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GEOMETRY OF GaAs NANOWIRE SEEDS IN SiO_x/Si (111) TEMPLATES

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Abstract. We present an energetic model to describe the initial stage of growth of GaAs nanowire seeds in SiO_x/Si (111) templates. The model explains the experimentally observed geometry of GaAs seed crystal emerging from Ga droplets in the holes, with either stepwise or ring geometry at the outer periphery of the holes and restricted by the steps that are much larger than monoatomic. Understanding and controlling this geometry is crucial for further growth of nanowires, improving their vertical yield and optimizing the morphology and crystal structure.

Keywords: GaAs nanowires, Ga droplet, elastic stress relaxation, surface energy, silicon templates

1. Introduction

Epitaxial growth of III-V nanowires [1] and other elongated structures [2] on silicon substrates may enable excellent crystal quality which is unattainable in thin films or even quantum dots [3]. Self-assisted, or self-catalyzed vapor-liquid-solid (VLS) growth of GaAs nanowires on Si (111) substrates, promoted by gallium droplets [4-8], has recently emerged as a gold-free alternative of a more traditional gold-catalyzed VLS growth [9-12], selective area epitaxy [13] or self-induced growth of nanowires [14]. During self-catalyzed growth of GaAs nanowires in lithographically defined templates in SiO_x/Si (111) substrates, the liquid gallium droplets are pre-deposited and then GaAs nanowire seeds nucleate from thee droplets in the holes. This initial stage of GaAs nanowires nucleation in largest measure determine the physical properties of the future nanowire arrays, such as the vertical yield, morphology and crystal structure [15-17]. In this work, we try to understand the unusual geometry of GaAs underneath gallium droplets in the holes, with either stepwise or ring geometry at the outer periphery of the holes and restricted by the steps that are much higher than monoatomic [17].

2. Model

In the standard VLS growth of developed nanowires far away from the substrate, theoretical considerations [18-20] and *in situ* growth monitoring [21,22] reveal mononuclear formation of planar nanowire monolayers which proceeds layer-by-layer so that the flowing steps are always monoatomic. However, the VLS growth within the holes is different – first, GaAs crystal nucleates on the lattice mismatched silicon substrate and, second, the crystal has lateral solid-solid interface with the SiO_x mask rather than free sidewalls in contact with vapor.

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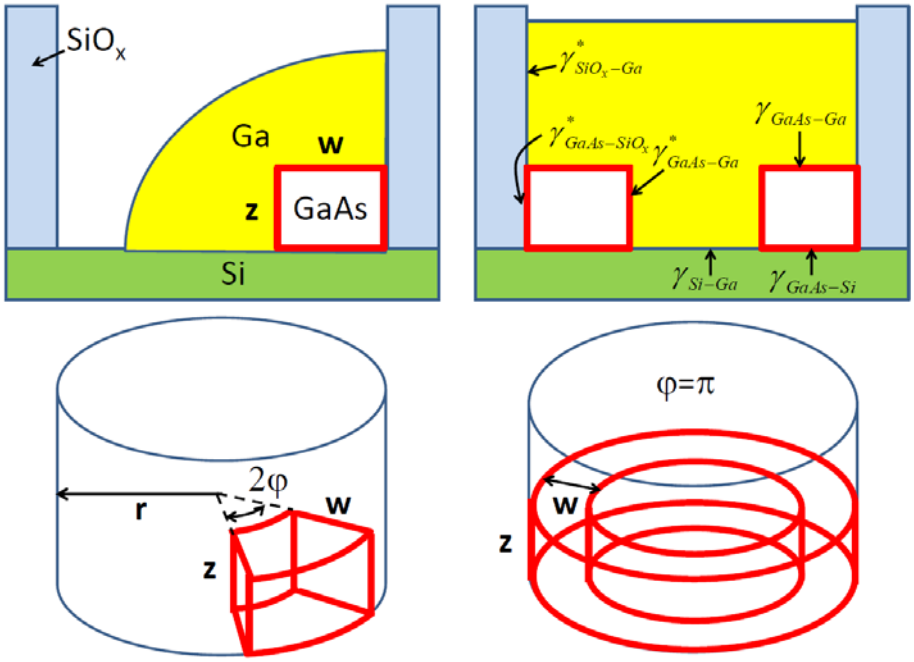

Fig. 1. Schematics of the geometry of GaAs growing from liquid gallium in a SiO_x/Si (111) hole. The hole walls are SiO_x and the bottom is silicon. The opening angle φ can vary from 0 to π depending on the gallium droplet and seed size. The GaAs crystal is a section of cylindrical ring (or the full ring at $\varphi = \pi$) of height h and width W, with the aspect ratio w/h

Initially, the gallium droplet may occupy a part of the hole (for smaller gallium volumes) or completely fill the hole (for larger gallium volumes) as shown schematically in Fig. 1. In the former case, the gallium droplet should be positioned at the edge of the hole for surface energetic reasons [23]. The initial droplet volume can be characterized by the angle φ showing which portion of the hole bottom is covered with liquid gallium ($\varphi < \pi$ for incomplete and $\varphi = \pi$ for complete filling). Assuming cylindrical geometry, we consider free energy of forming a GaAs crystal at the outer periphery of the hole, with the opening angle 2φ ($\varphi < \pi$ corresponds to incomplete and $\varphi = \pi$ to complete ring), width w and height z (see Fig. 1), at a fixed volume of GaAs. The latter is given by $V = zS$, where $S = \varphi r^2 - \varphi(r-w)^2 = \varphi r^2 x(2-x)$ is the surface area of the base and $x = w/r$ is the width of the crystal divided to the hole radius $r = d/2$ (the case $x \to 0$ corresponds to planar growth on the inner sidewalls of SiO_x and $x = 1$ to planar growth on the silicon bottom. Disregarding the volume term with chemical potential (which is the same for any configuration of the GaAs crystal at a fixed V), we can write

$$\Delta G = \frac{\lambda \varepsilon_0^2 V}{1 + Az/w} + 2\varphi rz(\gamma^*_{GaAs-SiO_x} - \gamma^*_{SiO_x-Ga}) + 2wz\gamma^*_{GaAs-Ga} + 2\varphi(r-w)z\gamma^*_{GaAs-Ga} + S(\gamma_{GaAs-Si} + \gamma_{GaAs-Ga} - \gamma_{Si-Ga}). \quad (1)$$

Here, the first term describes the elastic energy contribution induced by the lattice mismatch between GaAs and Si [24-27], with $\lambda = 1.4 \times 10^{11}$ J/m^3 as the effective elastic modulus of bulk GaAs, $\varepsilon_0 = 0.04$ at the lattice mismatch, and $A \cong 7.5$ as the relaxation coefficient [26]. Very importantly, coherent growth of GaAs on silicon requires the radius of the GaAs crystal to be smaller than the critical radius of 53 nm [27], which is fulfilled under the experimental conditions of Ref. [17] and hence all GaAs NWs should be free of dislocations at the base. The next three terms stand for the surface energies of vertical

sidewalls of GaAs, with γ^* representing the surface energies of the corresponding vertical interfaces as shown in Fig. 1 (the GaAs-SiO_x and GaAs-Ga surfaces are created and the SiO_x-Ga one is eliminated upon nucleation). The last term stands for the in-plane surface energy change, with γ representing the surface energies of the corresponding in-plane interfaces (the GaAs-Si and GaAs-Ga surfaces are created and the Si-Ga one is eliminated upon nucleation).

Introducing dimensionless free energy $f = \Delta G/(\lambda\varepsilon_0^2 V)$, after some simple manipulations we get

$$f(x) = \frac{\varphi x^2(2-x)}{\varphi x^2(2-x) + AV/r^3} + \frac{\varphi a + (1-\varphi)bx}{\varphi x(2-x)} + \frac{r^3}{V} c\varphi x(2-x), \quad (2)$$

with the control parameters

$$a = \frac{2\Delta\gamma_*}{\lambda\varepsilon_0^2 r}, b = \frac{2\gamma^*_{GaAs-Ga}}{\lambda\varepsilon_0^2 r}, c = \frac{\Delta\gamma}{\lambda\varepsilon_0^2 r}, \quad (3)$$

$\Delta\gamma_* = \gamma^*_{GaAs-SiO_x} + \gamma^*_{GaAs-Ga} - \gamma^*_{SiO_x-Ga}$ as the vertical and $\Delta\gamma = \gamma_{GaAs-Si} + \gamma_{GaAs-Ga} - \gamma_{Si-Ga}$ as the in-plane surface energy change. When $x << 2$, Eq. (2) is simplified to

$$f(x) = \frac{\varphi x^2}{\varphi x^2 + Av} + \frac{a}{2x} + \frac{c\varphi x}{v}, \quad (4)$$

where we do not write an unimportant x-independent constant. The parameter $v = V/(2r^3) \cong \pi(V/V_{hole})$ is proportional to the ratio of the GaAs volume to the effective total volume of the hole $V_{hole} = 2\pi r^3$ at the hole height $h = 2r$ corresponding to the hole aspect ratio of 1. Clearly, the x dependence of the free energy given by Eq. (4) is controlled by five parameters, the volume coefficient $v << 1$, the elastic energy relaxation A, the opening angle φ, and the two surface energy coefficients a and c describing the changes of the vertical and in-plane surface energies upon nucleation of a GaAs crystal in the hole. The case $c < 0$, $a > 0$ corresponds to the situation where GaAs initially wets the Si substrate but not the SiO_x walls of the hole [25], consistent with the fact that GaAs crystals grow in two-dimensional (2D) form on silicon and as irregular three-dimensional (3D) crystals on SiO_x [15,16].

3. Results and discussion

The energetically preferred configuration x_0 is now determined by the minimum of $f(x)$ in Eq. (4) for a given set of parameters. If we assume $va/(2\varphi) << |c|$, the minimum at intermediate x appears due to the elastic energy term in Eq. (4) for sufficiently large GaAs volumes when $Av >> \varphi x^2$ and corresponds to the ring width

$$w_0 \cong \frac{A|\Delta\gamma|}{\lambda\varepsilon_0^2}. \quad (5)$$

With the known A and $\lambda\varepsilon_0^2$, the experimentally observed ratio $\omega_0/r \cong 0.25$ for r=30 nm corresponds to a plausible $\Delta\gamma$ = -0.225 J/m^2. Figure 2 shows the free energy as a function of x for the full ring geometry of GaAs ($\varphi = \pi$) with these parameters and at $\Delta\gamma_* = 0.05$ J/m^2, corresponding to $a/2 = 0.0074$ and c = -0.033, for different values of V/V_{hole}.

These graphs show the following major properties. For very small GaAs volumes (the curve at $V/V_{hole} = 0.02$), the energetically preferred configuration is 2D GaAs layer. As the GaAs volume increases, the free energy acquires the local minimum at $x \cong 0.2$ for the

parameters considered, which becomes global at a slightly larger $x_0 \cong 0.23$, corresponding to the energetically preferred width $w_0 \cong 0.23R$, as observed in the experiments of Ref. [17]. Further increase of the GaAs volume does not affect the position of the energy minimum. According to Eq. (5), the width of the ring does not depend on the opening angle, yielding the same width for differently sized gallium droplets in the holes. The height of the rings $h_0 = V/(\varphi R^2 x_0)$ increases linearly with the GaAs volume and becomes larger for smaller φ.

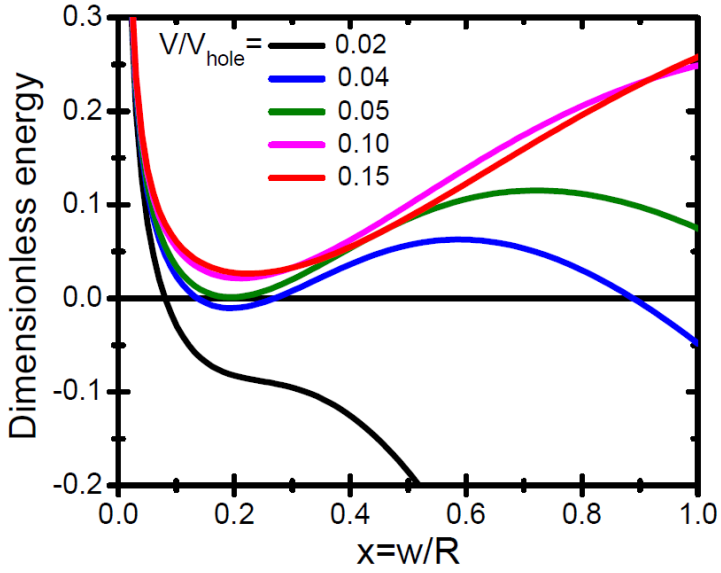

Fig. 2: Free energy versus relative width of full GaAs rings ($\varphi = \pi$) for different V/V_{hole} values (lowest curve - V/V_{hole} = 0.02, highest curve - V/V_{hole} = 0.15), showing the collapse to a volume-independent preferred configuration corresponding to the minimum free energy at $x_0 \cong 0.23$

In conclusion, our analytic model correctly describes the experimentally observed shapes of GaAs nanowire seed crystals nucleating from gallium droplets in SiO_x/Si (111) templates. These results are also supported by a more detailed numerical modeling [17]. A combination of the elastic energy relaxation due to the lattice mismatch between GaAs and Si (111) substrate and the surface energy constrains leads to the unusual geometry of GaAs crystals in the form of either steps or rings whose heights are much larger than monoatomic. These results can further be used as the initial condition for the description of subsequent time evolution of the GaAs nanowire morphology starting from the holes.

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