing at 973 K, the substrate was irradiated by Ne$^+$ ion beam at room temperature, which is directed at 30 degrees from the surface normal. The current density is controlled in the range of 1-10 $\mu$A/cm$^2$ for the incident energies of several keV. After irradiation, the substrate was heated by tungsten (W) heater and annealed at 1073 K.

As confirmed by RHEED observations shown in fig. l(a), degassing at 973 K does not completely remove oxygen and/or carbon impurities from the surface. When in-situ sputtering with Ne$^+$ ions is performed on the degassed substrate, it becomes amorphous as shown by the RHEED pattern in fig. l(b). But, a thermal annealing at 1073 K recovers the crystallinity of the surface as shown in fig. l(c), where a clear Si (100) - 2×1 superstructure is seen indicating that preexisting impurities were successfully removed.

Sputter deposition is performed using 35 keV Ar$^+$ ions and the sputtered species (Fe atoms) are deposited on the substrate heated in the range of 773-1173 K. The typical irradiation parameters are: ion current density; 200 $\mu$A/cm$^2$, deposition time; 30-70 min (to ensure that the obtained thickness of $\beta$-FeSi$_2$ film is in the range of 50-100 nm. An example of the RHEED pattern for $\beta$-FeSi$_2$ film is shown in fig. l(d). Analysis of the pattern revealed the so-called “type A” epitaxial relationship, i.e. FeSi$_2$ (100) // Si (100) with FeSi$_2$ [010] // Si [011] [7].

While RHEED monitors in-situ the surface structures during the course of film fabrication, the films were taken out of the deposition chamber for X-ray diffraction (XRD; MXP3T, MAC Science) and transmission electron microscopy (TEM; JEM-3000F, JEOL Ltd.) observation.

3. RESULTS AND DISCUSSION

3.1 Some characteristics of $\beta$-FeSi$_2$ films fabricated by IBSD (ion beam sputter deposition) method

3.1.1 Film properties as a function of reaction temperature, deposited thickness and target compositions
The conditions for the formation of epitaxial $\beta$-FeSi$_2$ films on Si (100) substrate with IBSD method was investigated [8]. It was found that crystal structure of the films as determined by XRD analysis was dependent on the substrate temperature as well as on the deposited thickness of sputtered Fe. The film with best crystalline properties was obtained either at 873 K with the FeSi$_2$ thickness of 50 nm, or at 973 K with the FeSi$_2$ thickness of 100 nm. This is displayed in Table I.

Table I Difference in crystallinity for the $\beta$-FeSi$_2$ film fabricated as a function of temperature and deposited thickness of FeSi$_2$ [8]. Shaded regions denote the conditions where $\beta$-FeSi$_2$ film with high crystal orientation is observed. Note that all the substrates were SE-treated with 3 keV Ne$^+$ ions.

<table>
<thead>
<tr>
<th>FeSi$_2$ thickness (nm)</th>
<th>Substrate temperature, K</th>
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<tbody>
<tr>
<td></td>
<td>773</td>
</tr>
<tr>
<td>25</td>
<td>Poly. $\beta$</td>
</tr>
<tr>
<td>50</td>
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<td>100</td>
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The phase composition of the iron silicide films fabricated by IBSD method was found to depend on the target compositions [9]. Briefly summarizing, the results revealed that when FeSi$_2$ target was employed, $\alpha$-FeSi$_2$ phase was predominant at temperatures above 973 K, while $\beta$-FeSi$_2$ phase was observed only in the limited temperature range at around 873 K. In this case, Si is originated both from the sputtered target and the substrate, thus, the supply of Si was considered to be in excess to sustain $\beta$ structure. On the other hand, the films prepared with Fe target became polycrystalline as they grow thicker than 100 nm. In order to optimize the supply of Fe and Si for epitaxial growth, Fe$_2$Si target was employed, where highly (100) -oriented a layer of 120 nm in thickness was obtained at 973 K.

3.1.2 The interfacial structure of $\beta$-FeSi$_2$ films on Si substrate

The effect of Si substrate surface treatment prior to iron silicide film formation on a Si (100) substrate with IBSD method was also investigated by means of cross-sectional transmission electron microscopy (XTEM) method [5]. High resolution XTEM images showed that although the lattice of the Si substrate was an almost perfect crystal immediately after TE treatment, it formed an undulated interface and the deposited silicide contained coalesced $\beta$-FeSi$_2$ islands. On the other hand, the dislocations and stacking faults produced by radiation damage were observed near the Si substrate surface for the SE treatment. Further study with XTEM observation revealed a presence of horizontal line along the $\beta$-FeSi$_2$ / Si interface in the dark field image of TEM [10]. Higher magnification image clearly showed that the line was due to aggregated defects. It was observed that the distance from the interface to the aggregated defects decreased and their size increased with the increase of Ne$^+$ energy for the Si surface treatment.

3.1.3 Surface characteristics of IBSD-grown $\beta$-FeSi$_2$ film

A combination of X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) using synchrotron radiation was applied to clarify surface chemical states of $\beta$-FeSi$_2$ films fabricated by an IBSD method [11]. The differences in the chemical states of the films fabricated at substrate temperatures of 873, 973 and 1173 K were investigated. For the film fabricated at 873 K, Si 2p XPS spectra indicate the formation of a relatively thicker SiO$_2$ layer. In addition, Fe Ledge XAS spectra exhibit the formation of FeSi$_{1-x}$ by preferential oxidation of Si or the presence of unreacted Fe.

The results for the film fabricated at 1173 K implied the existence of FeSi$_2$ with $\alpha$ and $\epsilon$ phases [12]. In contrast, the results for the film fabricated at 973 K indicated the formation of relatively homogeneous $\beta$-FeSi$_2$. These implied that the relatively excellent crystalline property of the film fabricated at 973 K is due to the formation of homogeneous $\beta$-FeSi$_2$.

3.1.4 PL properties

Current understanding on the photoluminescence (PL) properties of $\beta$-FeSi$_2$ has been discussed by Y. Maeda and co-workers [13, 14]. They defined three [14] to four [13] PL peaks observed in their $\beta$-FeSi$_2$ samples fabricated by ion beam synthesis (IBS) method. They argue that a PL peak at 0.802 eV (A-band) observed at 100 K is intrinsic emission, while those at 0.85-0.87 eV (B-band) and 0.75-0.78 eV (C-band) are extrinsic ones. Large enhancement of PL intensity occurred for A-band when the samples were annealed at temperatures > 1073 K. It was considered that such annealing was effective to eliminate some defects acting as non-radiative recombination centers.

On the other hand, the IBSD-grown $\beta$-FeSi$_2$ on Si substrate also showed a marked enhancement of PL intensity at 0.81 eV upon annealing the sample in a vacuum at 1153 K for 24 h [15]. The observed peak was considered to be that of A-band, but it almost coincided with D1 line [16] as originated from dislocations in Si substrate. In fact, annealed IBSD-grown samples exhibit some PL peaks which can be attributed to originate from dislocation related luminescence in Si [17].

3.2 Applicability of SE with lower incident ion energy

A previous study of the present authors clearly indicated that highly-oriented $\beta$-FeSi$_2$ film will be obtained if the incident energy of Ne$^+$ ion for SE treatment was in the range between 1-3 keV [18]. Moreover, it appeared that lower the incident energy, more highly-oriented the film would be. However, the sputtering yield by the ions will be decreased with decreasing the incident energy, so it is interesting to see how low one can decrease the incident ion energy and still obtain highly-oriented $\beta$-FeSi$_2$ film. In the experiment, SE treatments were
performed with incident Ne$^+$ ion energies below 1 keV. The irradiation conditions were as follows: 0.8 keV Ne$^+$ ions with ion current density of 0.4 $\mu$A / cm$^2$ were irradiated for 250 min, and 0.6 keV Ne$^+$ ions with the current density of 0.3 $\mu$A / cm$^2$ were irradiated for 330 min to match the irradiation fluence of (100 $\mu$A min) / cm$^2$ typically employed in the SE treatment with 3 keV Ne$^+$ ions. It is estimated that an irradiation fluence of 100 ($\mu$A min) / cm$^2$, i.e., $3.7 \times 10^{20}$ Ne$^+$ m$^{-2}$, corresponds to removal of approximately 15 nm-thick Si layers for 3.0 keV Ne$^+$ ions, according to SRIM calculation \cite{18}. The depth profile analysis with XPS indicates that the thickness of native oxides is in the range of 1 nm \cite{11}. The irradiation dose employed in the SE treatment should be sufficient to completely remove oxide from the substrate surface. 

Figs. 2 and 3 compare the RHEED and XRD patterns of $\beta$-FeSi$_2$ films obtained under various SE conditions, respectively. Note that “no SE” in figs. 2(d) and 3(d) means that the substrates were only degassed at 973 K prior to deposition, so that the substrate surface cannot be considered to be free of native oxide, as indicated by the RHEED pattern of fig. 1(a).

As results indicate, $\beta$-FeSi$_2$ film can be grown on Si (100) substrate even when it is contaminated by surface oxide. But as shown in fig. 3(d), it consists of $\beta$-FeSi$_2$ crystals with various orientations. Whereas SE treatment with 3.0 keV Ne$^+$ ions resulted in highly-oriented $\beta$-FeSi$_2$ film with the epitaxial relationship of $\beta$-FeSi$_2$ (100) // Si (100) (see fig. 3(a)), SE with 0.8 keV Ne$^+$

![Fig.2 Comparison of RHEED patterns of $\beta$-FeSi$_2$ film formed on Si (100) substrate surface with various SE conditions; (a) 3.0 keV Ne$^+$, (b) 0.8 keV Ne$^+$, (c) 0.6 keV Ne$^+$, and (d) no SE. Note that in all cases, the substrates were annealed at 1073 K for 30 min.](image-url)

![Fig.3 Comparison of XRD patterns of $\beta$-FeSi$_2$ film formed on Si (100) substrate surface with various SE conditions; corresponding to the cases of (a) to (d) in Fig.2.](image-url)
ions is also effective in obtaining highly-oriented \( \beta \)-FeSi\(_2\) film (see fig. 3(b)). The RHEED patterns shown in figs. 2(a) and 2(b), and the XRD patterns in figs. 3(a) and (b) are similar to each other. The TEM observation of the \( \beta \)-FeSi\(_2\) film on Si (100) substrate treated with 0.8 keV Ne\(^+\) have shown that the film had a uniform thickness and a smooth interface over a wide area [19]. On the other hand, the RHEED pattern shown in fig. 2(c) was less clear and the XRD pattern (fig. 3(c)) showed polycrystalline nature of the \( \beta \)-FeSi\(_2\) film on Si substrate, which was treated with 0.6 keV Ne\(^+\) ions. Since, according to calculation [20], the sputter yield of Si atoms with 3.0 keV Ne\(^+\) ions is larger than that with 0.6 keV Ne\(^+\) ions by a factor of about 1.5, etching may have been ineffective in the latter case. When this value is used, a sputtered thickness would be 10 nm for the case of SE with 0.6 keV Ne\(^+\) ions, irradiation fluence should have been enough to remove surface contaminants. Since it was difficult to obtain clean substrate surface by sputter etching with 0.6 keV Ne\(^+\), the quality of ion beam may need to be examined.

3.3 Possible role of sputter etching in the film formation

Ne\(^+\) ions have been employed by the present authors as an ion species in the SE treatment. The reason is that for Ne, along with Kr, recovery of the damaged surface layer is better than Ar [21]. Also, Ne is easily released from Si with annealing at around 1073 K, which is consistent with authors’ observation.

The obtained results for the IBSD-grown \( \beta \)-FeSi\(_2\) films definitely indicate the importance of Fe and/or Si diffusion in determining its crystalline properties [8], since the formation of iron silicides involves reactions between Fe atoms sputtered from solid target and Si atoms in the bulk substrate. For these atoms to meet each other, Fe and/or Si atoms must diffuse through the Si surface layer which is modified by sputter etching, or the preexisting silicide layer.

Diffusion behavior of Fe and/or Si atoms in the silicide, or the modified layer of Si to begin with, is not fully understood. Nevertheless, it would be reasonable to assume that diffusion would be restrained as the silicide formation reaction proceeds to increase its thickness. Although the SE treatments with keV-order ions inevitably produce defects, the interface of the \( \beta \)-FeSi\(_2\) (100) film and Si (100) substrate had a smooth interface after the deposition at 973 K [5]. It was then considered that a moderate disorder of the silicon substrate surface treated by SE is rather beneficial, for the presence of point defects, presumably Si vacancies [22], may enhance the intermixing of Fe and Si atoms by providing additional sites for diffusion to promote the epitaxial growth of \( \beta \)-FeSi\(_2\). The fact that the distance from the interface to the aggregated defects [10] (section 3.1.2) decreased with the increase of Ne\(^+\) energy for the SE treatment should be the consequence of complicated interactions between reacting atoms and defects as a function of Ne\(^+\) incident energies. It should be noted that the substrate prepared by WE treatment did not always produce better result than that by SE treatment. Better interfacial properties are often seen in the films prepared with SE treatment. It seems as though the WE treated surfaces are rigid, where diffusion is limited in the treated region so that intermixing of reacting atoms is not promoted.

Reducing both incident ion energy and fluence in SE treatments has its own limit as the efficiency of sputter etching is also lowered. Insufficient sputtering will leave native oxide on the substrate, so that the film cannot grow epitaxially on disordered surface. In fact, the SE treatments with extensive irradiation and higher incident energies often resulted in mixture of polycrystalline and amorphous structures in Si substrate after annealing [23]. Furthermore, under these conditions, formation of dense Ne bubbles was observed. Above discussion indicates that there must be an optimum dose and energy for applying SE treatment to obtain silicide film with high crystalline properties.

4. SUMMARY

It was demonstrated in the present study that a highly-oriented \( \beta \)-FeSi\(_2\) (100) film can be grown on Si (100) substrate by means of IBSD method, with employment of in-situ sputter etching (SE) treatment. A detailed examination with cross-sectional transmission electron microscope (TEM) indicates that SE-treatment introduces a small amount of irradiation defects even after thermal annealing. In order to further reduce the amount of defects existing in the film / substrate interface, the incident energy of ions is reduced below 1 keV, where under the conditions of the present study, incident energy of Ne\(^+\) for SE can be lowered to 0.8 keV to obtain highly-oriented \( \beta \)-FeSi\(_2\) film on Si. These experimental observations seem to indicate that the presence of irradiation defects is not necessarily deleterious in fabricating highly-oriented \( \beta \)-FeSi\(_2\) films. Or rather, this “modified” layer may even serve as a template for epitaxial growth of \( \beta \)-FeSi\(_2\) films. Or rather, this “modified” layer may even serve as a template for epitaxial growth of \( \beta \)-FeSi\(_2\) films. Or rather, this “modified” layer may even serve as a template for epitaxial growth of \( \beta \)-FeSi\(_2\) films. Or rather, this “modified” layer may even serve as a template for epitaxial growth of \( \beta \)-FeSi\(_2\) films.

(Received January 20, 2012; Accepted March 6, 2012)