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Transmission X-ray Diffraction from Bismuth Lines Embedded in Silicon

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We have devoted our efforts toward developing transmission X-ray diffraction (TXD) for surface and interface from the viewpoint of realizing more efficient and precise structural analysis than the conventional surface X-ray diffraction. Here, we investigated bismuth lines embedded in a Si(001) substrate, which are promising templates applicable to nanometer-scale device, by TXD. In our experiments with synchrotron X-rays typical one-dimensional diffraction patterns were observed, which obviously indicates that the bismuth lines are still preserved in interface at the atomic scale.
Key words: Bi, Atomic wire, Interface structure, Transmission X-ray diffraction, Synchrotron radiation, Si(001)

1. INTRODUCTION

Research on low-dimensional physics has been accelerated by recent rapid progress in manipulation of nanometer-scale structures on crystal surface. Self-organized atomic wire on semiconductor is a current topic gathering much interest, e.g. wires of metal on semiconductor [1, 2] and group-V elements such as Bi, Sb, and As on semiconductor [3–9].

Among them Bi line fabricated on Si(001) has received considerable attention because the lines have remarkable structural properties [3, 4]. They are defect free and atomically flat lines over 500 nm in length without kinks. Unraveling the physical mechanisms that produce the high degree of structural order in the line could lead to a unified understanding of other group-V line systems [6, 7]. Therefore, it is fundamental at all to understand the atomic geometry of the line. There are the two most plausible structure models for the Bi line on Si(001), the ad-dimer model proposed by Miki et al. [3, 4] and the Haiku model (or double-core model) proposed by Owen et al. [5]. In the Haiku model, surrounding Si atoms make a significant rearrangement to relief surface strain and the surface strain may play an important role in their self-assembly [5].

Although Bi lines on Si(001) themselves are quantum antiwires [3], they can be used as templates for growth of one-dimensional (1D) materials in fabricating nanoelectronic or nanomagnetic devices [10–12]. Another possibility for device application is encapsulation of the Bi lines by further deposition of Si. Bismuth lines can indeed be embedded in Si epitaxial layer [13–15], and a structural model was proposed by density functional theory calculations [14]. A structural model of Bi lines capped by amorphous Si was also proposed by X-ray standing wave method [16]. The model proposed is different from that on surface, which is ascribed to the influence of the burying effect although the interaction between amorphous Si and the line is expected to be weak. On the other hand, when Bi lines are buried in an epitaxial Si layer the position of Bi atom should be influenced and they may reconstruct because the interaction would be rather strong. The electronic structure of the embedded Bi lines is not sure since the surrounding environment is quite different than the line on surface. Therefore, it is expected that they may change their electronic properties after burial.

There have been reported many structural studies of Bi lines on Si(001) both experimentally and theoretically [3–5, 17–19]. However, structural studies on Bi lines embedded in Si are scarce. It is because there are few methods sensitive to not only such a dilute system but also buried interface structure.

In this paper, we report the structural study of Bi lines embedded in epitaxial Si/Si(001) interface by transmission X-ray diffraction (TXD) since TXD is a tool to meet the requirements as mentioned in the next section. In our synchrotron X-ray experiments typical 1D diffraction patterns were observed, which reveals that the line structure can remain in interface.

2. TRANSMISSION X-RAY DIFFRACTION FOR SURFACE AND INTERFACE

After the seminal work of TXD for surface structure analysis performed by Toshio Takahashi et al. [20], it took long time until subsequent reports in TXD for surface had followed because of instrumental problems, e.g. lack of a handy and dependable two-dimensional (2D) X-ray detector. Recently, we have revisited surface TXD in air and in ultra-high vacuum (UHV) from the viewpoint of realizing more efficient and precise measurement than the conventional surface X-ray diffraction [21]. TXD is also available to interface structure analysis.

Two major advantages we assured in TXD for surface and interface are following: At first, since X-rays incident on a sample almost normal to surface/interface, an illuminated sample area and an effective beam profile hardly change in measurement. This improves precision of diffraction data. Secondly, we can acquire a large number of diffraction spots from surface/interface, i.e. crystal truncation rod (CTR) scatterings and super-lattice reflections,

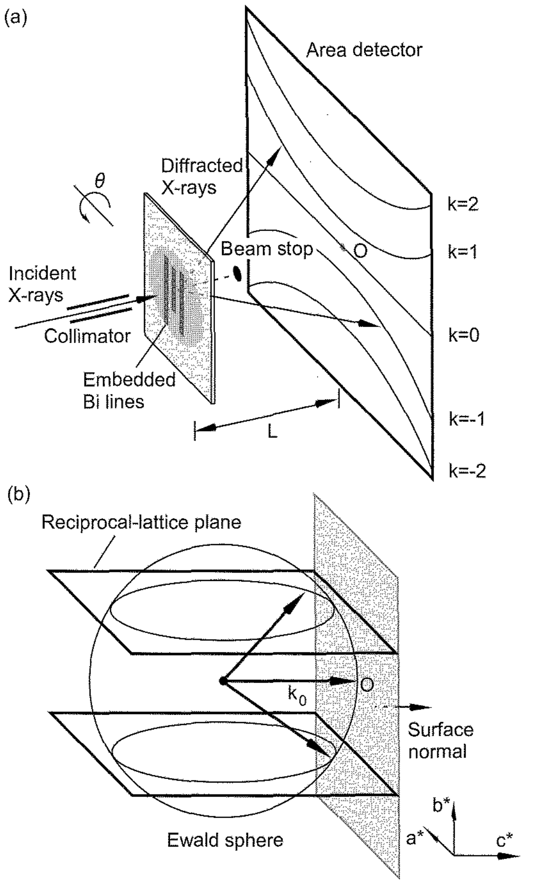

Fig. 1. (a) Experimental setup of transmission X-ray diffraction. Diffraction pattern is recorded by area detector. Here, θ and L denote the diffractometer theta and camera length, respectively. (b) Ewald construction. Diffraction condition of 1D periodic structure is satisfied at the intersection between the Ewald sphere and the corresponding reciprocal-lattice plane. k_0 represents incident wave-vector.

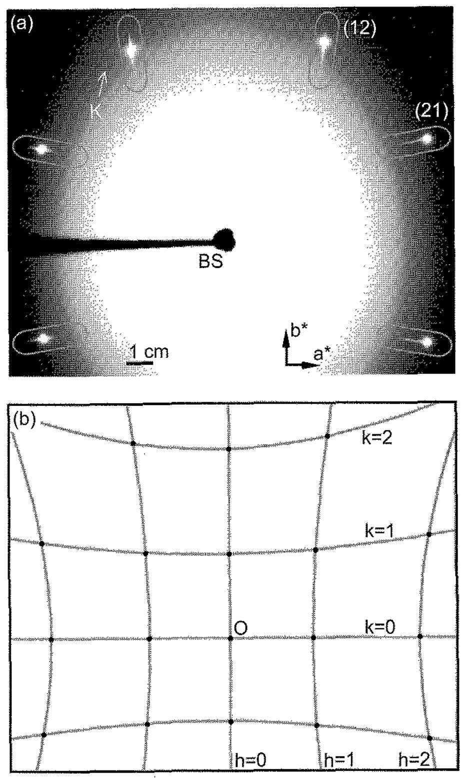

Fig. 2. (a) Transmission X-ray diffraction pattern from embedded Bi lines under normal-incident condition (θ=0°). Exposure time is 7 min. Diffraction lines from the Bi lines are enclosed with gray circles for guide to eyes. Diffuse peaks in the circles are thermal diffuse scatterings from the Si(001) substrate. The shadow in the center is a beam stop (BS). K represents Kossel line. (b) Indexation diagram for (a).

simultaneously by 2D detector, e.g. image plate and x-ray charge-coupled device camera. More generally, we can observe not only spot like diffraction but also diffuse scattering from surface/interface as whole pattern. This feature saves measurement time and can be utilized in rough characterization of surface/interface as is common with electron diffraction for surface. Therefore, TXD is just suitable for structural characterization of a dilute interface, e.g. the embedded Bi lines, which are promising materials for nanometer-scale electric wires or templates for such device applications.

For TXD experiment, although one needs to make a sample thin in the thickness of a few micron for deducing X-ray scattering background from the substrate, a sample is less damaged and easy to handle compared to that for transmission electron diffraction/microscopy.

On the other hand, reflection geometry similar to reflection high-energy electron diffraction (RHEED) has been evaluated in X-rays for characterization of surface and interface structures [14, 22]. The active use of an area detector has become increasingly important for studying dilute systems by surface X-ray diffraction [23, 24].

3. EXPERIMENTAL

Sample preparation process was as below: A miscut free Si(001) sample with size of $18 \times 20 \times 0.4$ mm^3 was oxidized in dry process to make 200 nm thick SiO_2 layer for impurity gettering, flattering, and surface protection. The sample was etched with the solution of HF, HNO_3, and CH_3COOH from the rear surface to the sample thickness of less than ca. 5 μm, followed by the standard RCA cleaning for removing oxide layer and remaking 1 nm thick oxide layer in wet environment , and then introduced to a molecular beam epitaxy system. After clean Si(001) with clear (2×1) RHEED pattern was obtained by thermal annealing at 800°C in UHV, Bi lines were fabricated on Si(001) by supplying Bi at the substrate temperature of 400°C. Finally a Si epitaxial layer of ca. 48 nm thick was grown on Bi/Si(001) as capping layer at 400°C.

The synchrotron X-ray experiments were performed at the beamline BL13XU [25] for surface and interface structures in SPring-8. A conventional six-circle diffractometer was used for the TXD experiments in air. Figure 1(a) shows experimental setup. A Pb collimator and a beam stop were arranged respectively in front of and ca. 15 mm behind a sample to eliminate unwelcome scattering from incident X-rays. Camera length was set to 130 mm. Diffracted X-ray patterns were recorded by image plate. X-ray energy used was 12.54 keV, which is lower than Bi L_3 X-ray absorption

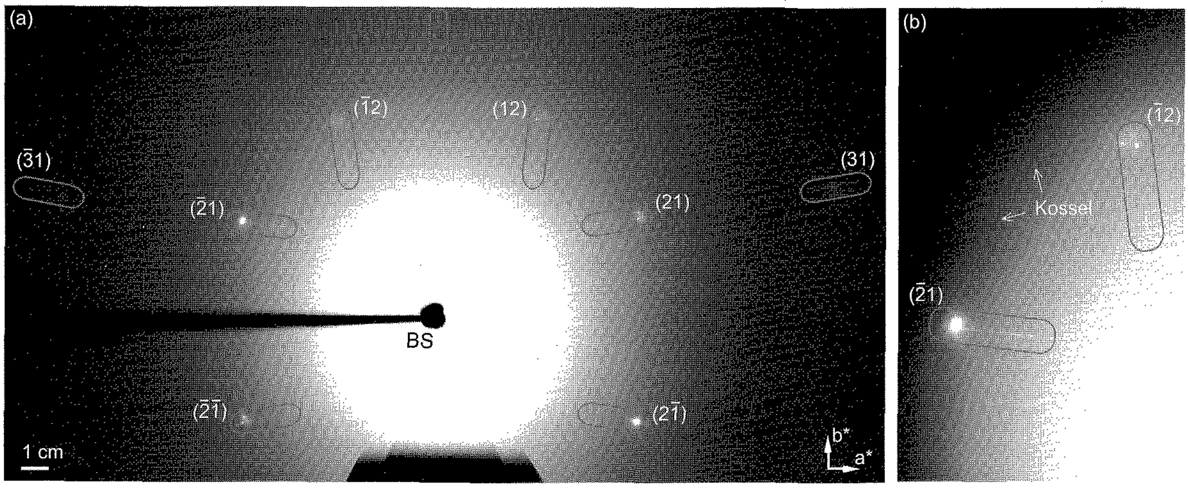

Fig. 3. (a) Transmission X-ray diffraction pattern from embedded Bi lines under off-normal incident condition (θ=2.0°). Exposure time is 40 min. Diffraction lines from the Bi lines are enclosed with gray circles for guide to eyes. The shadow in the center is a beam stop (BS). (b) Magnified diffraction image around the ($\bar{2}$ 1) and ($\bar{1}$ 2) CTRs in (a). Thermal diffuse scatterings from the substrate near the ($\bar{2}$ 1) CTR spot are recognized as a diffuse peak in addition to the Bi line pattern in the circle. Diffractions from the Bi lines along H=−1 and K=2 diffraction lines can be seen below and on the left of the ($\bar{1}$ 2) CTR spot, respectively. One can also find the {422} Kossel lines as denoted by arrows.

edge (13.419 keV). The beam size of incident X-rays was 0.1×0.1 mm^2. The optical surface normal was aligned by using laser so that normal-incident condition is satisfied at the diffractometer theta, θ=0°.

Since diffraction condition of 1D periodic object is satisfied at the intersection between the Ewald sphere and the corresponding reciprocal-lattice plane in Ewald construction as shown in fig. 1(b), X-ray diffraction from Bi lines produces line pattern on an area detector.

4. RESULTS AND DISCUSSION

Figure 2(a) shows a diffraction pattern from Bi lines with exposure time of 7 min. We can see the typical diffraction lines from Bi lines near the CTR scattering spots, e.g. the (2 1) spot. This result indicates that the Bi lines are still preserved in interface at the atomic scale. The indexation diagram for fig. 2(a) is shown in fig. 2(b). The direction of Bi lines is perpendicular to the surface Si-dimer rows on Si(001). Since we used a miscut free sample, clean Si(001) has (2×1) and (1×2) double-domain. Therefore, Bi lines have two possible directions to form and the corresponding diffraction lines have also. Diffraction patterns recorded on image plate were indexed based on the standard UB-matrix procedure [26]. Fundamental lattice vectors of Si(001) and the corresponding reciprocal-lattice vectors are respectively, $\boldsymbol{a}=\frac{a_0}{2}(1,\bar{1},0)$, $\boldsymbol{b}=\frac{a_0}{2}(1,1,0)$, $\boldsymbol{c}=a_0(0,0,1)$, and $\boldsymbol{a}^*=\frac{1}{a_0}(1,\bar{1},0)$, $\boldsymbol{b}^*=\frac{1}{a_0}(1,1,0)$, and $\boldsymbol{c}^*=\frac{1}{a_0}(0,0,1)$, where a_0 is the lattice constant of Si. The 220 and $\bar{2}20$ Bragg reflections from the substrate were used for determining crystal orientation. The pixel positions of an image plate were converted into Miller indices by least squares fitting to the following parameters, the camera length and three rotational freedom of an image plate. The misalignment of an image plate estimated was 2.86° at a maximum and typically less than 1.0°.

Figure 3(a) shows a diffraction pattern under off-normal incident condition, θ=2.0°. One can see apparently different intensity profiles along the lines from those in fig. 2(a)

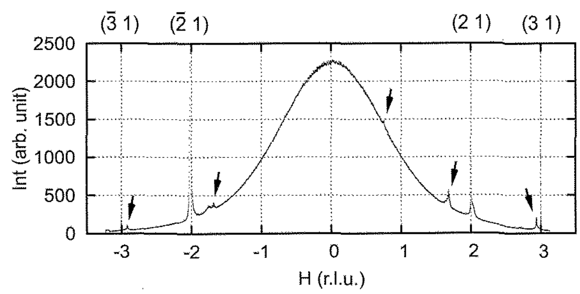

Fig. 4. Line profile of the K=1 diffraction line in fig. 3(a). Arrows indicate diffraction peaks from Bi lines. The peaks that H is integer are CTR scatterings.

because of diffraction from the different intersection on the reciprocal-lattice plane of the Bi line structure. Kossel lines generated by scattered incident X-rays are recognized near the {2 1} CTR scatterings as shown in fig. 3(b), incidentally. It is noticed that we can also find Kossel lines in both fig. 2(a) and fig. 3(a).

The line profile of the K=1 diffraction line thorough the ($\bar{3}$ 1), ($\bar{2}$ 1), (2 1), and (3 1) CTR spots, is plotted in fig. 4. Resolution of an image plate is 50 μm. Therefore, intensities of nine pixels were integrated for each data point in fig. 4, which is sufficiently enough to accept the whole diffracted beam. The very diffuse background whose peak is at H=0 is scattered X-rays mainly by air. The average length of the embedded Bi lines estimated from the diffraction width is over the instrumental resolution, 50 nm in assumption that beam profile has Gaussian shape. We evaluated the instrumental resolution from the full width at half maximum of the peak profile of the (1 2) CTR scattering.

It is expected that the intensities of the diffraction lines are broadly distributed and oscillatory along the lines since the contribution from heavy Bi atoms would be dominant.

Contrary to the expectation, the diffraction pattern shows rather spot like feature as indicated by arrows in fig. 4. These results imply that surrounding Si atoms are relaxed or reconstructed from the bulk positions in a different manner from that on Si(001). Possibility of segregation of Bi atoms composing lines should be neglected because the line length is long and the line could not be stable with vacancies instead of Bi atoms. In addition to these, a fractional-order pattern comes from twice periodicity to the fundamental lattice along the line was not observed, which was reported previously [14]. It is possible to infer that Bi atoms sit on almost (1×1) periodic positions. Fractional-order diffraction lines are too weak to detect as a result. Otherwise, we failed to find the diffraction condition that produces an intense pattern within available time in synchrotron X-ray experiments. As a consequence, it is difficult to construct plausible structural models from the few diffraction peaks alone rather than oscillatory line patterns at present.

We are planning to extract structural information of the embedded Bi line from the diffraction patterns by combination with structural modelings based on global optimization algorithm such as generic algorithm and theoretical calculations to assess energetic stabilities of the models. It is noted that a year after the first X-ray experiment on the sample, a sharp 1D diffraction pattern from the buried Bi lines was again observed, which indicates the interface structure is stable in air.

5. SUMMARY

We have successfully applied TXD to structural study of Bi lines embedded in a Si(001) interface as a representative dilute system. In our experiments with synchrotron X-rays typical 1D diffraction patterns were observed, which obviously indicates that the Bi lines are still preserved in interface at the atomic scale.

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