1.3.1 Semiconductor nanowires: growth mechanisms and dynamics

Semiconductor nanowires (NWs) are strongly anisotropic single crystals that can be obtained by exploiting bottom-up growth techniques. This approach allows to obtain NWs with very high aspect ratio and also complex axial and radial heterostructures in which materials that are incompatible in standard epitaxy can be combined together with a large flexibility. These properties make NWs attractive both for fundamental studies and for device applications in the field of electronics, photonics, chemical sensing and energy conversion. NW-related activities at NEST started in 2008 with the installation of the chemical beam epitaxy laboratory dedicated to the growth of III – V semiconductor NWs. Since then, research activities have involved an increasing number of other laboratories at NEST, from the nanofabrication facilities to the transport and superconductivity labs, making NEST nowadays an important player in the international NW community.

Within the class of 1D nanostructures, semiconductor NWs possess several unique characteristics, representing one key area in nanoscience and nanotechnology [1-3]. Their very high surface-to-volume ratio makes them interesting for efficient interaction with light, energy conversion, catalysis and sensing application. Another peculiarity of semiconductor NWs is their nanometer-sized diameter, which gives the opportunity for quantum confinement of the charge carriers. Moreover, it allows an unprecedented degree of freedom in the growth of dissimilar materials in defect-free axial heterostructures, thanks to the efficient relaxation of the stress on the sidewalls. Radial heterostructures where the chemical composition of the material is modulated perpendicularly to the wire axis can also be grown. In this case, the controlled growth of one or more shells can passivate existing surface states, enable new interface properties, and introduce unique electronic, phononic and plasmonic features. In the last 5 years, NWs activities at NEST focused on two complementary fronts: (i) the progress of growth processes for the synthesis of innovative nanostructures and (ii) the development of novel devices based on NWs and related heterostructures. In this contribution we will describe the main results related to the growth activities.
At the heart of the success of NWs as versatile building blocks for nanoscience and nanotechnology is the development of a general strategy for the controlled growth of these materials. The most widespread approach for the growth of NWs is the nanoparticle (NP)-mediated growth technique known as vapor-liquid-solid (VLS) mechanism. Usually Au is used to catalyze the NW growth, because of its chemical inertness and its capability of forming liquid eutectic alloys with major semiconductor materials at the growth temperature. Au NPs can be obtained with various methods, like the annealing of Au films (Fig. 1a), dispersion of colloidal solutions and electron beam lithographic techniques. Different NP preparation methods result in different NW size distribution and areal densities, therefore the choice of the growth method is crucial for controlling NWs density, diameter, length and crystal structure, as we have demonstrated for Au-assisted InAs NWs [4, 5].
The possibility to expand the range of material combinations in defect-free heterostructures not achievable in standard thin film epitaxy is one of the most attractive properties of NWs. Some examples of axial NW heterostructures realized at NEST in the last years are GaAs/InAs NWs (Fig. 1b), InAs NWs with built-in InP barriers forming quantum dot systems within a single NW (Fig. 1c), InP NWs with embedded InAs quantum dots and quantum wells (Fig. 1d), InAs/InSb NWs (Fig. 1e).

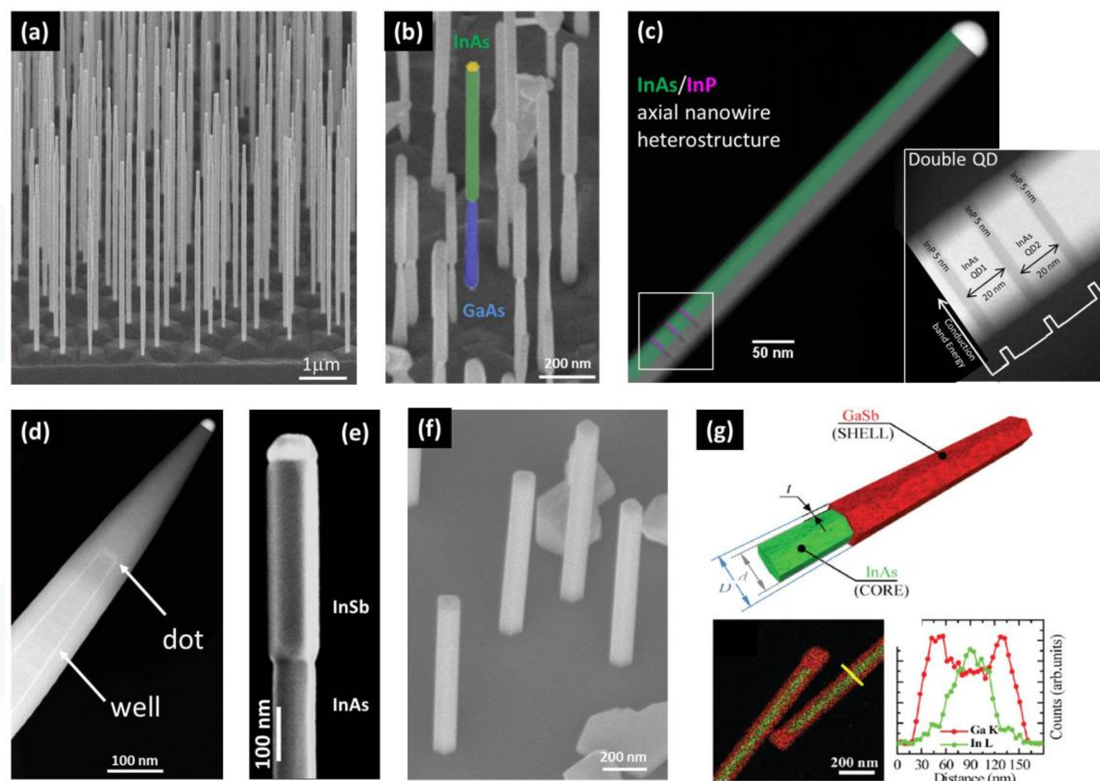

Figure 1. (a) 45°-tilted SEM image of Au-assisted InAs NWs grown on InAs(111)B substrate with 0.5 nm thick Au film. (b) 45°-tilted SEM image of GaAs/InAs axial heterostructured NWs grown on GaAs(111)B. The false-colors highlight the presence of the 2 materials in the same NW. (c) InAs NW with built-in InP barriers defining a double QD system (the inset is a STEM image of the double QD structure). (d) STEM image of a single tapered InP NW with an InAs quantum dot and well (bright contrast). (e) InAs/InSb axial heterostructured NW. (f) 45°-tilted image of catalyst-free InAs NWs grown on Si(111) substrate. (g) InAs/GaSb core/shell NWs (schematics of the single NW structure (top) and EDX elemental map and cross-sectional profile of the grown NWs (bottom).

The Au-assisted VLS growth approach allows an extremely high flexibility to grow different materials in axial NW heterostructure with very good crystal quality, size and shape control. However, the different interactions among the Au NP and the growing materials may affect the growth mode and the interface sharpness. Indeed, many axial NW heterostructures suffer from compositional gradients at the heterointerfaces and kinking or downward growth. Understanding such interactions is fundamental to achieve a full control over the morphology and the properties of the NW heterostructures. In this context, we have investigated the Au-assisted growth of GaAs/InAs and InAs/InP axial NW heterostructures and we found that the nanoparticle composition controls the growth mode and dynamics. In particular, for the straight growth of InAs segments on top of GaAs NWs, we found that the NP stability that determines the straight or downward growth is related to the change of composition of the III/Au alloy NPs at the flux commutation. Only high group III concentrations, hence large NP contact angles allow to obtain straight GaAs/InAs axial NW heterostructures [6]. Similarly, for the growth of InP segments on InAs NW stems we demonstrated that the sole parameter affecting the growth mode is the NP composition that changes at the material exchange. As a consequence, straight untapered InAs/InP NW heterostructures can be obtained only when the In/Au ratio in the NPs and hence the contact angle is kept under a certain critical value by properly choosing the

growth conditions [7]. Moreover, the NP reconfiguration at the InAs/InP switch strongly affects the growth of thin alternating InAs/InP segments. We analyzed the growth dynamics, the nucleation delay and the thickness/diameter dependence of thin alternating InAs/InP segments and we found a strategy to control the growth rate by forcing the nanoparticle reconfiguration before starting the next NW segment. This allows for the realization of InAs/InP nanowire heterostructures with a precise control over the segment thicknesses [8], essential for their implementation in quantum devices.

Despite the very good control of NWs aspect ratio and the high flexibility for the growth of NWs with the desired parameters, the Au-assisted growth may introduce the potential for unintentional incorporation of impurities degrading electronic and optical properties of the grown semiconductors and is not compatible with current CMOS technology. Consequently, Au-free techniques for the growth of III–V NWs are required to overcome these challenges. For this purpose, in the last few years we have developed two different strategies for the Au-free growth of InAs NWs on silicon substrates: the so-called catalyst-free and self-catalyzed growth. In the first case the NWs are grown without any NP (Fig. 1f). We have investigated experimentally and theoretically the heterogeneous nucleation and the growth mechanism of InAs NWs on Si(111), finding that surface defects, whose density can be controlled by the substrate preparation technique, act as nucleation sites and that the growth conditions (temperature and precursor fluxes) play a major role in driving the anisotropic NW growth and determining the final NW aspect ratio [9, 10]. In the second approach, Indium NPs are generated by using In-rich growth conditions and used to drive the NW growth via the VLS mechanism [11]. Also, in this case we have described the growth with a theoretical model that allowed us to extract relevant growth parameters, providing useful guidelines to rationally control the growth of Au-free InAs NWs for various applications.

Catalyst-free NWs are particularly suitable for the realization of radial heterostructures (core-shell NWs) because the axial growth can be almost completely suppressed and the radial growth enhanced by properly choosing the growth conditions. In this context, a very interesting material system consists of InAs/GaSb core/shell NWs (Fig. 1 g). InAs and GaSb have a very low lattice mismatch (0.6%), broken-gap band alignment (type-II) and small effective masses of electrons and holes in InAs and GaSb regions, respectively. Indeed, electronic devices fabricated with these heterostructures combine closely-spaced n-type and p-type conductors, and can display negative differential resistance due to transport across the broken gap junction, as we have demonstrated in [12].

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