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Twinning Superlattice Formation in III-V Compound Semiconductor Nanowires Revisited: Effects of Surface and Twinning Energies

Toru Akiyama, Kohji Nakamura, and Tomonori Ito

Departmenr of Physics Engineering, Mie University,
1577 Kurima-Machiya, Tsu 514-8507, Japan
Phone: +81-59-232-1211 E-mail: akiyama@phen.mie-u.ac.jp

Abstract

The formation of twin plane superlattice in III-V semiconductor nanowires (NWs) are analyzed by considering two dimensional nucleation using surface and twinning energies obtained by performing electronic structure calculations within density functional theory. Our calculations demonstrate that surface energies strongly depends on the growth conditions such as temperature and pressure during the epitaxial growth. The calculated twinning energy is found to be much smaller than previously reported values, which leads to smaller segment length. The calculations also suggest that nonlinear relationship between segment length and nanowire diameter depending on constituent elements is due to the difference in the surface energy difference. The calculated results imply that the surface and twinning energy are crucial for the formation of twin plane superlattice in III-V compound semiconductor NWs.

1. Introduction

III-V semiconductor nanowires (NWs) have proven a versatile building blocks for the realization of novel devices within electronics, photonics, and energy harvesting. It has been experimentally reported that periodic arrangements of twin planes, in which the distance between neighboring twin planes is almost constant, can be controlled by using zinc doping during the vapor-liquid-solid (VLS) growth for various III-V NW systems including InAs [1], InP [2,3], GaP [4], and GaAs [5]. Furthermore, an approximately linear relationship has been found between twin plane spacing and NW diameter in GaAs NWs [5], while twin plane spacing in InP NWs becomes constant with the NW diameter [2]. The formation twin plane superlattice has been explained by with a model on the basis of two-dimensional nucleation and droplet defor-mation [2]. Using this model, the contribution of individual parameters to the NW growth can be determined. However, there are several unknown parameters used for the fitting of estimated segment length of twin plane superlattice to the experimental data.

In particular, surface and twinning energies are some of parameters to adjust the experimental results, but they can be definitely calculated from electronic structure calcula-tions within density functional theory (DFT) using an effec-tive approach using a wedge shaped geometry [6]. In this study, we apply this approach to calculate surface energies of (111)A and (111)B surfaces, which form side faces of twin plane superlattice of III-V NWs, and the effects of these energies on the segment length of twin plane superlat-tice. We also calculated the formation energy of a twin plane to evaluate its contribution to the segment length, and discuss the difference in twin plane spacing depending on constituent elements.

2. Computational Procedure

The total-energy calculations are performed within the generalized gradient approximation (GGA) [7] in the DFT. To describe the electron-ion interaction, we adopt norm-conserving pseudopotentials generated using the Troullier-Martins scheme [8]. 3d (4d) electrons in Ga (In) atoms are treated by using partial core correction [9]. The conjugate-gradient minimization technique is used for both the electronic structure calculation and the geometry optimization [10]. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 20.25 Ry, which gives enough convergence of total energy to discuss the relative stability. The surface energies are calculated using (2×2) slab models consisting of four bilayers and 13 Å of vacuum region along the [111] direction. The surface energies polar (111)A and (111)B are calculated by using wedge shape geometry. Details of calculation procedure are described elsewhere [6,11]. For the twin plane formation energy we use the bulk (1×1) unit cell consisting of 24 bilayers including two twin planes.

In order to estimate the segment length of a twin plane superlattice at temperature T with bilayer spacing in the <111> direction h, we use the formula proposed by Algra *et al.* [2] expressed as

$$H_s = 2H_c\left[1+\frac{1}{\Delta}\ln\left\{1-\exp\left(-\frac{-\Delta}{H_c/h}\right)\right\}\right], \quad (1)$$

$$\Delta = \frac{c^2}{k_B T}\gamma_{\mathrm{T}}\left(\frac{\Gamma}{\Delta\mu}\right)^2, \quad (2)$$

where k_B is the Boltzmann constant, c is geometrical constant previously defined as 1.98 [4], γ_{T} is formation energy of twin a twin plane per unit area, $\Gamma = \gamma_{\mathrm{SL}} + (1/6)\{\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SV}}\cos\delta_0\}$ is the effective interfacial energy barrier to nucleus formation, γ_{SL} and γ_{SV} are surface energies per unit area of solid-liquid and solid-vapor interfaces, respectively, and δ_0 is the angle of the droplet with respect to a {111}B facet at a hexagonal cross section. $\Delta\mu$ is the supersaturation in the droplet, as defined by the energy difference in chemical potential between III-V pairs in solution relative to those in the solid. H_c is the axial distance from the point where the nanowire cross section is hexagonal using nanowire diameter D as

$$H_c \cong \frac{b}{h}\frac{\gamma_{\mathrm{T}}}{\gamma_{\mathrm{LV}}\sin\delta_0}\left(\frac{\Gamma}{\Delta\mu}\right)D, \quad (3)$$

where b is another geometrical constant previously calculated to

Table I Calculated surface energy γ_{SV} of (111)A and (111)B under III-rich and V-rich limit and twin plane formation energy γ_T of III-V compound semiconductors. The (2×2)-trimer surface is stabilized under V-rich limit.

	γ_{SV} (J/m^2)				γ_T (J/m^2)
	(111)A		(111)B		
	III-rich	V-rich	III-rich	V-rich	
GaP	1.18	0.75	1.25	0.37	1.7×10^{-2}
GaAs	0.57	0.35	0.97	0.28	2.2×10^{-2}
InP	0.80	0.58	0.93	0.27	4.1×10^{-3}
InAs	0.41	0.27	0.88	0.37	9.5×10^{-3}

be1.16 [4]. γ_{LV} is surface energy per unit area of liquid-vapor interface.

3. Results and Discussion

Table I shows the calculated surface energies γ_{SV} of (111)A and (111)B, along with the twinning energies γ_T for III-V semiconductors. The calculated surface energies for GaAs and InP are smaller than those in previous calculations by introducing an energy density [12,13]. Furthermore, the calculated surface energies are smaller than parameters to evaluate the segment length in the experiments, and the surface energies strongly depends on the chemical potentials, which corresponds to the growth conditions. This suggests that the segment length is drastically changed by the growth condition. The calculated twinning energies also smaller than those determined by measuring the dissociation width of edge dislocations. The smaller twining energy results in smaller segment length in Eq. (1), and is crucial for the nonlinearity of segment length with respet to the NW diameter.

Figure 1 shows the estimated segment length H_s of a twin plane superlattice of III-V semiconductor nanowires.

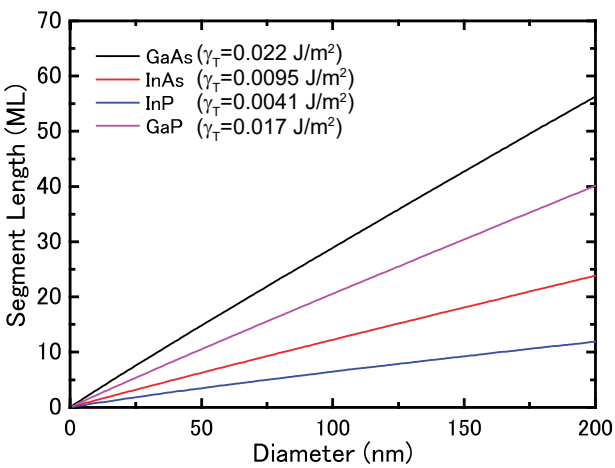

Fig. 1 Estimated segment length H_s of a twin plane superlattice of III-V semiconductor nanowires using calculated values of γ_{SV} and γ_T in Table I. γ_{SV} for (111)B under III-rich condition is used to calculate effective interfacial energy barrier for nucleus Γ in Eq. (1).

Here, we use the surface energies under (111)B under relatively III-rich conditions. It is found that the segment length of GaAs NWs is almost proportional to the NW diameter, while that of InP NWs is much smaller. The difference in the segment length is due to the difference in γ_T between GaAs and InP. γ_T mainly contribute to the magnitude of segment length. According to the difference in γ_T, it is expected that the segment length in InAs NWs is located between those in GaAs and GaP NWs. It should be noted that larger surface energy lead to the linear relationship between segment length and NW diameter, consistent with previous studies [2,4,5].

3. Conclusions

We have investigated the formation of twin plane superlattice in III-V semiconductor NWs by considering two dimensional nucleation using surface and twinning energies obtained by performing DFT calculations. We have found that surface energies strongly depend on the growth conditions such as temperature and pressure of epitaxial growth. The calculated twinning energy is found to be much smaller than previously reported values, which leads to smaller segment length. The calculations also suggest that nonlinear relationship between segment length and nanowire diameter depending on constituent elements is due to the difference in the surface energy difference. These results imply that the surface and twinning energy are crucial for the formation of twin plane superlattice in III-V compound semiconductor NWs.

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