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Grazing incidence small angle x-ray scattering study for determining structure and composition of multi-stack Ge nanowires on Si(113)

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We studied multilayers of self-assembled Ge nanowires grown on silicon (113) surface by solid-source molecular beam epitaxy using grazing-incidence small-angle x-ray scattering combined with x-ray reflectivity. Quantitative analyses show that the embedded nanowires retained their trapezoidal shape along the $[1\bar{1}0]$ direction, but are significantly subjected by interdiffusion of Si at their surrounding facets even at the growth temperature of 400℃. The Si interdiffusion is remarkable at the sides of the nanowires but not at the top and/or bottom of them. The diffusion lengths are 5.2 and 0.2 nm at sides and top/bottom, respectively, for the nanowire with 20.5 nm in width and 1.6 nm in height.

1. INTRODUCTION

Self-assembled nanostructures, such as quantum dots and wires, on Si substrates have been of much interest because of their great potential in microelectronics and optoelectronic devices [1]. In the resent years, there are a lot of studies about Ge nanodots delicately assembled on Si(100) [2]. On the other hand, it has been demonstrated that Ge nanowires are formed on an anisotropic higher-index surface Si(113), when Ge coverage are 5-8 monolayers (ML) and substrate temperature are 400-500°C [3]. The structure of the nanowires has been investigated by atomic force microscopy (AFM), scanning tunneling microscopy (STM) [4], cross-sectional transmission-electron microscopy (XTEM), and reflection high-energy electron diffraction (RHEED). The nanowires have about 20 nm wide and coherently aligned in the lateral $[1\bar{1}0]$ direction, and 10 - 600 nm long in the $[33\bar{2}]$ direction, and height about 1.5 nm. In addition, it is suggested that nanowires are surrounded by facets [5] and Si atoms are penetrating into them [6]. Even though the structures have been studied by the above techniques, more quantitative analysis in relatively large area is still important for applying such structures to functional devices. Grazing incidence small angle x-ray scattering (GISAXS) is well suited for this purpose [7, 8]. It can analyze the shape of nanometer size objects even when they are embedded and could not see directly from the surface. In addition, GISAXS is sensitive to the contrast of electron density and possible to detect the compositional profile inside the objects. Grazing incidence x-ray diffraction (GID) is also useful to analyze precise structures of nanodots [9, 10]. However, it is sensitive to strain rather than shape and composition and strain fields in- and outside the objects should be simulated for obtaining GID patterns [11]. It is not obvious for complex multi-stack nanostructures. In this paper, therefore, we report on quantitative analyses of shape and compositional inhomogeneities of multi-stack Ge nanowires in the Ge/Si(113) multilayers by using GISAXS combined with x-ray reflectivity (XRR). We show that the Ge nanowires maintain their trapezoidal shape and are significantly diluted by Si at their side facets.

2. EXPERIMENTALS

Multilayers of Ge/Si were grown on Si(113) by solid-source molecular beam epitaxy (MBE) [5]. Ge and Si were deposited on Si(113) to 6.4 ML and 30 ML,

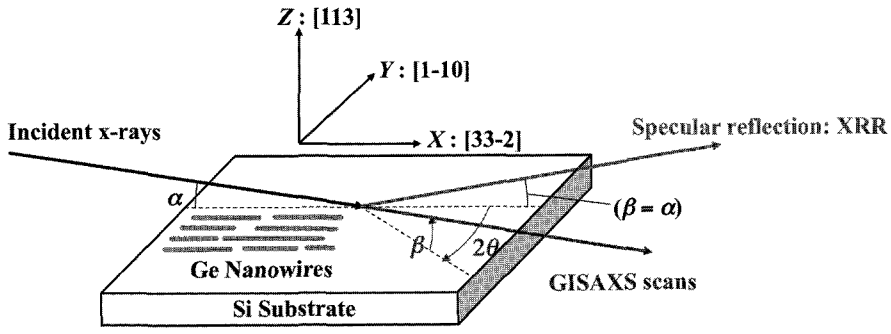

Fig. 1. The schematic of geometry of the measurements and orientation of Si substrate. The measurements were performed at the BL13XU beamline of the SPring-8 synchrotron facility.

respectively, at the substrate temperature of 400°C. The multilayers contain up to 5 periods. X-ray scattering measurements were performed at the BL13XU beamline of the SPring-8 synchrotron facility in Japan. The x-ray photon energy was 10.90 keV (λ =1.137Å). The sample surface was aligned with the center of x-ray beam (0.05 mm H x 0.1 mm V cross section) and x-rays irradiate the surface with a glancing angle α. In order to determine two-dimensional shape of the Ge wires, we collected XRR and GISAXS data. The former is suited for obtaining the structure of the stacking (Z: [113]) and the latter is that for the lateral structure (Y: [1$\bar{1}$0]). The schematic of geometry of the measurements and orientation of Si substrate are shown in Fig. 1.

3. OBSERVED DATA

Figure 2 shows the observed and calculated XRR curves from the Ge/Si multilayers. The calculation was

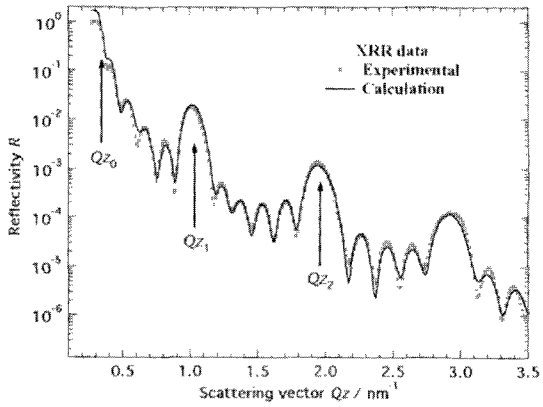

Fig. 2. Observed (circle) and calculated (solid line) XRR curves for analyzing the stacking structure. GISAXS measurements were performed at the three Q_z positions indicated by the arrows.

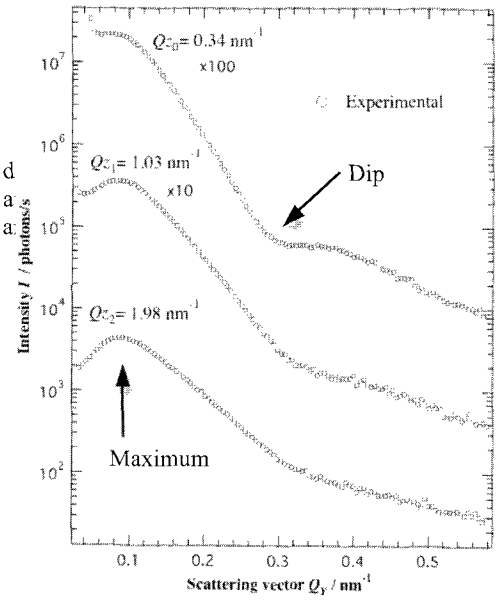

Fig. 3. Experimental GISAXS curves at the three Q_z positions. They have peaks at Q_Y=0.09 nm^{-1} and dips at Q_Y =0.30 nm^{-1}.

interlayer distance among five layers are 6.43, 6.65, 6.33, 6.56, 7.56 nm, respectively. These values are in a good accordance with the thickness of depositions and XTEM observation. In the GISAXS measurement, the data were collected at three different α's while maintaining exit angles $\beta = \alpha$. They correspond to just above the critical angle, the first and second peaks of multilayer period as indicated by the arrows at wave vector Q_{Z0}, Q_{Z1}, and Q_{Z2} in Fig. 2, respectively. The measured GISAXS profiles are shown in Fig. 3. The scattering intensities are rapidly decreased with increasing Q_Y. We can also see that they have a maximum at Q_Y =0.09 nm^{-1}, which is correlated with the interference among the wires. In addition, it is noticed a dip at Q_Y =0.3 nm^{-1}, which indicates monodisperse of nanowire width in the [1$\bar{1}$0] direction. Also, the dip becomes unclear with increasing Q_Z.

4. PRCEDURE FOR THE DATA ANALYSIS

In general, surface scattering intensities can be expressed using form factor F and interference function S of the objects as a function of wave vector $\boldsymbol{Q}$. In addition, transmittivity T of incident and exit x-rays should be introduced for surface scatterings [13]:

$$I(\boldsymbol{Q}) = N_W \cdot r_c^2 |T(\alpha)|^2 |T(\beta)|^2 S_X(Q_X) S_Y(Q_Y) S_Z(Q_Z) \times |F_X(Q_X)|^2 |F_{YZ}(Q_Y, Q_Z)|^2 \quad (1)$$

where r_c is the classical radius of an electron and N_W is the number density of nanowires. On the basis of our previous results [3, 4], the lengths (X:[33$\bar{2}$] direction) of nanowires are large enough and no correlations with width and thickness, and then, dependence of Q_X can be factorized from that of Q_Y and Q_Z. We assumed that the embedded nanowires retain their trapezoidal shape in the [1$\bar{1}$0] cross section. It means that the nanowires are surrounded by top, bottom, and side facets. We also assumed that Ge concentration in nanowires changes gradually because of the interdiffusion of Si at the boundaries with Si layers because they are stacked by MBE at a finite temperature [5]. On these assumptions, the deviation of the electron density ρ in Ge wires from Si matrix can be written as

$$\rho_{YZ}(y,z) = \Delta\rho \frac{\mathrm{Erf}\left[\frac{y-\left(-\frac{W}{2}+\frac{\Delta W}{H}z\right)}{\sigma_W}\right] - \mathrm{Erf}\left[\frac{y-\left(\frac{W}{2}-\frac{\Delta W}{H}z\right)}{\sigma_W}\right]}{2} \times \frac{\mathrm{Erf}\left[\frac{z+\frac{H}{2}}{\sigma_H}\right] - \mathrm{Erf}\left[\frac{z-\frac{H}{2}}{\sigma_H}\right]}{2} \quad (2)$$

Here, we introduce an error function Erf(x) to express Gaussian-like interdiffusion of atoms along Y and Z directions. The H is height, $W+\Delta W$ is the length of the bottom plane, and $W-\Delta W$ is that of the top facet of the nanowires. The $\Delta\rho$ is maximum deviation of electron density of the wire from Si, and σ_W and σ_H are

interdiffusion lengths along the Y and Z directions, respectively. The form factor of the density deviation $F_{YZ}(Q_Y, Q_Z, W, H)$ can be calculated straightforwardly by the Fourier transform of eq. (2) using y and z. We also considered that wire width W should have a distribution and used the following Gaussian convolution with the variance W_σ.

$$\left|F_{ZY}(Q_Y, Q_Z, W, H)\right|^2$$

$$\Rightarrow \int_0^\infty \left|F_{ZY}(Q_Y, Q_Z, Y, H)\right|^2 \frac{1}{\sqrt{2\pi}W_\sigma} \exp\left[-\frac{(Y-W)^2}{2{W_\sigma}^2}\right] dY \quad (3)$$

The Z-direction interference function can be constructed using the depth z_j of the j-th layer:

$$S_Z(Q_Z) = \left|\sum_{j=1}^{N_{layer}} \exp\left[iQ_Z^t z_j\right]\right|^2, \quad (4)$$

$$Q_Z^t = \frac{2\pi}{\lambda}\mathrm{Re}\left[\sqrt{n^2-\cos^2\alpha} + \sqrt{n^2-\cos^2\beta}\right]$$

where n is the index of refraction. Moreover, considering that Ge nanowires align periodically with spacing L in the $[1\bar{1}0]$ direction, $S_Y(Q_Y)$ in Eq. (1) can be written as

$$S_Y(Q_Y) = \frac{1}{N}\sum_{j,k=1}^{N} e^{iQ_Y L(j-k)}$$

$$\Rightarrow 1 + 2(1-V_p)\sum_{j=1}^{N}\left(1+\frac{{Q_Y}^2 L^2 j^2}{M^2}\right)^{-\frac{M}{2}} \times\cos\left[M\cdot\tan^{-1}\left(\frac{Q_Y\cdot L\cdot j}{M}\right)\right] \quad (5)$$

where N is the total number of nanowires along the Y direction. We have also taken into account the disorder for the periodicity by introducing a density of vacancy V_p ($0 \le V_p \le 1$) and distribution of spacing L, assuming Γ-distribution with the shape parameter M. Then, the in-plane Q_Y scan pattern for each (α, β) combination can be calculated by eq. (1) with the set of parameters {W, ΔW, σ_W, W_σ, L, M, V_p, H, σ_H}. The intensity ratio at different Q_Z is calculated by eq. (4) using the obtained interlayer distances by XRR.

5. RESULTS AND DISCUSSION

The calculated GISAXS curves with the optimized set of parameters are shown by solid line in Fig. 4. They are in good agreement with the experimental results (open circles). The values of the optimized parameters are listed in the first row in Table 1. The estimated width (W) and thickness (H) of the nanowires, and the set {L, M, V_p} determined by the shape and position of the peak around Q_Y = 0.09 nm^{-1} well agree with those obtained

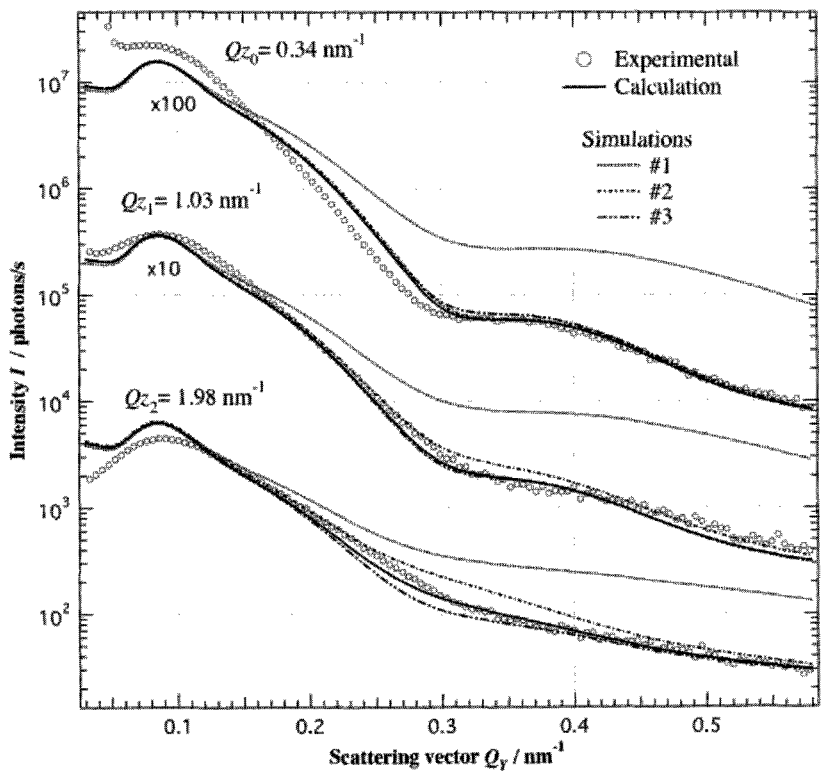

Fig. 4. Experimental (circle) and calculated (solid line) GISAXS curves at the three Q_z positions. The additional three simulations (broken lines) are carried out for comparison. The meaning of each simulation is described in the text.

Table 1. List of the structural parameters for multi-stack Ge nanowires. The optimized parameters are shown in the first row. The parameters for the other simulations #1, #2, and #3 are also listed.

	W (nm)	ΔW (nm)	σ_W (nm)	$W\sigma$ (nm)	L (nm)	M	V_p	H (nm)	σ_H (nm)
Optimum	20.5	6.6	5.2	2.65	68	15	0.4	1.6	0.2
Simulation #1	20.5	6.6	0	3.95	68	15	0.4	1.6	0.2
Simulation #2	20.5	9.0	4.3	2.54	68	15	0.4	1.6	0.2
Simulation #3	20.5	4.4	5.5	2.90	68	15	0.4	1.6	0.2

from AFM results [3], which sufficiently validates this analyses. Furthermore, it can be seen in Fig. 4 that the peak positions, they related to the average spacing L of the Ge nanowires, are almost unchanged for different Q_Z curves, indicating that they are stacked coherently (in the same Y position) along the Z direction, as can be seen in XTEM images [5]. In addition, we could also estimate parameters of nanowires ordering, variance of average spacing and density of vacancy; they are 26 % and 0.5, respectively.

Moreover, the results of the x-ray scattering give us further compositional and structural details of the nanowires. The primary characteristic feature of the observed structure is the nonzero σ_W value (see at the first row in table 1), which means that Si diffuses into the Ge nanowires at the boundary. Simulation #1 in Fig. 4 was carried out using $\sigma_W = 0$ as listed in the second row in Table 1. The slope of the simulation #1 is much more gradual than that of the experimental curve. We could not explain the observed experimental curves without interdiffusion at the boundary maintaining the reasonable cross-sectional profile observed by XTEM. In fact, if we introduce atomic interdiffusion of the matter at the boundary, the additional damping factor of GISAXS curves $\exp\left[-(\sigma_W Q_Y)^2/2\right]$ is coming out in the form factor $|F_{YZ}|^2$ in eq. (3), where σ_W is diffusion length on the sidewall of the nanowires. As can be seen in table 1, interdiffusion lengths are σ_W = 5.2 nm on the sidewall and σ_H = 0.2 nm at the top facet and bottom wall. This result indicates that the diffusion length of Si at the side is much larger than that at the top/bottom.

The second characteristic feature is the existence of the facets. The nonzero ΔW value means the cross section of the nanowires is not rectangular but trapezoidal. If we calculate with ΔW equal to zero, the shape of Q_Y scan curve would not depend on the value of Q_Z, because the Q_Y and Q_Z dependence would be completely separated in such a case. It is not true for the observed curve at the higher Q_Z. In the present calculation, the optimized angle $\phi = \tan^{-1}[H/\Delta W]$ is about 14°, which is consistent with RHEED observation [6]. We also tried to determine how reliable the obtained angle is. Simulations #2 and #3 correspond to the lower (ϕ = 10°) and upper (ϕ = 20°) angles, respectively. The sets of parameters (in the third and fourth rows in Table 1) were optimized to obtain similar Q_Y scan curves at Q_{Z0} = 0.3 nm^{-1}. Even if the curves are similar at the lowest Q_Z, there is noticeable difference between them at the higher Q_Z as shown in Fig. 4. From the comparison of the simulations, we conclude that the angle ϕ is within 10° and 20°, which satisfy the ϕ=14°. Shape and density profile of the nanowires, obtained by the analysis of GISAXS, indicate the facets on the sidewalls still remain even when the nanowires are subjected by Si interdiffusion. The resultant structure and density profile in the $(33\bar{2})$ plane are shown in Fig. 5.

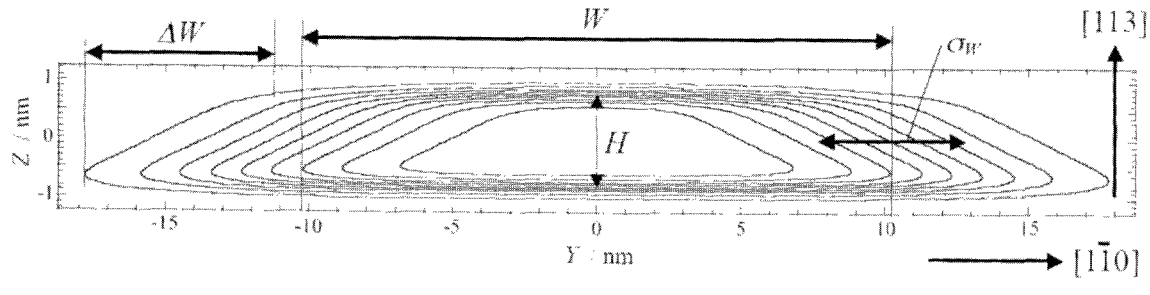

Fig. 5. Contour map of the Ge fraction of the nanowire in the $(33\bar{2})$ plane. The Z-direction scale is elongated by two times as a matter of convenience. Interdiffusion is remarkable at the sides of the nanowires and facets are clearly seen.

6. SUMMARY

In summary, we have evaluated the multi-stack Ge nanowires grown on Si(113) by surface x-ray scattering. The in-plane Q_Y scan patterns were collected at the several out-of-plane wave vectors Q_z, and a new structure of the Ge nanowires in the $(33\bar{2})$ cross section was determined by precise quantitative analyses. The density gradually and anisotropically changes at the boundary, providing evidence of interdiffusion between Ge and Si atoms. Furthermore, the cross section of the Ge nanowires is trapezoidal, indicating that the Ge nanowires are still surrounded by facets even when they are subjected by interdiffusion of Si.

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