

NUCLEATION OF ISLANDS WITH VERTICAL OR TRUNCATED CORNER FACETS IN VAPOR-LIQUID-SOLID NANOWIRES

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Abstract. We develop a model for nucleation of islands in vapor-liquid-solid nanowires with either vertical or truncated corner facets. Under the assumption of two-dimensional geometry of the growing island, it is shown that the earlier energetic condition for the truncated edge at the growth interface is modified by chemical potential. Therefore, the islands may nucleate at the trijunction during growth even if the truncation is preferred at the no growth conditions on surface energetic grounds. This conclusion may be used as the first step for understanding the peculiar oscillatory behavior of the growth interface and the related crystal phases of III-V nanowires.

Keywords: nanowires, vapor-liquid-solid growth, nucleation, truncation, surface energy, chemical potential, contact angle

1. Introduction

Vapor-liquid-solid (VLS) III-V nanowires (NWs) are promising as fundamental building blocks for nanoscience and nanotechnology [1,2]. In particular, these NWs enable dislocation-free growth of highly mismatched semiconductor materials in III-V heterostructures or on silicon substrates [3,4], which is unattainable in thin films or even quantum dots [5]. VLS III-V NWs exhibit interesting properties, such as the zincblende-wurtzite (ZB-WZ) polytypism which can be controlled by the growth parameter tuning [6]. Earlier theoretical models for Au-catalyzed [7-9] or self-catalyzed [10,11] VLS growth of III-V NWs considered planar liquid-solid interface at the NW top, and nucleation of two-dimensional (2D) islands with vertical sidewalls. For such planar geometry, the models of polytypism of Glas *et al.* [12,13] assumed nucleation at the trijunction, where the vapor, liquid and solid phases meet, as the necessary condition for the WZ phase formation. This view gained much support and was widely used for controlling the crystal phases of different III-V NWs (see, for example, Ref. [14] for a review)

Further progress in understanding the VLS growth of NWs was achieved through *in situ* monitoring inside a transmission electron microscope (TEM) [15-17]. In particular, it was found that VLS NWs often present a truncated corner facet at the trijunction, whose size oscillates with the period of the monolayer (ML) formation [15]. There is only one theory developed so far that explains the oscillatory behavior of the truncated edge in NWs [15,16] according to which, whenever a truncated facet is present, it never shrinks to zero size. If this is true, 2D islands cannot nucleate at the trijunction [15] and hence the crystal phase should be pure ZB [16]. According to the model of Tersoff [15,16], the occurrence of truncated edge requires a certain condition for the surface energies of different interfaces (the inclined wetted facet should be energetically preferred to the vertical non-wetted one). This condition depends on the contact angle of the droplet catalyzing the VLS growth of a given NW. Truncated geometry is preferred for larger contact angles and this is often believed to explain the

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presence or absence of polytypism at smaller or larger contact angles, respectively [16,18]. This view is very different from the original model of Glas *et al.* [12] which assumes nucleation at the trijunction for both WZ and ZB types of 2D islands.

However, it is not impossible the truncation starts from zero size at the beginning of each ML growth cycle and shrinks to zero at the end, reaching substantial values in the middle. The crystal phase of the whole NW must be determined at the moment of nucleation [12]. This explains the importance of answering the question of whether or not the initial nucleation of an island develops the truncated edge. In this work, we try to answer this by considering a simplified model for nucleation of 2D islands with either vertical or truncated corner facets having the ML height. We show that, under this simplifying assumption for geometry, the Tersoff energetic condition for the truncation [15,16] is modified by chemical potential and hence islands with vertical facets may nucleate at the trijunction even if the truncation is preferred when no growth occurs.

2. Model

Let us consider nucleation and growth of 2D islands of the ML height h , assuming only two types of possible lateral facets: vertical solid-vapor (having the surface energy γ_{ov}), and truncated solid-liquid (having the surface energy $\gamma_{\theta L}$), making the angle θ to the vertical. The other surface energies of interest are those of the liquid-vapor interface, with the surface energy γ_{LV} , and the planar solid-liquid interface, with the surface energy γ_{SL} . The contact angle of the droplet is denoted β . The geometry and relevant parameters are illustrated in Fig. 1. The single island can emerge with either (1) vertical non-wetted facet at the trijunction or (2) only truncated facets surrounded by liquid. Generally, the island changes its shape as it grows [17]. Our aim is to compare the free energies of forming the islands in the two configurations and to find out the conditions for the preferred nucleation of the truncated island.

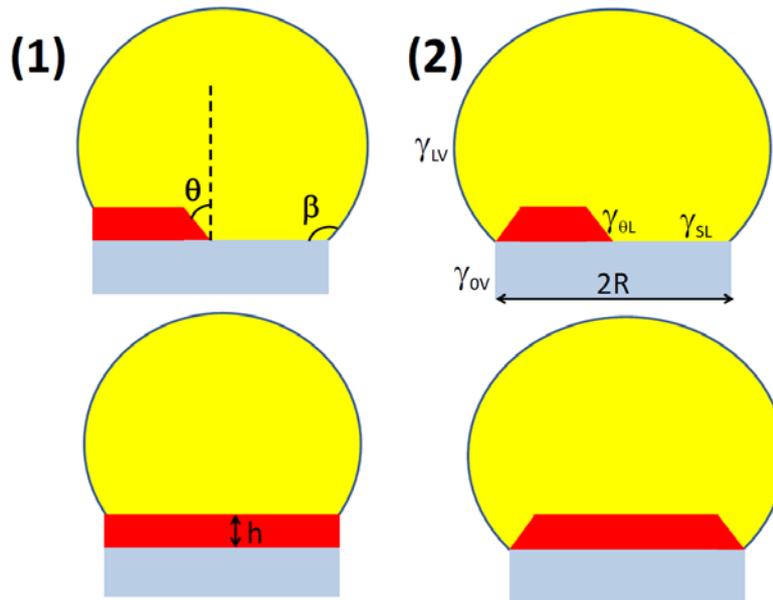


Fig. 1. Geometries and parameters of 2D ML islands with vertical (1) and truncated wetted (2) corner facets (top), extending to the full NW MLs (bottom)

Let us introduce the linear size of island r , its perimeter $k_1 r$ and surface area $k_2 r^2$, with k_1 and k_2 as the corresponding shape constants. These constants may change in the

course of growth, i.e., they generally depend on r . Let $\chi k_1 r$ and $(1-\chi)k_1 r$ be the parts of the island perimeter at the trijunction and away from it, respectively. The fraction of the perimeter at the trijunction also changes as the island grows; in particular, $\chi \rightarrow 1$ when $r \rightarrow R$, where R is the NW radius.

Quite generally, the free energy of forming the island in configuration (1) is

$$\Delta G_1 = -\Delta\mu \left[k_2 r^2 h - (1-\chi)k_1 r h^2 \frac{\tan \theta}{2} \right] + (1-\chi)k_1 r h \left(\frac{\gamma_{\theta L}}{\cos \theta} - \gamma_{SL} \tan \theta \right) + \chi k_1 r h (\gamma_{0V} - \gamma_{LV} \sin \beta), \quad (1)$$

where $\Delta\mu$ is the liquid-solid chemical potential difference per unit volume of the solid. Similarly, for configuration (2) we have

$$\Delta G_2 = -\Delta\mu \left[k_2 r^2 h - k_1 r h^2 \frac{\tan \theta}{2} \right] + k_1 r h \left(\frac{\gamma_{\theta L}}{\cos \theta} - \gamma_{SL} \tan \theta \right). \quad (2)$$

These expressions show that the volume of the fully truncated island in configuration (2) is smaller than that of the island with vertical corner facet at the trijunction in configuration (1). Therefore, there is a difference in the chemical potential terms in the two cases.

Let us first compare the two formation energies for fully formed MLs, i.e., when $\chi = 1$ and $r = R$. In this case, we obtain

$$\Delta G_2 - \Delta G_1 = k_1 R h \left(\frac{\gamma_{\theta L}}{\cos \theta} + \gamma_{LV} \sin \beta - \gamma_{0V} - \gamma_{SL} \tan \theta + \Delta\mu h \frac{\tan \theta}{2} \right). \quad (3)$$

For the critical nucleus which typically consists of only a few III-V pairs, it is reasonable to assume a fixed shape, i.e. r -independent shape constants and χ . Re-writing equations (1) and (2) as

$$\Delta G_1 = -\Delta\mu k_2 r^2 h + k_1 r h \left\{ (1-\chi) \left(\frac{\gamma_{\theta L}}{\cos \theta} - \gamma_{SL} \tan \theta + \Delta\mu h \frac{\tan \theta}{2} \right) + \chi (\gamma_{0V} - \gamma_{LV} \sin \beta) \right\}, \quad (4)$$

$$\Delta G_2 = -\Delta\mu k_2 r^2 h + k_1 r h \left(\frac{\gamma_{\theta L}}{\cos \theta} - \gamma_{SL} \tan \theta + \Delta\mu h \frac{\tan \theta}{2} \right), \quad (5)$$

we notice that they have the same structure $\Delta G_k = -Ar^2 + B_k r$, where only the effective surface energies B_k are different. Maximizing this in r , we find the sizes of the critical nuclei $r_* = B_k / (2A)$ and the corresponding nucleation barriers $\Delta G_k^* = B_k^2 / (4A)$. Therefore, the nucleation of the truncated island is preferred when $B_2 - B_1 < 0$, or

$$\frac{\gamma_{\theta L}}{\cos \theta} + \gamma_{LV} \sin \beta - \gamma_{0V} - \gamma_{SL} \tan \theta + \Delta\mu h \frac{\tan \theta}{2} < 0. \quad (6)$$

The surface energy term here is exactly identical to the earlier results of Tersoff *et al.* [16,19] and Dubrovskii [18]. However, it is modified by the chemical potential term. The condition for the preferred nucleation of the truncated islands is also identical to the one for the full MLs, as seen from comparing Eqs. (6) and (3).

3. Discussion

The last term in Eq. (6) is not at all negligibly small under the typical growth conditions. Assuming, for example, a modest $\Delta\mu = 100$ meV per GaAs pair for the parameters of GaAs ($h = 0.326$ nm, the elementary volume per GaAs pair $\Omega_s = 0.0452$ nm³) and $\theta = 50^\circ$, we obtain a substantial correction for the surface energy, $\Delta\mu h (\tan \theta) / 2 \cong 0.07$ J/m².

Therefore, the condition for forming the truncated corner facet is given by

$$c + \Delta\mu h \frac{\tan \theta}{2} < 0, \quad (7)$$

where $c = \gamma_{oL} / \cos \theta + \gamma_{LV} \sin \beta - \gamma_{oV} - \gamma_{SL} \tan \theta$ as introduced earlier [15,16,18,19], not just $c < 0$. The latter is valid only at zero chemical potential corresponding to the "no growth" conditions. Our inequality given by Eq. (7) contains the chemical potential term which may overcome the capillary forces. Hence, there is a range of contact angles β where $\Delta\gamma$ is negative but the corner facet remains vertical and the growth interface is planar.

Let β_* be the contact angle of the droplet corresponding to $c = 0$, i.e. where the truncation starts to develop at the no-growth conditions ($\Delta\mu = 0$). Then it is easy to find the difference $\Delta\beta = \beta_1 - \beta_*$, where β_1 is the contact angle at which the truncated corner starts in a growing NW at the moment of nucleation for a given $\Delta\mu$ (in other words, where the truncation never shrinks to zero size as in the Tersoff model [15,16]). Indeed, Δc can be related to $\Delta\beta$ as $\Delta c = -\gamma_{LV} |\cos \beta_*| \Delta\beta$ (assuming that $\beta_* > \pi/2$) and the condition $\Delta c + \Delta\mu h \tan \theta / 2 = 0$ is reduced to the linear relationship between $\Delta\beta$ and $\Delta\mu$

$$\Delta\beta = h \frac{\tan \theta}{2} \frac{\Delta\mu}{\gamma_{LV} |\cos \beta_*|}. \quad (8)$$

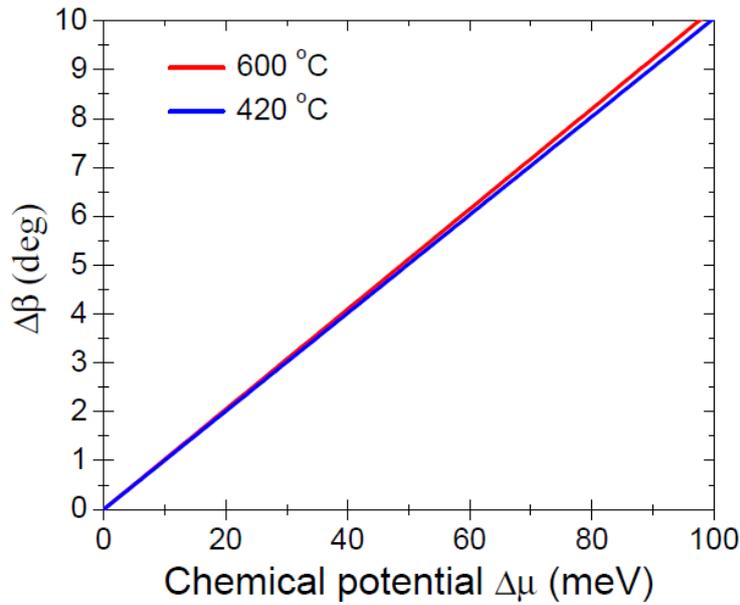


Fig. 2. Linear dependences of the range of contact angles with zero initial truncation $\Delta\beta$ on the chemical potential during growth $\Delta\mu$ for the parameters of GaAs NWs listed in the Table 1 for the growth temperatures of 600 °C and 420 °C

Figure 2 shows the linear correlation of $\Delta\beta$ with $\Delta\mu$ for the parameters of GaAs NWs listed in the Table 1. We took a value of 50 °C for the truncation angle θ in this example, which can be further refined by the *in situ* TEM measurements. As for the surface energy of the droplet, γ_{LV} , it should not be significantly different for Au-catalyzed or Ga-catalyzed GaAs NWs due to the surface enrichment by the lower energy liquid gallium [18]. The linear correlation is only slightly influenced by the growth temperature due to the weak temperature dependence of the surface energy of liquid gallium [20]. Finally, this linear dependence can be used for obtaining or refining some unknowns, such as θ or γ_{LV} (in the Au-catalyzed

case) from the measured $\Delta\beta$ at the known chemical potentials (which can be deduced from the NW growth rates [21,22]). It is seen that, with our parameters, the $\Delta\beta$ reaches a large value of about 10° for $\Delta\mu = 100$ meV.

Table 1. Parameters of GaAs NWs used in Fig. 2

Elementary volume Ω_s (nm ³)	Monolayer height h (nm)	Critical contact angle at no-growth β_* (deg)	Truncation angle θ (deg)	Droplet surface energy γ_{LV} at 600°C (J/m ²)	Droplet surface energy γ_{LV} at 420°C (J/m ²)
0.0452	0.326	125	50	0.671	0.684

In conclusion, our simple model predicts the existence of a range of contact angles for which 2D islands nucleate with vertical corner facet at the trijunction even if the truncation is preferred on surface energetic grounds. This supports the earlier models for the ZB-WZ polytypism in III-V NWs, with nucleation at the trijunction [12,13]. A more comprehensive treatment should include a more macroscopic truncation, the possibility to transfer the building material to the island in a kinetic treatment, and possible stopping effect at low arsenic concentrations. These interesting problems will be considered elsewhere.

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