TEM and CL of semiconducting 1D nanostructures

Laura Lazzarini

IMEM-CNR, Viale Usberti 37/A, 43124 Parma, Italy.

laura@imem.cnr.it
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The advanced discovery and development of nanometric-scale-structured materials with innovative properties requires investigation techniques able to perform characterizations on this scale. In this work, the results obtained by the combined use of TEM and high lateral resolution FESEM-CL on 1D nanostructures (NS) of various semiconducting materials systems, such as ZnO and AlGaAs-GaAs, will be shown. A correlation of structural, chemical and optical properties has been obtained on single NS.

ZnO is a very attractive material due to its unique optical, piezoelectric and magnetic properties. It very easily crystallizes in the wurtzite phase in a variety of NSs, such as nano-wires, ribbons, tetrapods, spings, combs. Achieving the presence of cubic and hexagonal phases in the same NS could offer novel routes in the design of nanodevices made by a single NS, as the two phases exhibit different band gaps, electronic and elastic properties. The nucleation of the bulk cubic (zinc blende) crystal phase along the wurtzite arms of ZnO tetrapods grown through a vapour-solid mechanisms has been observed for the first time (Figure 1). The structural and optical properties of single tetrapods have been studied by HREM and SEM-CL spectroscopy and imaging. The results showed a one-to-one spatial correspondence between the monochromatic CL imaging of the NBE emission of the ZB phase and HREM pictures. No other ZnO NSs like nanowires or nanocombs, grown with the same method, present the cubic phase. This fact has been ascribed to the different growth conditions used. The influence of the temperature gradient inside the furnace has been qualitatively correlated to the onset of alternating bulk ZB/WZ phases inside the arms, which seem to depend also on the tetrapod size.

GaAs–AlGaAs materials combination represents a prototypical system in semiconductor optoelectronics and the growth in form of core–shell nanowires adds further potentials for device applications. Moreover, the use of AlGaAs as shell material leads to almost strain-free nanowires, simplifying the analysis of their electronic/optical properties. AlGaAs shells were grown at 650 °C around GaAs nanowires by conventional MOVPE, with thickness ranging in the 70–160nm interval. The composition of the nanowires shells were studied by Z-contrast TEM observations, as well as by EDS, indicating a uniform composition for the AlGaAs alloy, with x_{Al}=0.32. Low-temperature PL and CL measurements were performed, respectively, on dense ensembles of core–shell nanowires and single nanowires; comparison between secondary electron and monochromatic CL images of single nanowires led to spatially resolve the major CL emissions as shown in Figure 2. The low-temperature CL luminescence spectrum consists of four contributions: the 1.96 eV excitonic recombination of the $Al_{0.33}Ga_{0.67}As$, assisted by GaAs-like LO phonons; a broad weaker band at _1.90 eV, ascribed to a donor–acceptor pair recombination associated to residual Si donors in the AlGaAs; a dominant and very broad band at _1.67 eV, due to the spatially indirect recombination between electrons in the core and holes in the shell, and the GaAs core emission peak energy at 1.49 eV interval. This latter energy varies in the interval 1.46-1.49 eV, and red-shifts by decreasing the V:III ratio. This effect is tentatively ascribed to the build-up of a space-charge induced electric field region at the core-shell hetero-interface,

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the latter associated to the unintentional incorporation of C in GaAs and Si in AlGaAs: a higher carbon concentration is actually found by EDS within the GaAs core than in the shell, that also presents lower Z-contrast signal.

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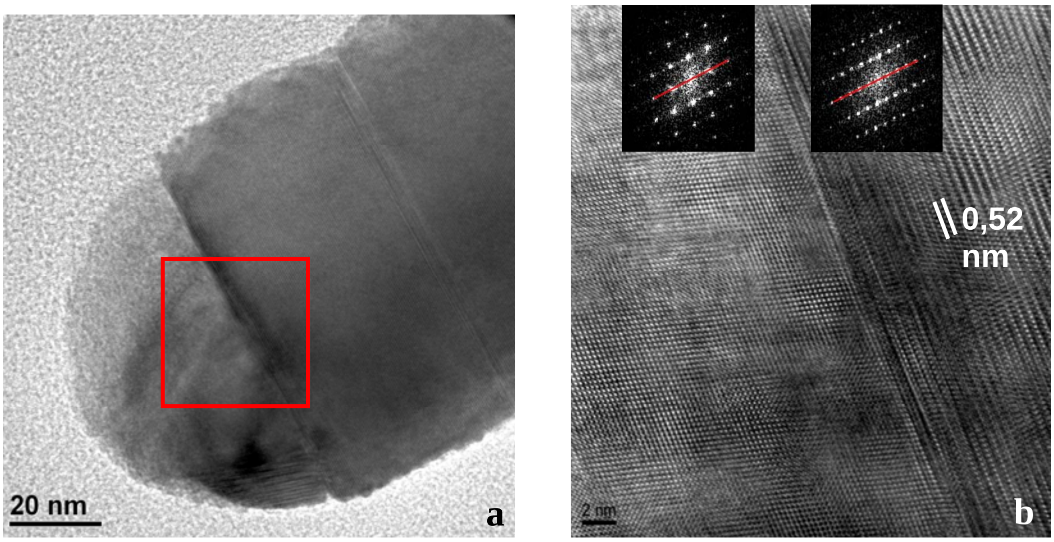

Figure 1: a) HREM image of a TP tip terminating with ‘bulk’ ZB phase. b) the square region in a) at higher magnification, showing the interface between the WZ phase (right) in the (21-10) projection and the ZB phase (left) in the (110) projection.

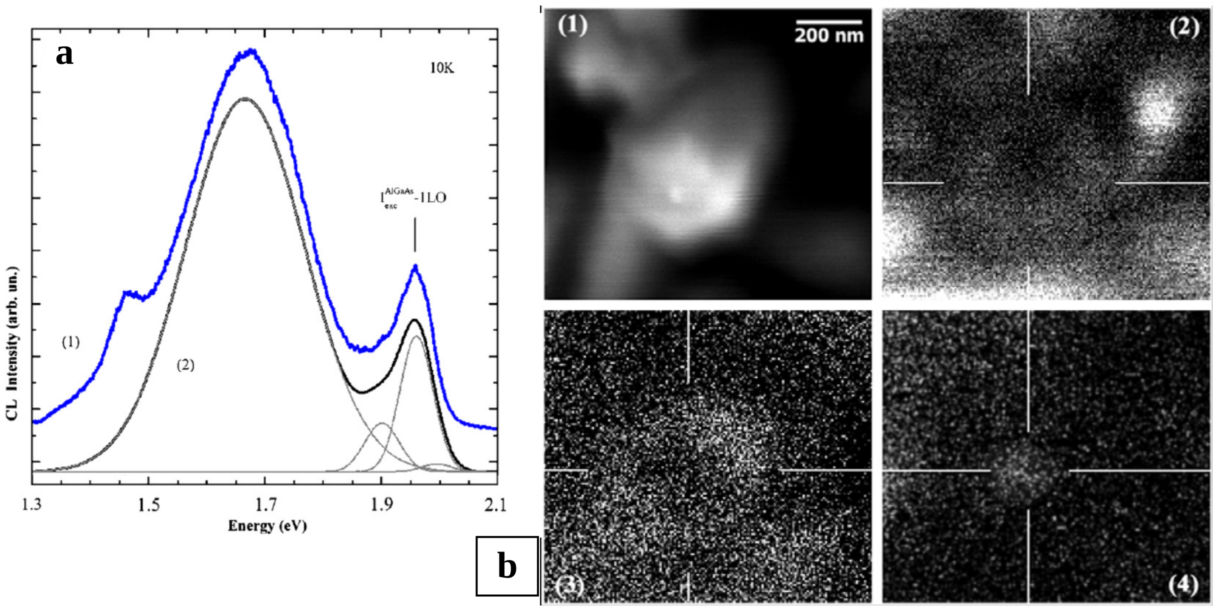

Figure 2. **(a)** Low temperature CL spectrum recorded on a few GaAs/AlGaAs core–shell nanowires (b) FESEM micrograph of one of the nanowires, from which the spectra in (a) is taken, viewed with its axis almost normal to the image plane (1); (2)-(4) are monochromatic CL images recorded at various photon energies, (2) 1.96 eV (633 nm), (3) 1.65 eV (750 nm)), and (4) 1.46 eV (850 nm).

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