

Modeling nanowire growth: nucleation, phase transitions, critical dimensions

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We report several recent advances in the modeling of semiconductor nanowires.

1. Nucleation

The current models of semiconductor nanowire growth assume that new layers develop from 2D crystalline nuclei formed on the top facet of the nanowire. In the case of the vapor-liquid-solid (VLS) growth mode, nucleation occurs at the nanowire-liquid interface (more generally, at the nanowire-catalyst interface). We show that the particular geometry of the nanowires makes it very likely that these nuclei do not form at random on the top facet (as usually assumed) but rather at the triple phase line (TPL) where vapor, liquid and solid phases coexist. The reason is simply that nucleation at the TPL eliminates part of the pre-existing LV interface and replaces it by an area of nucleus-vapor interface. We derive the criterion for TPL nucleation. Calculation of the respective nucleation probabilities for Au-seeded GaAs nanowires indeed demonstrates a very strong bias in favor of triple line nucleation. The arguments supporting nucleation at the TPL hold even if the catalyst is not liquid.

2. Phase transitions

We then show that triple line nucleation may be responsible for phase transitions in semiconductor nanowires. Indeed, it is often observed that nanowires of N-free III-V semiconductors predominantly adopt the hexagonal wurtzite (WZ) structure whereas the corresponding bulk compounds are of cubic sphalerite (or zinc-blende, ZB) structure. A possible favoring of the WZ structure via lower facet or edge energies can at best explain WZ formation for nanowires of very small radii. We propose instead to search the explanation in nucleation. However, 2D nuclei are not intrinsically of ZB or WZ structure: it is only their rotational *positioning* with respect to the underlying atomic layer that determines their character. If nucleation takes place away from the TPL, there is little difference between nuclei in ZB or WZ positions. On the contrary, in case of nucleation at the TPL, nuclei in WZ and ZB positions differ in several important respects, most notably the nature of the crystal plane exposed at the nucleus/vapor interface and the areas of the SL and LV interfaces. This can favor the formation of nuclei in WZ position, provided two conditions are met. The first one is a material-related condition involving the vapor-nucleus interface energies. The second is that the supersaturation in nanowire constituents of the liquid phase with respect to the solid be high enough to overcome the stacking fault energy related to WZ nucleus positioning. This second condition is confirmed by our systematic observation of ZB in two instances of non-stationary growth of GaAs nanowires by molecular beam epitaxy, namely the beginning of growth and its termination under As flux only (the latter observation already made for chemical beam epitaxy). Supersaturation is indeed low in both cases. To support this interpretation, we shall present the results of simulations of these transitory stages.

3. Critical dimensions for heterostructures in nanowires

In the final part of our presentation, we consider the formation of heterostructures involving mismatched materials in nanowires. In the so-called axial heterostructures, a certain height of misfitting material is grown over the foot of the nanowire, which is lattice-matched to the substrate. The lateral surfaces of the nanowire allow the epitaxial strain to relax much more efficiently than in similar heterostructures fabricated either in the quantum well or in the quantum dot geometry. Approximate semi-analytical calculations of the elastic state of the coherent heterostructure have been performed. As expected, the elastic energy depends much on the aspect ratio of the misfitting segment. By comparing this energy with an approximate calculation of the energy of the state with interfacial dislocations, we develop an equilibrium theory for the plastic relaxation of such heterostructures. We obtain an analytical implicit equation giving the variation of the critical thickness of the misfitting volume (beyond which dislocations appear) with the nanowire radius. The critical thickness becomes infinite for radii smaller than a certain critical radius, for which we also propose an analytical formula. These predictions are shown to agree with the few experimental results available at present.