Self catalyzed GaAs nanowires on GaAs (100): growth and characterization

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Nanowires (NWs) are quasi-one-dimensional crystals with diameter ranging between 30 and 100 nm and length up to several μm. NWs made of semiconductor materials are promising building blocks for the next generation optoelectronic devices and have received in the last years growing attention and interest [1]. They combine semiconductor properties with nanoscale dimensions and this can be exploited for device construction, such as solar cells [2], opto-electronics components [3-7], field emission devices [8] and sensor probes [9].

NWs are typically obtained either by top-down processes, involving patterning of a crystal, or by bottom-up methods, typically involving the presence of a metal nanoparticle, mainly Au, that induce and drive the 1D growth, or through the preparation of the substrate surface by nanofabrication methods. Avoiding Au as catalyst is particularly important when integration with the actual silicon technology is wanted, because Au creates in Si deep carrier traps that reduce Si semiconducting capacities [11].

We present here the growth of GaAs NWs on GaAs (100) without any catalyst deposition and without mechanical or chemical treatments of the substrate surface. Our 1D nucleation sites are obtained by depositing by MBE a sub-nm thick Si layer on GaAs (100) and then oxidizing it by atmospheric oxygen.

Most of the obtained NWs (fig.1A foreground) appear to grow following a VLS-like mechanism [12]: metallic nanoparticles present on the surface act as preferential adsorption sites for the reactants in gaseous phase. Once the nanoparticles are sovrasaturated, reactants precipitate and eventually nucleate at the interface among the nanoparticles and the substrate. In our case the metal is Ga. The high temperature employed during the growth (T_g > 580 °C), suggests an incongruent evaporation of As atoms from the oxidized Si surface [13] at early stages of the growth. This allows Ga atoms to diffuse onto the surface and merge to create the nanoparticles. These wires have a growth rate of 20 μm per hour. A minority fraction of NWs don't display a Ga nanoparticle at the tip (fig.1A background), but are pyramid terminated and have a growth rate one order of magnitude smaller.

The structural properties of the two kind of wires are also different: the presence of Ga nanoparticle (fig 1C) is associated with pure zincblende crystal phase, the absence of the nanoparticle (fig 1B) is instead associated with wurtzite crystal phase (fig. 2 left, top part of the NW). Intermediate cases are also observed, where the Ga nanoparticles is consuming (fig. 1D). This situation is associated with a very high mix of zincblende and wurtzite phases through very dense stacking faults along the NW body (fig 2 left, middle part of the NW).

Optical properties of the as grown samples reflect the coexistence of the different structures. A representative low temperature photoluminescence spectrum is shown in Fig. 2 right. It presents a sharp photoluminescence peak around GaAs free exciton energy together with a structured band at lower energy. According to Ref 15, we interpret this band as due to the coexistence of zincblende and wurtzite sections with staggered band alignment.

The Ga-catalyzed wires are a very good example of VLS growth: it proceeds at high rate and leads to absence of stacking faults. When the Ga nanoparticle starts consuming, the catalysis driving force in NW growth competes with the very small energy difference between wurtzite and zincblende stacking [14] and this results in a mixing of the two phases to a lower growth rate. When the Ga nanoparticle has completely disappeared, NW growth is very slow with a direct vapour-to-solid reaction. This reaction happens faster on the pyramidal tip facets than the wall facets [17], resulting in a dominant axial to radial growth and no tapering.

Experiments show that the dominance between the two growth mechanisms can be tuned through to the As to Ga beam pressure ratio (BPR). If the As/Ga BPR is low, the Ga nanoparticle is clearly visible at the end of the growth for durations as high as 1 hour. When the As/Ga BPR is high, the total number of Ga adatoms arriving to the NW tip (direct impinging from the vapour phase plus diffusion) is too low to maintain the Ga nanoparticle on top and the Ga nanoparticle gets consumed.

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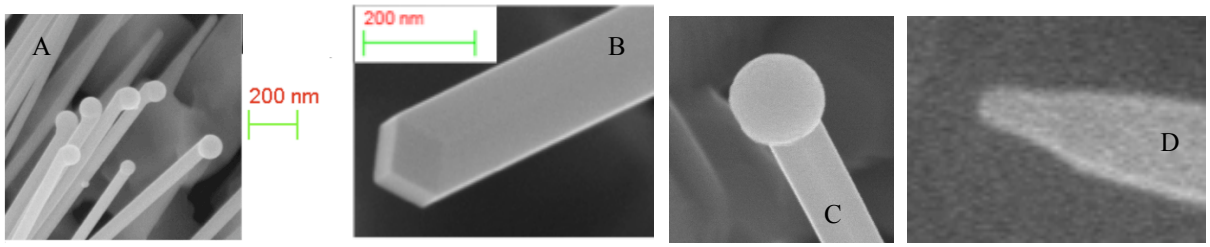
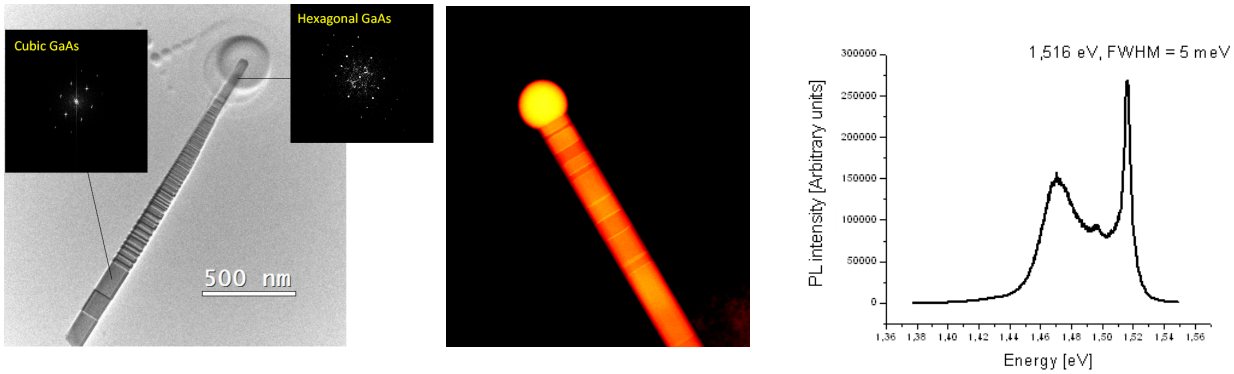
Figures



(Fig. 1) A: scanning electron microscopy images of the different GaAs NW types grown on GaAs (100). B: example of high As/Ga BPR growth, NWs are pyramid terminated; C: example of low As/Ga BPR growth, NWs are droplet terminated; D: example of growth with average As/Ga BPR, the nanoparticle is being consumed.



(Fig. 2) transmission electron microscopy images of the different GaAs NW types. Left: pyramid terminated NWs showing from the base, a pure zincblende phase, followed by a mix of zincblende and wurtzite and finally pure wurtzite phase in the top part; middle: droplet terminated NWs with pure zincblende structure; right: low temperature photoluminescence spectrum of the wires ensemble.