Structural Verification of Bi Nanolines in Si using Obvious-at-a-glance X-ray Diffraction Method

Most nanoscaled structures that have so far been created have single-unit or independent structures. A multiple-layer structure fabricated by the combination of such single-unit structures is required for practical nanodevice application and is called a nanoarchitecture. Miki's (a coauthor of this article) research group has succeeded in developing a new processing method for encapsulating Bi nanolines in silicon by epitaxial growth of Si. This success has been the first step toward the fabrication of nanoscale interconnections in epitaxial silicon; eventually, this method would allow us to form nanoarchitectures. During growth using the conventional process, a nanostructure is fragile or destroyed because a surface segregation phenomenon occurs. To use a Bi surfactant to avoid the destruction is a key point of the processing method that the research group developed; consequently, it has been possible to embed the Bi-nanoline structures in silicon.

It is in general difficult to nondesructively observe such a nanostructure embedded in a crystal from its surface. This is because the standard surface-structural-analysis tools such as scanning probe microscopy and electron diffraction are not available for direct observation of the embedded nanostructure. There could be a possibility to observe the nanostructure with a transmission electron microscope; however, the structure would be unintentionally destroyed during sample preparation before the observation. On the other hand, any synchrotron-based diffraction technique is nondestructive but had not revealed the Bi-nanoline structure.

Sakata (the first author of this article) applied the “obvious-at-a-glance” X-ray diffraction method based on reciprocal-lattice space imaging to quick observation and characterization of one-dimensional (1D) nano-structures. It disclosed the structural information such as a crystalline-domain size across ultrathin NiO nanowires and their crystal system successfully [1]. The basic idea behind the method is that Bragg conditions of such 1D structures are sheet shapes and are fulfilled more easily than those of 2D and 3D structures. Figure 1 depicts a typical geometry of reciprocal-lattice space imaging. The diffraction conditions or scattering patterns (the Fourier transform) of a 1D crystal are sheets, which are perpendicular to the 1D, located at Bragg positions of the corresponding bulk crystal of the 1D in the reciprocal-lattice space. For example, the segmented streaks would simultaneously arise from the intersection of the sheet-shape structures with the Ewald sphere.

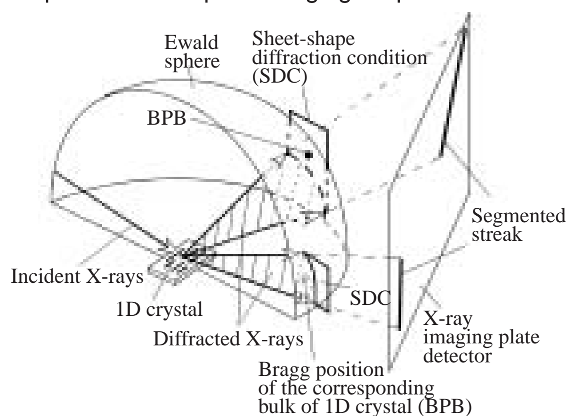

Fig. 1. Geometry of reciprocal-lattice space imaging for 1D crystal perpendicular to incident X-rays.

A principal objective of this research was to elucidate whether the Bi-nanoline structure remains after encapsulation. We used the “obvious-at-a-glance” X-ray diffraction method with possibly high-energy monochromatic X-rays for incidence to excite as many segments as possible and a 2D detector for straightforward analysis. Sample preparation, X-ray experimental conditions, results, and its atomic-scale structural model were already reported in [2].

Bi nanolines were grown on a Si(001) surface by molecular beam epitaxy in ultrahigh vacuum following the established recipe [3]. By scanning tunneling microscopy observation, the lines were 1.5 nm in width and more than 400 nm in length. The surface was at about 1/8 monolayer Bi coverage. Then an 11-nm-thick Si(001) epitaxial layer was grown epitaxially on the substrate at a temperature of *ca.* 400 °C for about 2 min. We also prepared a second sample capped with an 11-nm-thick Si amorphous layer at room temperature. A more explicit procedure for sample preparation was described in [2].

X-ray measurements were performed in air at the undulator beamline **BL13XU** for surface and interface structure determination. A special purpose camera was used, including a pair of slits to limit the beam size to 0.1 mm × 0.1 mm, a sample, a direct-beam stopper, and a cylindrical X-ray imaging-plate (IP) detector to record diffraction. The distance of the sample to the IP detector camera length was 133 mm. The X-ray exposure time was typically 2 min. An X-ray beam with a photon energy of 25.3 keV was incident on the sample at an angle of 0.1°, giving a

penetration depth of 2.7 μm; it is clear that the X-rays reached the Bi lines under the cap layers.

We recorded X-ray patterns diffracted from the samples at different azimuthal angles around the surface normal. The right pattern in Fig. 2 shows a typical one for the incident X-rays perpendicular to the Bi nanolines. A 1D structure in a crystal gives rise to diffraction sheets perpendicular to itself; these are imaged as segmented streaks because of the intersection of the sheets with the Ewald sphere (see Fig.1 again). The magnified pattern (the left of Fig. 2) has segmented streaks.

The average length of the buried 1D lines was about 100 nm, which was estimated from the width of the k = 0 streak, where we use standard notation of h k l to indicate a point in reciprocal space that is defined by the surface unit cell. It should be noted that such streaks or circular arcs were not observed in the case of a Si(001) sample where no Bi nanolines were buried.

Magnifying the pattern (the left image in Fig. 2) gives more information on the 1D structures. Three streaks from the diffraction sheets appeared around the reciprocal lattice points of 0 -1/2 1, 0 0 1, and 0 1/2 1, which correspond to diffraction sheets of k = -1/2, k = 0, and k = 1/2, respectively. This shows that the buried 1D structure has a superstructure along the line, the periodicity of which is two times as large as the length of the primitive vector of the Si(001) surface. In additional to the epitaxial Si cap, we also used a cap of amorphous Si. In this case, the k = 0 streak was barely detectable, and no fractional-order streaks were observed around the direct-beam position, implying a complete loss of the Bi nanoline structure. Our X-ray results indicate that while Si amorphous growth seriously disturbed the atomic lines, Si epitaxial growth with a Bi overlayer confined the 1D atomic lines to the interface, while retaining the two-by periodicity along their length.

On the basis of the structural information obtained from these experiment results, we modeled the optimum atomic structure (Fig. 3) using tight binding and density-functional-theory (DFT) calculations. The starting structure was the “haiku” structure [4] for Bi nanolines on the Si(001) surface.

In summary, Bi nanolines embedded in a Si crystal were found to remain by observation of X-ray sheet-like diffraction for the first time. Sharp images appeared in the X-ray diffraction patterns obtained from the nanolines covered with only the Si epitaxial layer. The nanolines with the epitaxial cap were found to have a 2 × n superstructure having their Bi-dimer bonds parallel to themselves. The atomic-scale structural model for the embedded Bi nanolines has been proposed using tight binding and DFT calculations.

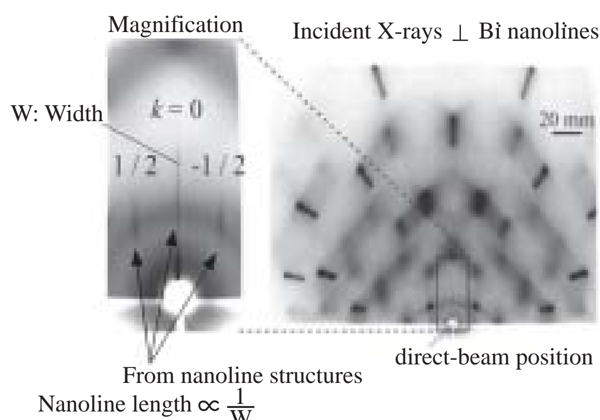

Fig. 2. X-ray patterns diffracted from Si epilayer cap/Bi lines/Si(001) sample. Whole pattern (right figure) recorded on imaging-plate detector and magnified pattern (left figure) around direct-beam position for incident X-rays perpendicular to Bi atomic lines. The surface unit vectors [1 0 0]S and [0 1 0]S having lengths of 3.84 and 3.84 Å are parallel to the bulk vectors [1 -1 0]B and [1 1 0]B, respectively.

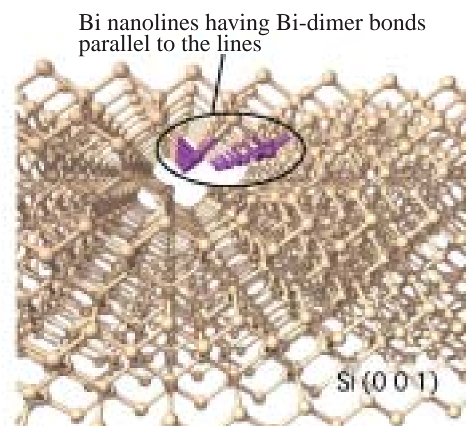

Fig. 3. Perspective view of our proposed model for buried Bi lines, showing their one-dimensional nature.

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