Real-time observation of formation of indium phosphide nanowires by means of GISAXS

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Abstract. Real-time observation of InP nanowire formation was performed using grazing incidence small angle x-ray scattering (GISAXS). Prior to the nanowire growth, gold colloidal particles were spread on the substrate as the catalyst and annealed at 500 °C. Changes of GISAXS images were clearly observed after annealing, suggesting the formation of molten metal droplets, which were used for nanowire growth. After starting the growth, little change except for the increase of GISAXS intensity was observed, suggesting that x-ray scattering from nanowires overlapped with that from the catalysts. From the GISAXS images calculated using a sphere and cylinder model, scattering from the nanowires shows the streak along the \( q_y \) direction, and that from droplets shows an increase of intensity around the specular reflection, which qualitatively explains the measured GISAXS image after the growth.

1. Introduction

Recent developments in semiconductor nanowires have shown their diversity for optical [1] and Electrical [2] devices using quantum effects. Ever since the fabrication of Si sub-micrometer whiskers by means of the vapor-liquid-solid (VLS) mechanism [3], various kinds of nanowires, including Si [4,5], GaAs [6] and InP [1], have been grown using chemical vapor deposition, chemical beam epitaxy, and laser-assisted catalytic growth. Figures 1(a)-(d) schematically illustrate the principle of VLS growth. First, catalyst metals are evaporated on the substrate as a thin film (Fig. 1(a)). After the formation of metal layer, the substrate is annealed to make small droplets of catalyst metal (Fig.1 (b)). It is noted that catalyst metal usually melts at a temperature lower than the usual melting point of metal because of the size effect. After molten metal balls are formed, material gases are supplied for nanowire growth (Fig. 1(c)). Since
atoms tend to be incorporated into the small balls because of the dependence of local chemical potential on ball size [4, 7], growth of small nanowires is more dominant than that of larger ones. When the incorporation process starts, the catalytic balls become saturated and the super-cooling sometimes occurs in them, inducing crystallization of the nanowires from the bottom of the balls. Once the crystallization process starts, it continues until the materials gas supply is stopped or the catalytic metals are exhausted (Fig. 1(d)).

Although the previous researches, the detailed growth mechanism is not yet well understood because nanowire growth depends on several factors, such as the growth temperature, vapor pressure, local chemical potential of the catalytic balls, substrate, and vapors, and the size of the balls which dynamically changes during the growth process. Additionally, ordinary evaluation techniques, such as SEM and TEM, can not be applied in the gas-phase environment, which is very important for VLS growth. In contrast to these electron-based techniques, x-ray based techniques can be easily adapted to growth in the gas-phase environment and provide much structural information, such as the size and shape of particles [8] and nanowires. In particular, grazing incidence small angle x-ray scattering (GISAXS) is effective for monitoring nanowire growth since the growth time using the VLS mechanism is usually very short. It allows us to observe structural changes in catalysts and nanowires very quickly with a two-dimensional detector. In this article, we report the preliminary results of real-time GISAXS measurement of InP nanowire formation in the gas-phase.

2. Experimental

All measurements were performed using a specially designed x-ray diffractometer that combines a MOCVD chamber and z-axis diffractometer [9] at beamline 24XU of the Spring-8 synchrotron facility. InP nanowires were grown on InP (111)B substrate using tertiarybutyl phosphine (TBP) and trimethylindium (TMI) as precursors. Gold colloidal particles about several ten nanometers in diameter were firstly spread on the substrate as catalysts. At the beginning of the growth procedure, the substrate was annealed at 500 °C to desorb extra-organic molecules of gold catalysts. It was then cooled to 450 °C and InP nanowires were formed within 2 min. Figure 2 shows a schematic of the growth procedure. The inset is a SEM image of typical nanowires. Details of the growth and SEM observation are described in ref [10,11].

The GISAXS images were taken using a back-illuminated CCD camera (C4880-10, Hamamatsu Photonics, Japan) with 12.5 µm resolution during the growth. Arrows in Fig. 2 indicate the GISAXS measurement points. Incident x-rays of 0.124 nm wavelength were collimated with a 50 µm circular pinhole upstream of the diffractometer, and impinged upon the substrate at 0.15 ° incident angle, which is about 0.1 ° lower than the critical angle of InP, and the CCD camera was set at 1 m downstream of the sample. The strong scattering near the specular reflection was masked by a tantalum square plate and wire. It should be noted that dynamic range of CCD detectors is small so that they are more suitable for monitoring qualitative changes of structures than analyzing structures quantitatively.
3. Results and Discussion

Figure 3 shows a GISAXS image taken at room temperature 100 sec before starting the growth procedure. In the figure, coordinates of \( q_y \) and \( \Delta q_z \) (\( = q_z - q_z^{\text{specular}} \)) correspond to the directions of in-plane and out-of-plane scatterings. A gray region in Fig. 3 shows the masked area on the CCD detector. Obviously, x-ray scatterings from the gold particles are clearly observed, and the scattering is broader along the \( q_y \) direction than along the \( q_z \) direction. Considering that the average particle size was about 3 nm and the number of particles was larger than the number that would form a single layer on the substrate, it seems that gold particles segregated and formed a stacked layer of particles.

Figure 4 shows the GISAXS image taken at 500 º during the annealing process. During the annealing process, GISAXS images were taken every 6 seconds with 1 sec irradiation time to observe the time evolution of GISAXS images. After the measurements, all data were summed to increase signal counts, since the acquired signals in each measurement were too weak. Owing to the dark current and reading error of CCD signals, artifacts appeared in the x-ray image along the \( q_y = 0.07 \), as shown by the light gray area in Fig. 4. The dark gray region in the figure again corresponds to the masked area on the CCD detector, and all GISAXS images are normalized so that we can compare each one directly. During the annealing process, the broadening of scattering along the \( q_z \) direction was observed, although the intensity along the \( q_y \) direction was almost the same. This suggests a decrease of the height/radius ratio of droplets and the forming of wetting layer on the substrate.

After annealing, substrate temperature was lowered to 450 º, and GISAXS images were taken during a 2-min nanowire growth. The measurement condition for the CCD detector was the same as that during annealing. Figures 5(a) and (b) show the GISAXS images taken during the nanowire growth and (c) which taken after the growth. Light and dark gray regions correspond to the artifacts of the detector and the tantalum-masked area, respectively. The GISAXS patterns during the growth, as shown in Fig. 5(a) and (b) were basically the same as that after annealing except for an increase of scattering intensity. This suggests that scattering mainly came from the catalyst droplets on the surface, which did not contribute to the growth of nanowires. After the growth was stopped, the shape of the GISAXS image taken in the first 1 min changed slightly as shown as Fig. 5(c). The major change was the appearance of a spear-head like corner at \( \Delta q_y = 0.0 \text{nm}^{-1} \), suggesting that scattering from the nanowires was added to the GISAXS image.

Finally, a GISAXS image was taken after cooling the substrate to room temperature (Fig. 6(a)). The integration time was 100--sec, and the masked area is again the dark gray region. Changes in the GISAXS image from that before the growth (Fig. 3) were clearly observed. The main features are the broadening of scattering along the \( q_z \) direction and the narrowing of it along \( q_y \) direction. Considering
the change in GISAXS images during the growth, these changes are mainly caused by the formation of large alloyed droplets and InP nanowires.

To estimate the scatterings from nanowires and droplets, GISAXS images were calculated using a sphere and cylinder models. Figures 6(a), (b) and (c) show the measured and calculated GISAXS images. The number of contour lines in Fig. 6 (a) is increased to show the scatterings far from the specular reflection. The calculation was performed using the IsGISAXS program [12] with parameters of a 60 nm radius for the sphere model and a 15 nm radius and 150 nm heights for the cylinder model.

Scatterings from the spheres have symmetry corresponding to the specular point and, considering the form factor of the spherical shape, the scattering pattern does not depend on the size of particles. In contrast to the calculation using the sphere mode, sharp streaks along q_y direction were observed in the calculation.
GISAXS image calculated using the cylinder model. Although the dispersions of size and height for each model were not included, calculated GISAXS images of the cylinder model is similar to the measured one, suggesting that the scattering from nanowires overlapped in the GISAXS images after the growth, which would explain the spear-like corners along the \( q_y \) direction.

4. Summary
In summary, we observed the formation of InP nanowires by means of GISAXS. The GISAXS image taken before the growth shows that colloidal particles were stacked and segregated. After the annealing, the gold particles melted, forming droplets which act as catalysts for nanowire growth. When the nanowire growth started, additional scatterings occurred along \( q_y \) direction. From the result of GISAXS calculations using a sphere and cylinder models, the origin of this streak is estimated to the formation of nanowires. Although much information could be obtained from the real-time measurement, a quantitative analysis has not yet been performed because large dynamic-range measurement using CCD detectors is difficult. This difficulty would be overcome by combining different types of detectors, such as CCD detectors and imaging plates.

References

[1] Duan X, Huang Y, Cui Y, Wang J and Lieber C M 2001 Nature 409 66
[2] Bjork M T, Ohlsson B J, Thelander C, Persson A I, Deppert K, Wallenberg L R and Samuelson L, 2002 Appl. Phys. Lett. 81 4458
[3] Wagner R S and Ellis W C 1964 Appl. Phys. Lett. 4 89A
[4] Westwater J, Gosain D P, Tomiya S, Usui S and Ruda H 1997 J. Vac. Sci. Technol. B15 554
[5] Morales A M and Lieber C M 1998 Science 279 208
[6] Hiruma K, Yazawa M, Katsuyama T, Ogawa K, Haraguchi K, Koguchi M and Kakibayashi H 1995 J. Appl. Phys. 77 447
[7] Givargizov E I 1975 J. Cryst. Growth 31 20
[8] Glatter O and Kratky O 1982 Small Angle X-ray Scattering
[9] Kawamura T, Watanabe Y, Utsumi Y, Uwai K, Matsui J, Kagoshima Y, Tsusaka Y and Fujikawa S 2000 J. Cryst. Growth 221 106
[10] Bhunia S, Kawamura T, Watanabe Y, Fujikawa S, and Tokushima K 2003 Appl. Phys. Lett. 83 3371
[11] Bhunia S, Kawamura T, Fujikawa S and Watanabe Y 2004 Physica E 21 583
[12] "IsGISAXS: a program for Grazing-Incidence Small-Angle X-Ray Scattering analysis of supported islands", Lazzari R 2002 Appl. Cryst. 35 406