Mechanisms determining the structure of Au-catalyzed GaAs nanowires studied by in situ X-ray diffraction

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Abstract

The evolution of polytypism during GaAs nanowire growth was investigated by in situ X-ray diffraction. The growth of nanowires was found to start with the formation of zincblende structure, followed by the growth of wurtzite structure. The growth process was well reproduced by a simulation based on a layer-by-layer nucleation model. The good agreement between the measured and simulated results confirms that nucleation costs higher energy for the stackings changing the crystal structure than for those conserving the preceding structure. The transition in prevalent structure can be accounted for by the change of local growth conditions related to the shape of triple

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phase line rather than by the change in supersaturation level, which quickly reaches steady state after starting growth.

Introduction

Semiconductor nanowires have been extensively studied because their highly anisotropic shapes are expected to lead unique applications, such as vertical transistors,¹ tunneling transistors,² tunneling diodes³ and high-efficiency solar cells.⁴ One of the typical ways enabling the growth of vertical free-standing nanowires is the vapor-liquid-solid (VLS) growth. Liquid alloy droplets of Au and Si have been known to act as catalysts for the growth of Si wires since the work of Wagner and Ellis.⁵ Later, the Au-assisted VLS mechanism was found to also work for the growth of III-V semiconductors.^{6,7} Recently, catalytic functions of elements present in the growth material has been discovered in systems such as Ga droplets for GaAs nanowires,⁸⁻¹¹ Ga for GaAsSb¹² and In for InAs.^{13,14} Nanowires of III-V semiconductors are known to show polytypes including the 4H and wurtzite (WZ) structures in addition to the zincblende (ZB) structure that is the most stable in the bulk.¹⁵⁻¹⁷ Since the electronic and optical properties of nanowires are sensitive to the crystal structure,^{18,19} much effort has been devoted to phase purification²⁰⁻²³ and active control of polytypes.²⁴⁻²⁹ For these purposes, an understanding of the polytype formation is strongly required.³⁰

The polytypism found in III-V semiconductor nanowires has been discussed in relationship to the surface energy of the side facets of nanowires. Ab initio calculations,³¹ an energy calculation based on an empirical potential,³² and a thermodynamic model³³ have suggested that the relative stability of the ZB structure in the bulk does not hold for nanowires with small enough diameters, for which the WZ structure is stabilized by relatively large surface contributions to the total energy. For this reason, the stability of the WZ structure is greatly influenced by the crystallographic orientation of the side facets.³⁴⁻³⁶ For the VLS-grown GaAs nanowires, formation of the ZB and WZ segments bounded by $\{111\}$ and $\{10\bar{1}0\}$ facets, respectively, has been well established,^{24,25,37,38} while the facets oriented in $\{1\bar{1}0\}$ and $\{11\bar{2}0\}$ have been known for nanowires grown by selective growth.³⁹

In addition to the structural stability in equilibrium, however, growth kinetics must also be considered for a full understanding of the polytype formation.^{9,40} The energy difference

between ZB and WZ is so small that stacking faults and phase mixing can be brought about by thermal fluctuations at typical growth temperatures. The dependence of the polytype formation on growth conditions including temperature and incoming molecular-beam flux can be incorporated into the model by considering the energy barrier for the formation of a two-dimensional nucleus at the VLS triple phase line. On the basis of this nucleation model, the preferential nucleation of the ZB or WZ structure has been attributed to the supersaturation of the catalytic liquid,^{40–43} the interfacial energy between the liquid and vapor phases,⁴⁴ and the shape of the liquid.⁴⁵

For the study of nanowire growth involved with kinetics, progress has recently been made by in situ measurements.^{46–52} Among them, X-ray diffraction has emerged as a suitable tool for identification of polytypes.^{37,53,54} An advantage of X-ray diffraction is its good statistics resulting from simultaneous measurement of the entire part of more than 10^6 nanowires included in the X-ray beam size, which can be as large as $\sim 0.5 \times 0.5 \text{ mm}^2$. In this paper, we present in situ X-ray diffraction results revealing the transition of the crystal structures formed in Au-seeded GaAs nanowires during molecular-beam epitaxial (MBE) growth. While the diffraction peaks corresponding to specific crystalline phases were focused on in previous in situ X-ray work,^{50–52} the X-ray diffraction profiles along the reciprocal lattice rod and its radial extent were also measured in the present work. By virtue of the X-ray measurements covering a wide range of reciprocal space, stacking faults, average length of ZB or WZ segments and the average diameter of nanowires were characterized. Through comparison with X-ray diffraction profiles simulated on the basis of the nucleation model, the critical role played by the side surface energy of the nuclei for polytype formation has been clarified.

Experimental details

Experiments were performed at the synchrotron radiation beamline 11XU at SPring-8 using a molecular beam epitaxy chamber integrated with a surface x-ray diffractometer.⁵⁵ An

X-ray wavelength of 0.124 nm was selected using a liquid-nitrogen-cooled Si(111) double crystal monochromator. The size of the X-ray beam was set to 0.1 (horizontal) $\times$ 0.7 (vertical) mm² by Rh-coated bent mirrors and Ta-blade slits. X-ray diffraction measurements were performed under in situ conditions while the nanowire growth was temporarily interrupted. We measured the intensity distribution along the reciprocal rod, (1,-1, L), where the diffraction indices are represented by the hexagonal coordinates based on a hexagonal unit cell defined by $\mathbf{a}=[1/2,0,-1/2]_{\text{cubic}}$, $\mathbf{b}=[0,-1/2,-1/2]_{\text{cubic}}$, and $\mathbf{c}=[-1,-1,-1]_{\text{cubic}}$. Diffracted X-rays were collected by a two-dimensional X-ray charge coupled device (CCD) detector, which was placed at a distance of 700 mm from the the sample. With the help of the two dimensional imaging enabled by this detector, the diffraction signal from the crystal and the background including the thermal diffuse scattering could be separated. At each point of L , the X-ray intensity was integrated over the diffraction peak and the background intensity was subtracted. The X-ray diffraction profile is related to the structure factor of nanowires by the following equation,

$$I/I_0 = \frac{16\pi^2 r_e^2 P^2}{Q_z^2} \frac{|F|^2}{S^2}, \quad (1)$$

where Q_z is the surface normal component of $\mathbf{Q}$, r_e the electron classical radius, P the polarization factor and $S = |\mathbf{a} \times \mathbf{b}|$. Note that Q_z and P are functions of the diffraction indices, H , K and L . The diffraction peaks are broadened by the finite size of the nanowires. The width of the diffraction peak in reciprocal space, $\Delta\mathbf{Q}$, is related to the coherence size of the scatterer as $D \sim 0.9(2\pi/|\Delta\mathbf{Q}|)$. Using this formula, the diameter of nanowires can be estimated.

The substrate was cut from a mechanochemically polished GaAs(111)B wafer and pasted on a molybdenum block with In. After the substrate was transferred to the growth chamber, native oxide layers were desorbed by heating the sample up to 590°C in an As pressure of 8.5×10^{-4} Pa as confirmed by a spotty pattern of reflection high energy electron diffraction. Subsequently, Au was deposited at a substrate temperature of 560°C from a Knudsen cell source. The deposited amount of Au was calibrated as 1.8 nm thick using a separate X-ray

reflectivity measurement. The growth of GaAs was performed at a substrate temperature of 480°C and an As pressure of 8.5×10^{-4} Pa. By X-ray diffraction, it was confirmed that Au-Ga alloy remained melted at this temperature. The deposition rate of Ga corresponded to a two-dimensional growth rate of 200 nm/h in the homoepitaxial growth of GaAs(001). The GaAs nanowires were grown for 30 to 60 sec with ~ 30 minute intervals for the X-ray scan along L . The influence of the growth interruption on the nanowire structure was not discernible by in situ X-ray diffraction and post-growth scanning electron microscopy.

Results and discussion

Figure 1 shows the evolution of the X-ray diffraction profiles along $[1, -1, L]$ during the GaAs nanowire growth. The peaks at $L = 2$ and 5 correspond to the $00\bar{2}$ and $\bar{1}\bar{1}\bar{3}$ Bragg reflections of the ZB structure of the GaAs substrate. The intensity around these peaks changed little throughout the subsequent nanowire growth. With only Au deposition, small peaks already appeared at $L = 1$ and 4, which can be attributed to the rotationally-twined ZB GaAs. This suggests that, even before starting the deposition of Ga, a small amount of crystalline GaAs was precipitated from the Au-Ga alloy while the substrate was cooled down to the growth temperature of 480°C from 560°C, at which point Au was deposited. The intensity enhancement around $L = 3$ does not originate from the Bragg reflection of the WZ GaAs, because peaks are absent at $L = 1.5$ and 4.5. Rather, it is ascribable to an interfacial ordering similar to that reported for InP nanowire growth.⁵⁶

The growth of GaAs nanowires was initiated by the formation of the ZB structure, which was characterized by an increase in intensity at $L = 1$ and 4. The exclusive growth of the ZB phase continued for 90 s. After this point in time, the WZ peaks were found to show up at $L = 1.5, 3.0$ and 4.5. A closer look at the diffraction profiles after 210 s shows additional weak peaks attributable to the 4H structure at $L = 2.25$ and 3.75. Thus, it is concluded that the preferred crystal structure of the nanowires changes from the ZB to more hexagonal

Figure 1: Evolution of measured X-ray diffraction profiles along $(1, -1, L)$ during the growth of Au-assisted GaAs nanowires on GaAs(111)B. Solid lines are simulated results based on the nucleation model described in the text. In the simulation, the fraction of the triple phase line simultaneously shared by the top and side facets, χ , was assumed to increase from $\chi = 1$ at 0 s to $\chi = 0.950$ at 270s according to Eq. (8).

Figure 2: Evolution of nanowire diameter estimated from the width of X-ray diffraction peaks corresponding to (a) zincblende and (b) wurtzite structures. The diameter of wurtzite segments was found to be significantly small for a while after the emergence of wurtzite peaks at 120 s, suggesting preferential formation of wurtzite at small catalysts.

structures with the progress of the growth.

The transition from ZB to WZ growth depends on the diameter of the nanowire. Figure 2 shows the coherence size of the scattering objects estimated from the width of the corresponding diffraction peaks. Specifically, the size at $L = 1$ and 4 indicates the diameter of the ZB segments, and the size at $L = 1.5$, 3.0 and 4.5 indicates the diameter of the WZ nanowires. Overall, the average diameter of the nanowires was 70-80 nm, in agreement with ex situ scanning and transmission electron microscopy measurements. While the coherence size estimated from WZ peaks before 90 s is attributed to crystal truncation rod scattering rather than Bragg diffraction from WZ segments in nanowires, the increase in the coherence size for ZB includes the contribution from developing ZB segments as well. A notable feature is that the diameter of the WZ nanowires significantly decreases with the appearance of WZ peaks at 120 s. As the growth of nanowires proceeded, the diameter of WZ segments gradually increased and the difference in diameter between ZB and WZ was indiscernible after

210 s. These results suggest that thin nanowires are prone to adopting the WZ structure. It should be noted that there is a considerable size variation in catalyst droplets, and thus in the diameter of nanowires. Among those nanowires, WZ segments are formed earlier in relatively thin nanowires than in thick ones. At the later stage of growth, WZ segments were formed in thick nanowires as well and the difference in diameter was no longer observed.

Figure 3: Top view (a) and side view (c) of hexagonal unit cell of the zincblende GaAs and top view (b) and side view (d) of the wurtzite GaAs. For zincblende GaAs, the $\mathbf{c}$ axis is aligned in the surface normal direction, $[\bar{1}\bar{1}\bar{1}]_{\text{cubic}}$. Inplane lattice vectors $\mathbf{a}$ and $\mathbf{b}$ are defined as $[1/2, 0, -1/2]_{\text{cubic}}$ and $[0, -1/2, 1/2]_{\text{cubic}}$, respectively. The minimal component of the unit cell is a pair of Ga and As atoms, which are separated by $\Delta\mathbf{r}$ in the surface normal direction.

To get insight into the growth mechanism resulting in the measured X-ray diffraction profiles, comparison was made with simulations based on a nucleation model, where two-dimensional nuclei are stacked on the top facet of the nanowire, stochastically following the ZB or WZ stacking sequence. As shown in Fig. 3, the ZB and WZ GaAs structures can be regarded as stackings of Ga-As pairs, which consist of Ga and As atoms separated by $\Delta\mathbf{r} = \mathbf{c}/4$ in the $\{111\}$ direction. The normal stacking of the ZB structure gives rise to a horizontal shift of $\Delta\mathbf{R} = (\mathbf{a} + 2\mathbf{b})/3$ along with a vertical shift of $\mathbf{c}/3$, while faulted stacking causes a horizontal shift in the opposite direction, $-\Delta\mathbf{R}$. Consequently, the structure factor

Figure 4: Possible stacking sequences of Ga-As pairs of nuclei on the top facet and the grown crystal. The ZB and WZ stacking sequences are expressed by $s_i = 1$ and $s_i = -1$, respectively. (a) ZB nucleus on ZB crystal (b) WZ on ZB (c) WZ on WZ and (d) ZB on WZ.

Figure 5: Simulated X-ray diffraction profiles under the assumption that the side surface energy of a nucleus is independent of the preceding crystal structure of the nanowire. The fraction of the triple phase line in contact with side facets of the nanowire was varied from 0 to 1.

of the whole nanowire crystal, consisting of a series of stacked layers, is given by

$$F = \sum_j F_0 \exp[2\pi i \mathbf{Q} \cdot (s_j \Delta \mathbf{R} + j \mathbf{c}/3)], \quad (2)$$

using the structure factor of a Ga-As pair,

$$F_0 = f_{\text{Ga}} + f_{\text{As}} \exp(-2\pi i \mathbf{Q} \cdot \Delta \mathbf{r}), \quad (3)$$

and a series of numbers, $\{s_j\}$, which represents the stacking sequence. For perfect ZB stacking, s_j are all unity, while the WZ structure is expressed by alternating numbers as $s_j = (-1)^j$. Stacking faults bring about irregularity in the sequence of $\{s_j\}$.

Considering up to the second nearest neighbors of s_j , there are four possible stacking sequences, $\{s_0, s_1, s_2\} = \{1, 1, 1\}, \{-1, 1, 1\}, \{-1, 1, -1\}$ and $\{1, 1, -1\}$, corresponding to (a) ZB nuclei on ZB predecessors, (b) WZ on ZB, (c) WZ on WZ and (d) ZB on WZ, respectively, as shown in Fig. 4. The side walls of the ZB and WZ segments are known to be terminated by $\{111\}$ and $\{10\bar{1}0\}$ planes, respectively. To estimate the probability of each stacking pattern, we employ the nucleation theory.^{40–43} In VLS growth, nuclei are formed at the triple phase line, where the vapor-liquid (VL), solid-vapor (SV) and solid-liquid (SL) interfaces are involved. Nucleation theory states that, if the two-dimensional nucleus is approximated by a semicircle with its diameter shared with the triple phase line, the energy barrier for appending a nucleus of type $n = a, b, c$ or d is given by

$$\Delta G_n = \frac{\Gamma_n^2}{2\pi(\Delta\mu - \sigma_n)}, \quad (4)$$

where $\Delta\mu$ is the the difference of the chemical potential of Ga between the catalyst droplet and the crystal. The stacking energy, σ_i , can be written as

$$\sigma_i = \sigma_0 - J_1 s_0 s_1 - J_2 s_0 s_2 \quad (5)$$

when up to the second nearest neighbors are considered. These coefficients have been given by a first principles calculation, $J_1 = 0.869 \text{ [meV/\AA}^2\text{]}$ and $J_2 = -0.0419 \text{ [meV/\AA}^2\text{]}$.⁵⁷ Since the stacking energy for ZB on WZ is the lowest among these four stacking patterns, one can put $\sigma_d = 0$ and thus $\sigma_a = -2J_2$, $\sigma_b = 2J_1$ and $\sigma_c = 2(J_1 - J_2)$ are obtained. The side surface energy, Γ_n , is expressed by

$$\Gamma_n = [2\chi\gamma_n^{\text{SV}} + 2(1 - \chi)\gamma_{\text{ZB}}^{\text{SV}} + \pi\gamma^{\text{SL}}]d, \quad (6)$$

where d is the height of the monoatomic step. Since the side surface component at the solid-liquid interface, γ^{SL} , is expected to be independent of the crystal structure of the nucleus, it should be identical to the step energy of ZB GaAs, $\gamma_{\text{ZB}}^{\text{SV}} = 7.46 \text{ [meV/\AA}^2\text{]}$.⁵⁷ The parameter χ represents the fraction of the triple phase line simultaneously shared by the top and side facets. Its value can vary depending on the contact angle and volume of the liquid catalyst droplets staying on the top of nanowires.⁴⁵ For the fraction of χ , the side surface energy at the solid-vapor interface is lower for the WZ nucleus because the surface energy of WZ GaAs is known to be lower than that of ZB GaAs. Johansson et al. employed the surface energy, $\gamma_b^{\text{SV}} = 0.4\gamma_a^{\text{SV}} = 2.98 \text{ [meV/\AA}^2\text{]}$,⁴³ and assumed that the side surface energy is determined only by the nearest neighbor stacking sequence as $\gamma_b^{\text{SV}} = \gamma_c^{\text{SV}} < \gamma_a^{\text{SV}} = \gamma_d^{\text{SV}}$. For the rest of the triple-phase line, $(1 - \chi)$, the solid-vapor interface energy is $\gamma_{\text{ZB}}^{\text{SV}}$ since there is no contribution from the side facet.

Now that the energy barrier, ΔG_n , can be calculated for stackings (a)–(d), the probability of the formation of stacking n is obtained by

$$p_n = \frac{\exp(-\Delta G_n/kT)}{\sum_m \exp(-\Delta G_m/kT)}. \quad (7)$$

Following these stacking probabilities, we simulated the growth of 500 nanowires, each of which consists of 450 atomic layers. Figure 5 shows simulations of X-ray diffraction profiles along the $1\bar{1}1$ rod, varying the fraction χ of the triple phase line shared by the top and side

facets simultaneously. The critical supersaturation for nucleation was fixed at $\Delta\mu = 7.0$ [meV/Å²]. With increasing χ , WZ peaks at $L = 1.5, 3$, and 4.5 grow larger than the ZB peaks at $L = 1, 4$ and 5 , owing to the lower side surface energy of the WZ nuclei. However, both the ZB and WZ peaks in the simulated curves are so broad that the measured X-ray diffraction profiles shown in Fig. 1 cannot be reproduced, even if the critical supersaturation for nucleation allowed to vary.

Figure 6: Simulated X-ray diffraction profiles with a higher energy barrier for the formation of a wurtzite (zincblende) nucleus on the zincblende (wurtzite) nanowire than on the wurtzite (zincblende) nanowire.

Improved simulations of the X-ray diffraction profiles can be obtained by introducing a high solid-vapor interface energy for the stackings of (b) ZB on WZ and (d) WZ on ZB in comparison with the congeneric stackings, (a) ZB on ZB and (c) WZ on WZ. For surface energies of $\gamma_b^{SV} = \gamma_d^{SV} = 10$ [meV/Å²], $\gamma_a^{SV} = 7.46$ [meV/Å²] and $\gamma_c^{SV} = 2.98$ [meV/Å²], simulated curves shown in Fig. 6 were obtained for several values of χ . The good agreement between the simulated and measured curves suggests that nucleation causing the transition between ZB and WZ is hindered by the large values of γ_b^{SV} and γ_d^{SV} . The presence of this extra energy barrier has also been suggested by a recent X-ray study.⁵² The side walls of

III-V nanowires formed by Au-seeded VLS growth are known to be bounded by the $\{111\}$ and $\{10\bar{1}0\}$ planes for ZB and WZ segments, respectively.^{24,37,38} Step edges that mediate the differently-oriented facets may account for the energy barrier hindering the alternation of the ZB and WZ structures.

Figure 7: Simulated profiles of X-ray diffraction with varying the critical supersaturation for nucleation of Ga in the Au-Ga catalyst droplets.

Supersaturation is another factor that can influence polytypes. Figure 7 shows X-ray diffraction profiles calculated for various $\Delta\mu$ ranging from 5.5 to 9.0 [meV/Å²], with χ fixed at 1.0. High supersaturation promotes the nucleation of WZ and, as a result, WZ peaks grow in intensity while ZB peaks weaken. In contrast, the value of χ affects the average length of the ZB or WZ segments, as indicated by the change in the width of the diffraction peaks rather than in the integrated intensity.

Apart from the statistical behavior of the stacking sequence, the experimental results show that the ZB GaAs preferentially grows during the initial stage of the growth, and that the WZ GaAs appears after a delay. Since the external growth parameters, including the substrate temperature and the flux of III- and V-group elements, were unchanged throughout the growth, this growth mode transition can be ascribed to two possible changes in local

growth conditions. Firstly, at the beginning of the growth of the nanowires, the whole triple phase line is on the substrate surface. Thus, χ should increase from zero with the progress of growth. The increase of χ is likely to be sustained by the tapered structure, which is known to form at the base of nanowires.⁴⁰ This change can enhance the WZ formation, as simulated in Fig. 6. Secondly, Ga in the liquid phase should be in equilibrium with Ga in the substrate before starting growth. As soon as the supply of Ga is turned on, supersaturation will increase along with the concentration of Ga in the droplets. For comparison with the X-ray diffraction profiles measured with the progress of nanowire growth, a simulation was performed with χ changing as

$$\chi = 1 - \exp(-n/n_0) \quad (8)$$

during the growth of nanowires, where n is the number of atomic layers in the nanowire and $n_0 = 150$. The critical supersaturation for nucleation was fixed at $\Delta\mu = 7.0$. A growth rate of 1.7 bilayers/s was employed, as estimated from a post-growth transmission electron microscopy measurement. The simulated curves are shown by solid lines in Fig. 1. X-ray diffraction profiles in the intermediate stages before emergence of WZ phases are as well reproduced as those at the later stages of growth. The emergence of 4H peaks at $L = 2.25$ and 3.75 are not expected to be reproduced because long-range correlation beyond the second nearest neighbor was not considered in the present model. When $\Delta\mu$ was varied and χ was kept constant, on the other hand, similar agreement between the measured and simulated profiles through the entire growth stage was not achieved. This suggests that the change of χ is critical for the ZB to WZ transition during growth. It should be noted, however, that a change of supersaturation cannot be ruled out since supersaturation should be zero at the beginning of growth. The implication is that, while χ gradually increases from zero to unity with completion of the side walls of the nanowires, supersaturation reaches steady state so quickly that it can be treated as constant except at the very initial stage of growth. This mechanism for the transition from ZB to WZ growth is consistent with the earlier transition for nanowires with a smaller diameter. Although the effects of nanowire size on

polytypism is not explicitly incorporated into the nucleation theory described in the present paper, the size of catalysts affects the preferential crystal structures through χ and $\Delta\mu$. For smaller droplets, even slight change in the volume or the contact area with the top facet of nanowires is more influential on the shape of the triple phase line and thus χ . In addition, steady state of $\Delta\mu$ under given molecular flux is attained earlier because of their large ratio of surface to volume. These changes in local growth conditions can help the transition from ZB to WZ growth.

Conclusion

In summary, the growth process of Au-seeded GaAs nanowires was investigated by in situ X-ray diffraction. The growth of nanowires was found to start with the formation of ZB structure, followed by growth of WZ structure. Comparison with a simulation based on the nucleation model shows the presence of high surface energies for the ZB nucleus on WZ, and the WZ nucleus on ZB. Transition of the prevalent growth from ZB to WZ is ascribed to the change of shape of catalyst droplets, while supersaturation reaches steady state under a given Ga flux at an early stage of growth.

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Graphical TOC Entry

The evolution of polytypism during the growth of Au-seeded GaAs nanowires was investigated by in situ X-ray diffraction. Measured profiles were well reproduced by a layer-by-layer nucleation model. The results confirm that an energy barrier preventing the stacking changes is present and that the transition in prevalent structure is due to the change of local growth conditions.