On the possibility of growing antimonide nanowires in the metastable wurtzite phase

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Abstract. Controlled formation of metastable phases is one of the challenges of the physics of crystal growth. Gold-catalyzed nanowires are considered to be one of the most convenient systems to study this phenomenon. Studies of antimonide-based nanowires indicate that they preferentially crystallize in the zinc blende crystal structure rather than wurtzite, which is common in other III–V nanowire materials. Here we propose a new approach to the formation of antimonide nanowire segments in the metastable wurtzite phase and support it with theoretical results. The hexagonal crystal phase is stabilized due to the elastic strain. We suggest that this approach can be applied to other III-V nanowires as well.

1. Introduction
Crystal structure is one of the basic characteristics of a material, which strongly influences physical properties such as symmetry, band gap, Fermi level, surface energies, modulus of elasticity, and density. Most III-V compounds in the bulk phase form a face-centered cubic lattice [1]. However, in the form of nanowires (NW), many III–V compounds show the possibility of growth in the crystal phase of zinc blende (ZB) or metastable wurtzite (WZ) depending on epitaxial conditions [2]. In thin nanowires of arsenides and phosphides, crystallization at a triple-phase line at the NW edge is thermodynamically preferable [3]. In this case, the reduction of surface energy for the WZ nucleus overcomes the loss in bulk energy. Thus, the formation barrier for the WZ layer becomes less than for the ZB layer, and the NW growth proceeds in the WZ phase. For sufficiently large diameters of a NW, this difference is compensated by a large number of potential nucleation sites in the interior part (which is proportional to the NW cross-section area) compared to the number of sites at the triple line (which is proportional to the perimeter). It means that NWs have a critical transverse size (diameter), above which the nucleation of a new monolayer occurs predominantly in the center, and NWs grow in the stable phase [4]. This critical diameter for antimonides is substantially less than for arsenides and phosphides [4]. As a result, the formation of antimonide NWs in the WZ phase requires an extremely small catalyst particle. In combination with the high solubility of antimony, this significantly complicates the growth of antimonides in the hexagonal phase in most of the catalysts used.

Some of the authors show the possibility to control the NW crystal phase upon the addition of dopants [5], which works perfectly for arsenide NWs. Unfortunately, even a small amount of antimony switches the arsenide NWs to the ZB phase [6].

So far, almost all the studies on the growth of gold-catalyzed antimonide NWs have shown a pure ZB structure [7,8]. It is worth noting that there is still the possibility of growing WZ antimonide on
templates. For example, it is possible to form a WZ antimonide shell around the WZ core [8]. Even more, a WZ antimonide NW was grown with the so-called “pulsing approach” [7].

2. Model

In this work, we propose to use another effect to stabilize the metastable hexagonal phase: the accumulation of elastic energy. When antimonides are deposited on phosphide substrates, large elastic stresses lead to the formation of quantum dots and, further, to a three-dimensional growth of bulk cubic material. NWs form in a different way: elastic stresses relax on the sidewalls and the growth proceeds in a layer-by-layer mode. Thus, the formation of the nucleus of a new monolayer requires overcoming the elastic stress. When the antimonide 2D segment is grown on the phosphide stem, the additional elastic energy $W$ per pair of atoms can be found as [9]:

$$W = \varepsilon^2 E \Omega / 2,$$

where $\varepsilon$ is the lattice mismatch, $E$ is the Young’s modulus (along [111] in case of ZB or [0001] in case of WZ) and $\Omega$ is the volume per pair.

We compare the difference in the formation energy between the WZ and ZB phases in the absence of elastic strain $\psi$ with the contribution from elastic strain $\Delta W = W_{\text{ZB}} - W_{\text{WZ}}$. Table 1 summarizes the results of calculations for GaSb growth on GaP and InSb growth on InP.

**Table 1.** Elastic contribution to the formation energy (W) for GaP and InSb growth on InP.

|                | $\varepsilon_{\text{ZB}}$ | $\varepsilon_{\text{WZ}}$ | $E$, GPa | $\Omega_{\text{ZB}}$, Å$^3$ | $\Omega_{\text{WZ}}$, Å$^3$ | $W_{\text{ZB}}$, meV | $W_{\text{WZ}}$, meV | $\Delta W$, meV | $\psi$, meV |
|----------------|--------------------------|--------------------------|----------|--------------------------|--------------------------|----------------------|----------------------|----------------|------------|
| GaSb on GaP    | 11.8%                    | 9.9%                     | 103.2    | 56.6                     | 53.7                     | 256.1                | 168.4                | 87.7            | 19.8       |
| InSb on InP    | 10.4%                    | 8.3%                     | 74.5     | 68Å$^3$                 | 64.2                     | 171.2                | 102.8                | 68.4            | 16.4       |

The values of $\psi$ were taken from [4]. The rest of the values were taken from [1]. Our calculations show that, in the hexagonal phase, the elastic energies per pair of GaSb and InSb atoms are 87.7 meV and 68.4 meV less than in the cubic phase. These differences in elastic energy $\Delta W$ are much greater than the values of $\psi$ of 19.7 meV and 16.4 meV for GaSb and InSb, respectively. Thus, the nucleation of antimonide on top of phosphide in the WZ phase is preferable to ZB in both indium and gallium compounds.

The strain energy per pair, accumulated in several monolayers, $W_{3D}$, can be presented as a function of $W$:

$$W_{3D} = z(\eta)W,$$

(2)

The pre-factor $z(\eta)$ measures the strain relaxation at the free NW sidewall as a function of height $H$ to diameter $D$ ratio $\eta = H / D$ [10]:

$$z(\eta) = \frac{p_1}{1 + p_2 \eta} + (1 - p_1) \exp(-p_3 \eta),$$

(3)

where $p_1 = 0.557$, $p_2 = 10.15$ and $p_3 = 9.35$ are given by Glas fit to finite element calculations of elastic relaxation of a uniformly strained cylinder standing on an infinite foreign substrate [10].

Thus, the difference in the formation energy of ZB and WZ layers per pair could be written in the following form:

$$G = z(\eta)W - \psi,$$

(4)
Negative $G$ values correspond to the preferential NW growth in the ZB phase, while positive values correspond to growth in the WZ phase.

In figure 1(a), the values of $G$ are plotted as a function of $\eta$ and the fraction $x$ of Sb atoms in the monolayer of GaSb$_x$P$_{1-x}$ or InSb$_x$P$_{1-x}$ NW. In the calculations, we use the linear approximation of $\varphi$ and lattice constants as functions of $x$. The top left corner, corresponding to a high fraction of Sb and a short distance to the phosphide substrate, shows the preferential growth in the WZ phase. An increase in the height of the WZ segment or a decrease in the Sb content leads to growth without a preferred phase ($G$ around 0), where the formation of stacking faults is possible. The ZB growth is expected in the region of low Sb concentrations (below 0.2) or large $\eta$.

![Figure 1](image)

**Figure 1.** The difference in the formation energy per pair between ZB and WZ as a function of $\eta$ and the fraction $x$ of Sb atoms in a monolayer of GaSb$_x$P$_{1-x}$ NW (a) and InSb$_x$P$_{1-x}$ (b) in the antimonide segment on top of the GaP or InP stem, respectively. Negative values correspond to preferential NW growth in the ZB phase; positive values correspond to growth in the WZ phase.
The indium compound shows similar behavior illustrated in figure 1(b). We predict the formation of a thin insert of wurtzite antimonide near the phosphide interface for both material systems.

The approach considered above can be used to form a WZ segment of GaSb or InSb NW on top of a GaP or InP NW stem. At high Sb concentrations and a short distance from the interface, the formation of WZ layers is favorable. Thus, a short segment of WZ GaSb is expected in thick enough NWs. In practice, experiments on the growth of GaSb or InSb segments on different stems show a rapid expansion of the droplet [7,11], therefore, the elastic strain relaxes faster than assumed in our calculations. Usually, the WZ part merges in experimental results with the next segment, where NWs grow predominantly in the ZB phase with stacking faults. However, the control over the droplet size allows the formation of an antimonide segment in the WZ phase on top of the phosphide NW.

3. Conclusion
In summary, we have proposed a mechanism for forming short WZ segments of antimonide on top of the phosphide NW stem. Our model is based on the stabilization effect of elastic compression in a dense metastable phase. According to our calculations, the formation of the WZ phase requires a high Sb content in the monolayer. The height of the WZ segment is limited by the ratio of height to diameter of below 0.1. Some of the key elements of the model, especially the control of the droplet size, still need to be developed.

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