Study of the Interface Structure of Epitaxial Ultra-Thin Film by an X-Ray Holographic Imaging Method*

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An X-ray holographic method that reconstructs a single layer of atoms at the interface between ultra-thin film and substrate crystal is studied. We applied the method to the analysis of the interface structure of iron-silicide grown on the Si(111) surface, the structure of which is considered to be the CsCl-type FeSi. First we confirmed by simulations that the method is useful to discriminate whether an additional layer at the interface exists or not, using calculated X-ray intensities. Next we applied the method to the analysis of experimental data obtained for Si(111)-2×2-Fe. The result indicated the existence of the interface atoms, corresponding to the B8 model for CsCl-type FeSi.

Keywords: X-ray scattering, diffraction, and reflection; Crystal-truncation rod; Direct methods; Silicides; Iron; Phase problem

I. INTRODUCTION

X-ray diffraction has been used for the structure analysis of surfaces and interfaces because its diffraction process is well described by a single scattering theory [1, 2]. Particularly crystal-truncation rod (CTR) scattering gives information on the structure of surfaces and interfaces with respect to the substrate crystal [3–5]. In the case of reconstructed and adsorbed surfaces where the number of atomic layers to be determined is small, the surface structures can be completely analyzed. In the case of thin film crystals epitaxially grown on a substrate crystal, the structure of thin film crystals is easily determined as the thickness of film crystals increases. In contrast to this, the structure of the interface becomes difficult to be analyzed without ambiguity in single atomic layer resolution. For instance, it becomes more difficult to determine which atomic layer starts at the interface in compound thin crystals with the increase of thickness. Another reason for difficulties in the analysis is that such epitaxially grown thin crystals are not flat and their thickness is not uniform.

In the analysis of X-ray diffraction data, the least squares fitting is usually applied to obtain structural parameters for some structural models, and the most probable structure model is distinguished from other models based on the value of the R-factor. Thus there remains some ambiguity to determine the interface atomic layer due to the reasons mentioned above.

In this work we describe a kind of direct method that determines whether a single atomic layer exists or not at the interface of a ultra-thin film epitaxially grown on substrate crystals. In a previous work [6, 7] we showed that atom images of a single atomic layer on a crystal surface are reconstructed three-dimensionally directly from X-ray CTR scattering data by using a holographic technique. In this work we apply the method to investigate the interface of a ultra-thin iron silicide film on Si(111) and show that the method is useful to reveal a single atomic layer at the interface.

II. IRON SILICIDES ON SI(111)

Iron silicides attract much attention from view points of their applications to optoelectronic and magneto- electronic devices. Recently fabrication of iron silicides on Si(111) by solid phase epitaxy (SPE) growth was systematically studied for the conditions of the amount of deposited Fe and subsequent annealing temperature [8]. In the region of a few monolayer deposition, thin films with 1×1, 2×2 and c(8×4) periodicity, observed by LEED, RHEED, STM etc., are fabricated almost separately. For the structure of those films, cubic CsCl-type, CaF$_2$-type, and defect CsCl-type structures are proposed [9–13].

As to the 1×1 phase, the cubic CsCl-type structure is believed to be the most probable, but the interface structure is still unsettled. Figure 1 shows the CsCl-type FeSi structure models where the FeSi films are rotated by 180° with respect to the Si(111) substrate and figures correspond to the coordination number of Fe at the interface. Fe atoms are bonding to the topmost Si atoms of the Si(111) substrate in both the B5 and B8 models, but an additional Si atomic layer bonding to the interface Fe atoms exits in the B8 model. In the B7 model, the topmost Si atoms of the Si(111) substrate are bonding to Si atoms of the FeSi film. In a recent study Walter et al. [12] support the B8 model from the analysis of LEED I-V curves and first-principles calculations. On the other hand, the B5 model is supported by a theoretical work [14] explaining a ferromagnetic nature observed at low temperature [15].

Next we explain the principle of a holographic imaging method that reconstructs the additional atoms at the interface if the B8 model is correct and reconstructs no atoms at the interface if the B5 model is correct.

III. PRINCIPLE OF THE METHOD

Figure 2(a) illustrates schematically the method we have developed to reconstruct atom images on the surface from measurements of CTR scattering [6]. The X-ray

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scattering amplitude $F(k)$ from crystal surfaces is divided into scattering from the bulk crystal $F_{\text{Bulk}}$ and that from a surface structure formed on the crystal $F_{\text{Surface}}$.

The method we used is based on a kind of holographic approach. Since the structure of the substrate is known, we can easily calculate X-ray scattering from the substrate. Thus we regard this as the reference wave $F_{\text{Reference}}$, and the x-ray scattering from the unknown surface structure as the object wave $F_{\text{Object}}$. Then the x-ray scattering intensity is given by

$$I(k) = |F(k)|^2$$

(1)

$$I(k) = |F_{hk}^{\text{Reference}} + F_{hk}^{\text{Object}}|^2$$

(2)

$$I(k) = |F_{hk}^{\text{Bulk}} + F_{hk}^{\text{Surface}}|^2,$$

(3)

where $h$ and $k$ are integers denoting the indices of crystal truncation rods, and $I$ is the index designating the point on the $hk$ rod.

If we define the hologram function by

$$\chi(k) = \chi_{hk}(l) = \frac{I(k) - I_0(k)}{F_{hk}^{\text{Reference}}}$$

(4)

then surface atom images will appear by the Fourier transform of $\chi(k)$ as follows

$$U(r) = \int \chi(k) \exp(-i2\pi kr)dk$$

$$= \sum_h \sum_k \int \chi(k) \exp(-i2\pi kr)dl.$$  

(5)

Here, observed intensities are used for $I(k)$ while calculated ones are for $I_0(k) = |F_{hk}^{\text{Reference}}|^2$. It is noted only the data points near the Bragg points should be used in the analysis [6].

Figure 2(b) illustrates the CTR scattering in the case of a thin film grown on a substrate crystal with an additional layer at the interface. In this case the CTR scattering amplitude is given by

$$F(k) = F_{hk}^{\text{Bulk}}(l) + F_{hk}^{\text{Films}}(l) + F_{hk}^{\text{Interface}}(l).$$

(6)

Since the structure of the thin film is usually determined from experimental data, the reference wave is composed of two known scatterings from the substrate and the thin film, and the object wave is attributed to X-ray scattering from the unknown interface as follows,

$$F_{hk}^{\text{Reference}}(l) = F_{hk}^{\text{Films}}(l) + F_{hk}^{\text{Interface}}(l),$$

(7)

$$F_{hk}^{\text{Object}}(l) = F_{hk}^{\text{Films}}(l).$$

(8)

In this work we use the present method to distinguish the B5 and B8 models. If we use the CTR scattering from the B5 model as the reference wave, then atom images will appear only when the B8 model is correct. In contrast, no atom images will appear when the B5 model is correct. Thus we can discriminate between the two models.

IV. SIMULATIONS

First we investigate the present method by simulations, regarding x-ray scattering from the B5 model as the reference wave. Calculated intensities were used for $I(k)$ instead of observed intensities in simulations. Figure 3 shows the images obtained from Eq. (5) when $I(k)$ and $I_0(k)$ were calculated for the B8 model and the B5 model, respectively, assuming that the CsCl-type FeSi takes the B8 structure. Here we assumed the lattice spacing $d_L$ of FeSi is the same for each layer within the film and the spacing between the additional Si layer in the B8 model has the same distance $d_L$ from the bottom Fe layer of the FeSi film. In Fig. 3, we used 2.42 Å for the distance $D$ between the bottom Fe layer of the film and the topmost Si layer of the Si(111) substrate, corresponding to the sum of atomic radii for Si and Fe atoms, and 0.78 Å for the lattice spacing $d_L$ of FeSi, corresponding to one-fourth of the lattice spacing of Si (111) plane. In the figure, $x$ and $y$ values are normalized by the unit of the 1x1 unit cell.
for the Si(111) surface, and z value by the Si(111) lattice spacing, 3.14 Å. The origin of x, y and z was taken at the topmost Si of the Si(111) substrate crystal.

As is seen in Fig. 3, the interface atoms in the B8 model are reconstructed at about the expected positions \((x, y, z) = (0.67, 0.33, 0.53)\). Simulations were repeated by changing the values of \(d_L\) and \(D\). The result indicated that images of the interfaces atoms move to the positions corresponding to changes in \(d_L\) and \(D\).

In the present method, the effects of surface roughness and selection of the scale factor adjusting experimental data to calculated ones have possibilities to make the results ambiguous. We carefully checked both the effects, but found to be not so serious in judging whether an additional atom exists or not. We also examined that surface roughness does not much affect atom images from calculations assuming that the thin film is composed of two films with different thickness.

In the above simulations, we used CTR intensities along the 00, 10, 01 rods and their symmetry-equivalent rods (7 rods in total), and selected 124 CTR intensities only around Bragg points. Simulations indicate that the atom image seen in Fig. 3 becomes sharp with the increase of the number of rods to be considered.

V. ANALYSIS OF EXPERIMENTAL DATA

Experiments of CTR scattering were performed at the beamline BL3A and BL4C of the Photon Factory in KEK. Measurements were done for two samples with 1×1, and 2×2 periodicity, fabricated by SPE growth. X-ray intensities were observed along the 00, 10, and 01 rods in atmosphere. Details of the experimental results and analyses using the least squares fitting are described elsewhere [16]. The results support the CsCl-type structure for both samples. In this work we use only the result obtained for Si(111)-2×2-Fe. Since the fractional order reflections were not observed for Si(111)-2×2-Fe, the 2×2 periodicity is considered due to Si adatoms on the film, and is lost in the atmosphere [11]. The observed intensities along the 00 rod are reproduced in Fig. 4.

We can determine with ease that the fabricated film has the B-type CsCl structure from the profile of the observed data. Furthermore we can roughly estimate the
lattice spacing and thickness of the film, because the peak A in Fig. 4 (l=5.3) corresponds to the main peak of the Laue function arising from the FeSi film, and the peak B (l=7.2) to the first sub-peak of the Laue function. From these peak positions, we can safely assume that the lattice spacing \( d_L \) is 0.88 (\( \pm 0.78 \times 6.0/5.3 \)) Å and the film is composed of three (\( \pm 5.3/(7.2-5.3) \)) pairs of Fe and Si layers as in the B5 and B8 models shown in Fig. 1. It is noted that the main peak A appears at \( l=6.0 \) if \( d_L \) is equal to the spacing of a Si bilayer 0.78 Å. As to the distances between the film and the substrate, \( D \), we assumed the sum of atomic radii, 2.42 Å, as in the simulations. The result is shown in Fig. 5. In the analysis we selected 79 points around Bragg points (independent 33 points) for the 7 rods (independent 3 rods). We can obviously find additional atoms at the positions expected for the B8 model.

As is expected from the result of the simulations, images of the additional atoms appear even if the values of \( d_L \) and \( D \), and also the film thickness were changed. We further checked that the atom images appear even with changes of the value of the scale factor.

VI. DISCUSSIONS AND CONCLUSION

In this work we applied a holographic imaging method to the analysis of the interface structure. First we showed that a single layer of atoms at the interface is reconstructed by simulations. Then the method was applied to the analysis of an iron silicide thin film on the Si(111) surface. The result indicated that the iron silicide of Si(111)-2\( \times \)2-Fe is of CsCl B8-type, consistent with the analysis done by using the least squares fitting [16].

It should be mentioned that a number of studies have been done to solve the surface structure using various kinds of direct methods [17–27], but most of them are underway. At the present stage we think that such direct methods are much helpful to distinguish the most probable model from others. Then one can use the conventional least squares fitting to get structural parameters precisely with less ambiguities.

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