Reciprocal-lattice Space Imaging of X-ray Intensities Diffracted from Nanowires

Structural investigation is essential for development of nanotechnological materials such as nanoelectronics and nanophotonics. X-ray diffraction/scattering is one of the most promising non-destructive methods for observing atomic-scale structures and morphology of the nanomaterials. A nanowire structure on a device surface is particularly interesting since this wire could be one of the minimum parts of electrical devices. The conventional approach for determining such a structure maps X-ray diffraction/scattering intensities under Bragg conditions in a reciprocal-lattice space. This provides quantitative information on the strain in the nanowires [1]. One of its disadvantages is its being time-consuming. In order to establish a rapid characterization method, we have developed an "obvious-at-a-glance analysis" technique for nanocrystalline structures [2]. By taking advantage of high-energy and brilliant X-rays of SPring-8, rapid measurements are achieved by mapping many diffracted intensities under Bragg conditions in the reciprocal-lattice space simultaneously. The present method uses many sets of limited diffracted intensities around a Bragg point and coaxes forth specific structural information such as crystallographic domain sizes. In this work, the method was successfully applied to observe sheet-shape diffraction emanating from ultrathin NiO wires and scattering arising from the 20 nm periodicity of stripes of nanowires.

Specimens had the stripes of ultrathin NiO nanowires deposited on an ultrasmooth sapphire (0001) surface with two-atomic-plane step edges at Yoshimoto Res. Group, Tokyo Institute of Technology [3]. We used two samples that were similar except for the nanowires' orientations; in addition, both substrates had a miscut of approximately 0.1°. Sample A had nanowires almost perpendicular to the sapphire [1 0 $\bar{1}$ 0] direction; and sample B had nanowires nearly parallel to the [1 0 $\bar{1}$ 0] direction. The coordination is expressed using a hexagonal symmetry. The samples were grown using a pulsed laser ablation method. The surface morphology of sample A was observed by atomic force microscopy (AFM) in air (Fig. 1). The nanowires were found to be of the order of mm in length, which was surprisingly long, by scrutinizing hundreds of successive AFM images (scan size 10 μm × 10 μm, not shown here). The images indicate that the nanowires were grown along step edges and were approximately 20 nm in width and 0.5 nm (two atomic planes) in height. The density was a nanowire per 50 nm.

Here, the nanowires that we are interested in are very thin, narrow, and long. If the wires are 1D crystalline, the scattering pattern or diffraction domain (the Fourier transform) in the reciprocal-lattice space shows sheets (which are perpendicular to the wires and whose diameters are inversely proportional to the width sof the wires). Let us assume that the sheets elongate along the sample surface normal from bulk-crystal Bragg points due to a surface truncation effect. The Ewald sphere can simultaneously intersect some of the sheets accordingly (Fig. 2). We used possibly high-energy X-rays to excite many diffracted X-rays.

Measurements were performed at the undulator

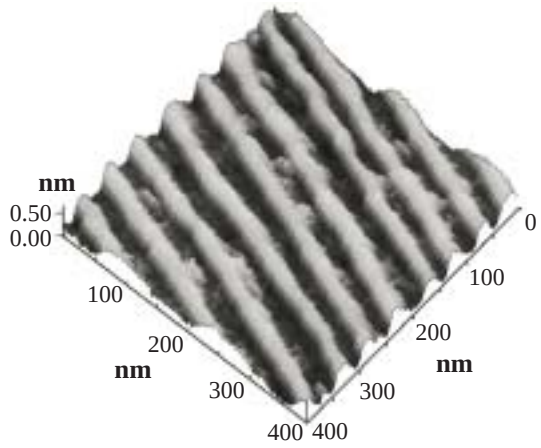

Fig. 1. AFM image (0.4 μm × 0.4 μm) of the nanowires grown on an ultrasmooth sapphire surface of sample A.

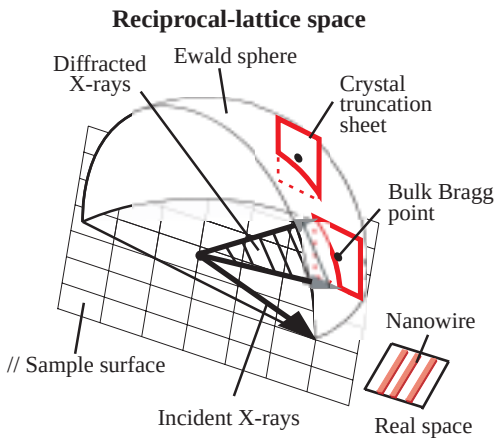

Fig. 2. Geometry of grazing-angle high-energy X-ray scattering.

beamline **BL13XU** for surface and interface structure determination [4]. The experimental setup included a pair of slits for limiting the beam size to 0.1 mm × 0.1 mm and an X-ray imaging plate for recording diffraction. An X-ray beam with a photon energy of 25 keV was incident on the sample at an angle of around 0.1°. The typical exposure time was 10 min. A similar experimental arrangement was used for surface structural observation by Hong *et al.* [5]. They utilized 20 keV X rays and a CCD camera to detect diffracted X-rays; their sample Si was located in ultrahigh vacuum.

Figure 3 shows the diffraction pattern recorded when X rays were incident almost perpendicular to the NiO nanowires. Diffraction images (in rectangles) pointed down at a direct beam position. When X-rays were incident nearly parallel to the nanowires, diffraction images looked like circular arcs round the direct beam position (not shown here). Blunt or dim images were produced by X-ray thermal diffuse scattering of the substrate crystal. We indexed crystal truncation sheets using a conventional notation expressed for crystal truncation rods. Here, the indices h and k are defined by h direction // [1 0 $\bar{1}$ 0] and k direction // [0 1 $\bar{1}$ 0], respectively. Actually, the images extend along the h and l directions; here, the closest integer h values are shown. The diffraction images have intensity profiles (for example, the inset in Fig. 3). From the geometrical consideration in the reciprocal-lattice space, the full-width-at-half-maximum (FWHM) crystallographic domain sizes across the nanowires are 7.5 and 7.2 nm for samples A and B, respectively, obtained using the in-plane FWHM of the intensity profile. The average nanowire-nanowire spacing of 46 nm for sample A was estimated from the peak-to-peak distance. The value is nearly equal to that (~ 50 nm) obtained using the AFM image. By further analysis of the diffraction images, the following structural and morphological information could be obtained: the straightness of the nanowires (in other words, the distribution of the nanowire width), spatial distribution of the nanowires, and atomic-scale roughness of the side surface of the wires.

The method described here will allow us to determine the structures of the nanowires buried in the interfaces between a thin film and a crystalline substrate. Furthermore, it could be applied to structure analysis during growth of nanowires and to rapid observation of a surface phase transition in any atmosphere.

In summary, we demonstrated the feasibility of a new X-ray scattering method for structure analysis of nanowires in air using a combination of grazing-incidence surface scattering and high-energy synchrotron X-rays. The size of X-ray crystalline domains in the nanowires was evaluated. We easily determined whether the nanowires are crystalline or amorphous by grazing-angle high energy X-ray scattering. The method has also been proven feasible for rapid confirmation of the crystallographic orientation and epitaxy of the nanowires.

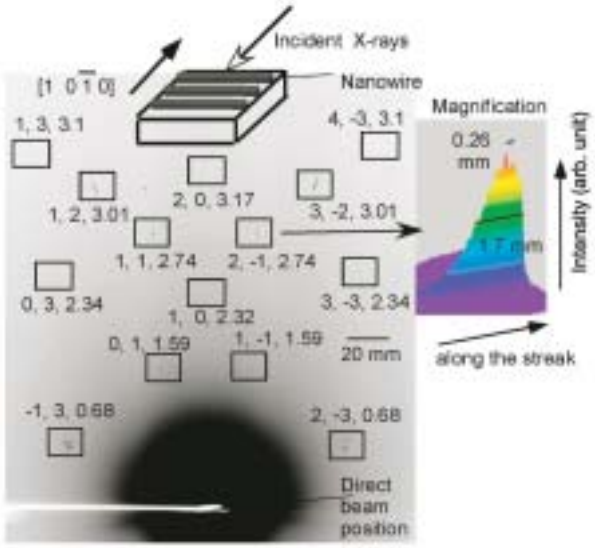

Fig. 3. Pattern diffracted from nanowires nearly perpendicular to the incident X-ray beam. The distance from sample A to the imaging plate (camera length) was 190 mm. A pair of of numbers h, k stands for an index of a crystal truncation sheet. The lengths used for unit vectors **a** (// [1 0 $\bar{1}$ 0]), **b** (// [0 1 $\bar{1}$ 0]), and **c** (// [0 0 0 1] were 0.476, 0.476, and 0.421 nm, respectively.

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References

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