Interface Structure of an Epitaxial Iron Silicide on Si(111) Studied with X-Ray Diffraction

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Atomic structures of iron-silicide ultra-thin films epitaxial grown on Si(111) were investigated by x-ray crystal-truncation-rod scattering measurements. Two films, each of them respectively exhibited 1×1 and 2×2 periodicities in ultra high vacuum, were measured with the x-ray diffraction under ambient air. Both of the films showed essentially the same Laue peaks. The Laue peaks directly indicate that both films have the CsCl-type (so-called c-FeSi) structure whose stacking orientation is rotated by 180° with respect to the substrate. Quantitative structural analysis, which includes degree of the film roughness as fit parameters, reveals that the interfacial Fe atom is 8-fold coordinated to Si atoms (so-called B8 model). The determined interlayer spacing in the silicide film and the Fe-Si bond length at the interface are respectively ∼6 % and ∼9 % larger than those in the hypothetical c-FeSi.
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I. INTRODUCTION

Iron-silicide films epitaxially grown on semiconductor materials have attracted much attention due to considerable technological interests [1, 2]. Depending on atomic structure and composition, the iron silicides exhibit various electronic, magnetic, and optical properties [2–4]. Integrating the iron silicides into semiconductor devices, therefore, can provide wide variety of potential applications. Growth of epitaxial iron silicide films of sufficient homogeneity and crystallinity is an important matter on a road to the device applications. Numerous studies have been devoted to get better knowledge of growth mechanism of the iron silicides on Si(111) [5–11]. At early stage of epitaxial growth, competition among surface, interface, and strain energies can result in formation of ultra-thin films whose structure is instable in bulk. In the Si(111)-Fe system, when the coverage of Fe atom is below ∼10 monolayer (ML) (1 ML is defined as the density of Si atoms in the topmost layer of the Si(111) substrate) well-ordered silicide ultra-thin films, 1×1, 2×2, and c(8×4) which have bulk-instable atomic structures, are formed depending on the Fe coverage and annealing temperature [11].

Atomic structure of the 1×1 phase, grown by annealing at temperatures between 300 and 600 K according to a phase diagram of ref. 11, was determined as the CsCl-type structure (so-called c-FeSi) by quantitative low-energy electron diffraction (LEED) analysis [9]. Further annealing up to ∼800 K leads to the formation of the 2×2 phase.

Different structure models have been proposed for the 2×2 phase: the CaF$_2$-type structure (so-called γ-FeSi$_2$) [5], modulation of the c-FeSi film caused by Fe vacancies [6], and 2×2 arrangement of Si adatoms at surface of the c-FeSi film [7, 8]. Quantitative structural analysis for the 2×2 phase has not been reported to our knowledge.

Very recently, ferromagnetism of the 1×1 and 2×2 films was reported [12]. Surprisingly, the ferromagnetism was maintained even after exposing the ultra-thin, ∼3-ML Fe coverage, films into ambient air. The origin of the ferromagnetism have been discussed, whether it comes from the film itself or interface. Therefore, revealing the crystalline and interface structures of the 1×1 and 2×2 ultra-thin films and if the structures are maintained under ambient air had been strongly required.

FIG. 1: A LEED pattern from the 2×2 iron silicide film. The incident energy is 90 eV. LEED spots originating from the 2×2 periodicity are circled.

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In this study, for this purpose, x-ray crystal-truncation-rod (CTR) scattering of the 1×1 and 2×2 ultra-thin films were measured under ambient air. CTR scattering amplitude from an epitaxial film at a reciprocal vector \( \mathbf{q} \) is represented as \( F_{\text{sub}}(\mathbf{q}) + e^{i\mathbf{q} \cdot \mathbf{h}} F_{\text{film}}(\mathbf{q}) \), where \( e^{i\mathbf{q} \cdot \mathbf{h}} \) is a phase factor corresponding to interfacial separation vector \( \mathbf{h} \), and \( F_{\text{sub}}(\mathbf{q}) \) and \( F_{\text{film}}(\mathbf{q}) \) are, in the present system, structure factors of the Si(111) substrate and iron silicide film, respectively. Therefore, atomic structure of the film and its epitaxial relationship to the substrate can be obtained [13, 14]. Since the CTR scattering can be described by single-scattering approximation [15, 16], the real structure of the hypothetical films are 3 bilayers (1 bilayer is defined as a pair of 1-ML Fe and 1-ML Si for the c-FeSi, and of 1-ML Fe and 2-ML Si for the \( \gamma \)-FeSi\(_2\)). The Fe-Si inter-layer spacing is set to 0.85 Å for the c-FeSi film, which is obtained through our structural refinement (described later), and is set to match the substrate’s lateral unit cell for the \( \gamma \)-FeSi\(_2\) film. In Fig. 2(a), at around \( L = 5.2 \), where a main peak originating in the \( F_{\text{film}}(\mathbf{q}) \) is located in the measured intensity curves, the c-FeSi film shows the main Laue peak while the \( \gamma \)-FeSi\(_2\) film shows the series of sub peaks. Even though the shape of the calculated curves should be modified when the films are roughened by air-exposure, the position of the main peak does not vary largely. Therefore, the c-FeSi film is supported, and the CaF\(_2\) film can be safely excluded. The c-FeSi film can have two stacking orientations with respect to the substrate, A or B type with the unit cells of the film and substrate aligned or mutually rotated by 180°, respectively. In Fig. 2(b), the intensity curve calculated for the B-type stacking shows a main peak at \( L \sim 3.2 \) and a sub peak at \( L \sim 6.2 \) in accord with the measured intensity curves, while the A-type stacking shows a dip at the experimental peak position of \( L \sim 3.2 \). Therefore, in summary, we conclude that the crystalline structure of both the 1×1 and 2×2 films is the CsCl-type structure with the B-type stacking. The 2×2 periodicity, observed by the \textit{in-situ} LEED (see Fig. 1), was not observed by the \textit{ex-situ} XRD measurements. Therefore, the 2×2 periodicity is suggested to originate in a modulation at surface of the c-FeSi film, e.g., \( 2 \times 2 \) arrangement of Si adatoms [7, 8].

In order to reveal the interface structure, a quantitative structural analysis was carried out. Four structure models illustrated in Fig. 3 were examined. According as the coordination number of the interfacial Fe atom, the models are named B4, B5, B7, and B8 as labeled in Fig. 3. \( h, d_1, d_2, \) and \( d_t \) represented in the figure were employed as structural parameters, where \( h \) is the interfacial spacing between the topmost Si atom of the substrate and the film atom directly bonded to it. The film is assumed to have a constant interlayer spacing \( d_t \). The films originally contain a few domains of different thickness [9–11], and furthermore, should be roughened by the air exposure. In order to include the effect of the film roughness into the structural analysis, area fraction of each atomic layer, which can contribute to the diffraction intensities, indicated that at certain fractions of the iron silicide films their atomic structures remained and made the interferences even though the ultra-thin films had been exposed to air. The results imply that the films are rather tolerant to oxidations, as inferred from inert property of the 2×2 surface against nitric-oxide exposure [18]. Even in the measurements done after five months, the Laue peaks in the 10 rod of the 2×2 film were observed, although their intensities were decreased by 50–80%.

As clearly seen in Fig. 2, the CTR intensity distributions are very similar between the 1×1 and 2×2 films, demonstrating that the films have the same crystalline structure after exposure to ambient air. In order to identify the crystal structure type, the CTR intensities calculated for free-standing CsCl-type c-FeSi (solid curve) and CaF\(_2\)-type \( \gamma \)-FeSi\(_2\) (dashed curve) films are compared with the experiment in Fig. 2(a). The thicknesses of the hypothetical films are 3 bilayers (1 bilayer is defined as a pair of 1-ML Fe and 1-ML Si for the c-FeSi, and of 1-ML Fe and 2-ML Si for the \( \gamma \)-FeSi\(_2\)). The Fe-Si inter-layer spacing is set to 0.85 Å for the c-FeSi film, which is obtained through our structural refinement (described later), and is set to match the substrate’s lateral unit cell for the \( \gamma \)-FeSi\(_2\) film. In Fig. 2(a), at around \( L = 5.2 \), where a main peak originating in the \( F_{\text{film}}(\mathbf{q}) \) is located in the measured intensity curves, the c-FeSi film shows the main Laue peak while the \( \gamma \)-FeSi\(_2\) film shows the series of sub peaks. Even though the shape of the calculated curves should be modified when the films are roughened by air-exposure, the position of the main peak does not vary largely. Therefore, the c-FeSi film is supported, and the CaF\(_2\) film can be safely excluded. The c-FeSi film can have two stacking orientations with respect to the substrate, A or B type with the unit cells of the film and substrate aligned or mutually rotated by 180°, respectively. In Fig. 2(b), the intensity curve calculated for the B-type stacking shows a main peak at \( L \sim 3.2 \) and a sub peak at \( L \sim 6.2 \) in accord with the measured intensity curves, while the A-type stacking shows a dip at the experimental peak position of \( L \sim 3.2 \). Therefore, in summary, we conclude that the crystalline structure of both the 1×1 and 2×2 films is the CsCl-type structure with the B-type stacking. The 2×2 periodicity, observed by the \textit{in-situ} LEED (see Fig. 1), was not observed by the \textit{ex-situ} XRD measurements. Therefore, the 2×2 periodicity is suggested to originate in a modulation at surface of the c-FeSi film, e.g., \( 2 \times 2 \) arrangement of Si adatoms [7, 8].

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FIG. 2: CTR intensity distributions along (a) 00 rod and (b) 10 rod. The red circles and blue squares are intensities measured for the 2x2 and 1x1 films, respectively. In (a), the solid and dashed curves are intensity curves calculated for free-standing hypothetical CsCl-type c-FeSi and CaF$_2$-type γ-FeSi$_2$ films, respectively. In (b), the solid and dashed curves are intensity curves calculated for the hypothetical c-FeSi film with the B- and A-type stacking, respectively. Details of structures of the hypothetical films are described in the main text.

TABLE I: Optimized structural parameters and R-factor for each structure model illustrated in Fig. 3. Error range is given in parenthesis.

<table>
<thead>
<tr>
<th>Model</th>
<th>$d_0$ (Å)</th>
<th>$h$ (Å)</th>
<th>$d_1$ (Å)</th>
<th>$d_2$ (Å)</th>
<th>R-factor</th>
</tr>
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<tbody>
<tr>
<td>B4</td>
<td>0.84(0.01)</td>
<td>2.62(0.02)</td>
<td>0.70(0.01)</td>
<td>2.42(0.01)</td>
<td>0.173</td>
</tr>
<tr>
<td>B5</td>
<td>0.76(0.01)</td>
<td>2.19(0.03)</td>
<td>0.91(0.02)</td>
<td>2.31(0.02)</td>
<td>0.263</td>
</tr>
<tr>
<td>B7</td>
<td>0.79(0.01)</td>
<td>1.61(0.03)</td>
<td>1.29(0.07)</td>
<td>2.25(0.03)</td>
<td>0.285</td>
</tr>
<tr>
<td>B8</td>
<td>0.85(0.01)</td>
<td>2.62(0.02)</td>
<td>0.78(0.01)</td>
<td>2.37(0.01)</td>
<td>0.151</td>
</tr>
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was employed as fit parameter in addition to the aforementioned four structural parameters. We thus expressed the $F_{\text{film}}(q)$ as

$$F_{\text{film}}(q) = \sum_j f_j(r) e^{i q \cdot r}, \quad (1)$$

where $f_j(r)$ is atomic form factor at $j$th layer locating at a position $r$, and $\theta_j$ is the area fraction of $j$th layer.

The parameters were optimized to minimize the $R$-factor defined as $\sum_q |(F_{\text{exp}}(q)) - |F_{\text{cal}}(q))|/|F_{\text{exp}}(q)|].$ The experimental data for the 2x2 film was applied to the analysis. The optimized structural parameters and $R$-factor for each model are listed in Table I, and the area fractions of each atomic layer are plotted in Fig. 4. As seen in Fig. 4, each model shows the broad tendency for the area fraction: it is close to 1.0 at the 4th substrate layer and decreases with approaching to the film surface. The tendency would not be inconsistent with real progress of oxidation of the film. The B5 and B7 models have the $R$-factors larger than 0.26 (see Table I). The interfacial separations $h$ in these models are unrealistically small compared with the summation of covalent radii of Fe and Si, 2.42 Å. Therefore, these models are excluded. The B8 model has the smallest $R$-factor of 0.151, being slightly smaller than 0.173 of the B4 model. Indeed the small difference in $R$-factor can not exclude the B4 model safely, but the analysis which employs the data for the 1x1 film also support the B8 model with the same structural parameters within error. And furthermore, the analysis which employs intensity data for the 2x2 film, acquired using a wavelength corresponding to the Fe K-absorption edge of 1.746 Å (not shown), also support the B8 model. Therefore, we conclude the B8 model is the real interface structure, in agreement with the LEED analysis and first-principles calculation for the 1x1 film [9]. The best-fit intensity curves calculated for the B8 model are compared with the experiment in Fig. 5. The experimental peak and dip positions are almost reproduced.

The optimized interlayer spacing $d_0$ of the B8 model is 0.85 Å (see Table I), which is close to the averaged interlayer spacing of 0.82 Å obtained by the LEED analysis for a 3-bilayer domain [9]. The interlayer spacing of the hypothetical c-FeSi, whose lattice constant is about 2 % larger than that of Si, is 0.80 Å [9]. The silicide film is thus extended from the bulk value by about 6 %. The interfacial Fe-Si bond length $h$ is 2.62 Å also being extended from the bulk value by about 9 %. Due to the 2-% lattice mismatch between Si and the bulk c-FeSi, the c-FeSi film should be laterally compressed when epitaxi-
FIG. 3: Interface structure models examined in the structural analysis. Dashed lines represent the boundary between the substrate and silicide film. In bottom right panel structural parameters employed for the analysis are indicated.

FIG. 4: Area fractions of each atomic layer optimized by the structural analysis. In the horizontal axis, left-to-right corresponds to the substrate-to-surface of the film.

FIG. 5: Comparison between experimental CTR intensities (red circles) and intensity curves calculated for the B8 model (dashed lines).

IV. CONCLUSION

Atomic structure of the 1×1 and 2×2 iron-silicide ultra-thin films and their epitaxial relationship to the Si(111) were investigated by x-ray CTR scattering measurements. The ~3-bilayer-thickness ultra-thin films exhibited clear Laue peaks even in air. The two films showed essentially the same CTR intensity distributions along reciprocal rods, indicating that the crystalline structures of the films are the same after the air-exposure. The Laue peaks clearly show that the crystalline structure is the CsCl-type (c-FeSi) whose unit cell is rotated by 180° with respect to the substrate. As a result of the quantitative structural analysis which takes account of the effect of film roughness, the interface structure was determined as the B8-type, in which interfacial Fe atom is 8-fold coordinated to Si atoms. In the determined structure, the interlayer spacing in the silicide film and Fe-Si bond length at the interface are respectively ~6% and ~9% longer than those in the hypothetical bulk c-FeSi. The obtained structural properties are expected to provide insights into the origin of the ferromagnetism of the iron silicide ultra-thin film.
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