What Determines the Crystal Structure of Nanowires?

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Abstract. The growth of thin GaAs and InAs nanowires (NWs) was studied both theoretically and experimentally. InAs and GaAs NWs grown by the Vapor Liquid Solid (VLS) method were studied by a high resolution transmission electron microscope (HRTEM). The wurtzite (*wz*) structure is dominant in such wires with occasional stacking faults (SFs) resulting from the intermixing of zinc-blended (*zb*) stacking. Growth direction is $\langle 0001 \rangle$ and $\langle 111 \rangle$ for the *wz* and the *zb* type sections of the NW, respectively. Nevertheless, we find that for NWs thinner than ca 100 Å, the *wz*/*zb* SFs do not appear. Using *ab initio* methods, we studied the stability of the structure of the NWs; in particular the competition between *wz* and *zb* phases. We have found that for the diameters of up to 50 Å the most stable NWs adopt the *wz* $\langle 0001 \rangle$ structure. For NWs with the diameter larger than 100 Å the free energies of *wz* and *zb* become nearly equal, which explains the occasional occurrence of SFs observed in as grown NWs.

Semiconductor NWs, in particular the NWs of III-V compounds, are of great interest due to possible applications in nanoelectronics, nanophotonics, and nanosensors, [1-2] and are intensively studied both experimentally and theoretically. However, in most of the GaAs and InAs NWs many defects related to stacking faults (SFs), which would hamper the functionalities of the future devices, are obtained during the growth. To find conditions, which would help to avoid these defects, we study what determines the crystal structure in such NWs. We observe that reducing the diameter of the wires results in diminishing the amount of SFs. To explain this result we study, using *ab initio* methods, the stability of the NW structures, in particular the competition between *wz* and *zb* ones.

The InAs and GaAs NWs are grown by the VLS technique in a solid source Riber 32 system, using Gold as the catalyst. A thin ($\sim$1 nm) layer of Gold is evaporated on the epi-ready substrate and heat to above the eutectic temperature to form a set of arbitrarily distributed in size and position Gold droplets on the surface. The GaAs {111}B and {011} substrates are used for the growth of GaAs wires where InAs {111}B or Si substrates are used for the growth of InAs wires. MBE growth is carried out at a temperature of 450°C and 550°C for InAs and GaAs, respectively, under a high As_4 to group III ratio in the range of 200 to 300. Growth rate is in the rage of 0.5 to 1 μm/h of a respective bulk-grown layer. Scanning electron microscopy (SEM), as well as transmission electron microscopy (TEM), are used to study the structural properties of the NWs, which are harvested from the grown wafer by conventional methods. Under optimized growth conditions rod shape NWs of GaAs and InAs are obtained with the typical *wz* structure, having occasional SFs along the wire. The length of GaAs wires is 2-4 μm; InAs wires are longer, 5 μm and above. Diameters of the grown whiskers are mostly in the range of 10-50 nm, though thicker wires have also been achieved. At lower growth temperature the shape of the wires become tapered and the concentration of SFs increases dramatically. Pencil shape NWs of GaAs are typical for high density growths, particularly on {011} substrates.

We have noticed that thinner wires have a lower concentration of SFs [3]. In particular, InAs wires as thin as 10 nm are easily grown, having no SFs all along a total length of 5 μm, as shown in Figure 1. GaAs wires of such thickness are rare but exhibit the same phenomenon even for larger diameters (up to 15 nm) (Figure 3).

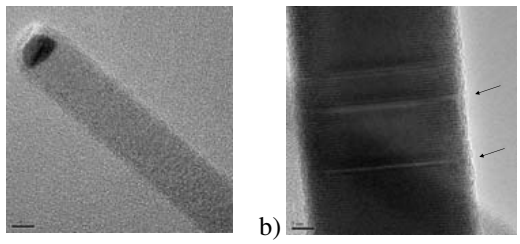

FIGURE FIGURE 1. InAs *wz* NWs of diameter (a) 10 nm – no SFs are observed; (b) 35 nm – SFs shown by the arrows.

To explain these results we study the stability of GaAs and InAs NWs in various structures by comparing their total energies. The studied NWs are oriented along six different crystallographic directions of either *zb* and *wz* structure and have diameters up to 50 Å. We use methods based on the Density Functional Theory to determine the atomic configuration corresponding to the min-

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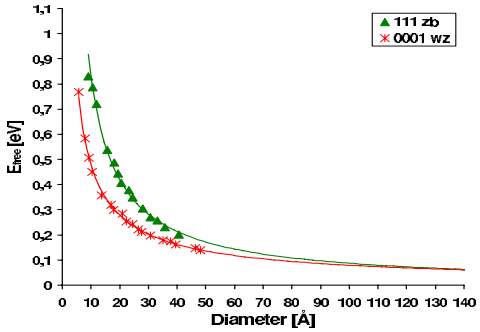

FIGURE FIGURE 2. InAs NWs' free energy vs diameter - calculated (points) and extrapolated (green (*zb*) and red (*wz*) lines) values.

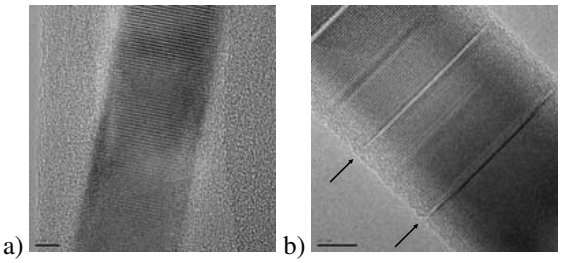

FIGURE FIGURE 3. GaAs *wz* NWs of diameter (a) 15 nm – no SFs are observed; (b) 35 nm – SFs shown by the arrows.

imum energy of each of the initial structure (full atomic position relaxation and NW surface reconstruction are allowed). In Figures 2 and 4 the free energies per atomic pair (E_{free}) for InAs and GaAs NWs with different diameters and structures are collected. We found that for the diameters of up to 50 Å the most stable NWs adopt the *wz* (0001) structure. In thin *zb* NWs along any crystallographic axis, the free energies are much larger than that of the *wz* (0001). However, among *zb* NWs thicker than 30 Å, the ones (111) oriented are energetically favorable, with the free energy difference from that of the *wz* (0001) diminishing with diameter. To estimate E_{free} for NWs with larger diameter we just extrapolate our results. The energy differences between *zb* and *wz* NWs for 3 different diameters in the region 10nm and above are presented in Table1. These differences are only few meV, much lower than the kT in the growth conditions. It should be noted, however, that in the bulk the total energy differences per atomic pair between *zb* and *wz* are only 19 meV for GaAs and 14 meV for InAs, still the *zb* structure is stable below the melting temperature. On the other hand in ZnS the energy difference between *zb* and *wz* phases as small as 6 meV/pair [4] is enough to make the compound unstable, i.e., allows for reversible changes from one phase to the other, at about 1300K. These facts suggest that at about 800 K, i.e.,for our growth temperatures, the calculated energy differences are close to the stability threshold – differences higher than about 10 meV should lead to NWs with stable structure, but for differences lower by few meV the instabilities and SFs should appear. Importantly, the diameters which correspond to the same energy difference are about 20% higher for GaAs than for InAs (see Table), in agreement with the experiment and in contrast to previous calculations based on empirical potentials [5].

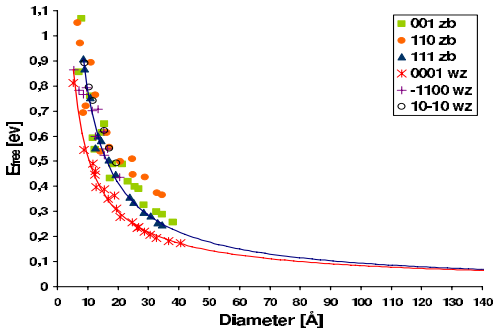

FIGURE FIGURE 4. GaAs NWs' free energy vs diameter - calculated (points) and extrapolated (blue (*zb*) and red (*wz*) lines) values.

TABLE TABLE 1. The energy differences between *wz* and *zb* structures for chosen NWs diameters.

Structure	Diameter (nm)	ΔE_{free} (meV)
InAs	10	7.87
	12	4.19
	14	1.8
GaAs	10	11.22
	12	7.85
	14	5.59

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