Crystal facet engineering in Ga-doped ZnO nanowires for Mid-IR plasmonics

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The MOCVD growth of various Ga-doped ZnO (GZO) nanostructures for plasmonics is investigated, such as spontaneous or Au-catalyzed GZO nanowires, and ZnO/ZnO:Ga core/shell 1D structures. Indeed, in degenerate wide bandgap semiconductors such as n-type ZnO, the electron concentration can be tuned, thus allowing to expand the spectacular properties of plasmonic nano-objects to the infra-red range.

Undoped ZnO nanowires typically grow along (0001) C-axis and exhibit (10-10) M-facets with hexagonal morphology. However, literature shows that growth direction, morphology and facet orientation can be tuned by adding a dopant in the source material (in CVD processes) or metal ions in the solution (e.g. hydrothermal growth). This work focuses on the nanowire facet transformations induced by the addition of trimethylgallium in the gas phase. For spontaneously grown ZnO nanowires, the morphology evolves rapidly towards Christmas-tree like and hierarchical structures upon intentional Ga doping. Regarding ZnO/ZnO:Ga core-shell structures, a change of the smooth initial M-oriented facets occurs, with the development of {20-21} surfaces, and further {10-11} and {0001} surfaces. Interestingly, a similar evolution of the lateral roughness is observed in Au-catalyzed doped nanowires. SIMS measurements reveal high Ga concentrations from 10^{19} up to 2.10^{21} at/cm³ in the doped ZnO reference layers. In addition, photoluminescence spectra show an increase of the donor bound exciton emission at 3.358 eV, assigned to Ga impurities. The influence of Ga doping on the facet transformations and the occurrence of unexpected {0001} polar surfaces are discussed. The results can be mainly understood by a Ga surfactant effect (at least partial) responsible for the modification of the surface energies and kinetics. In particular, density functional calculations support the floating behaviour of the negatively charged Ga⁻ ion on the growing surface. Finally, first photoacoustic measurements show an optical absorption at 6 µm, evidencing that the degenerate material is suitable for plasmonic applications in the IR range.

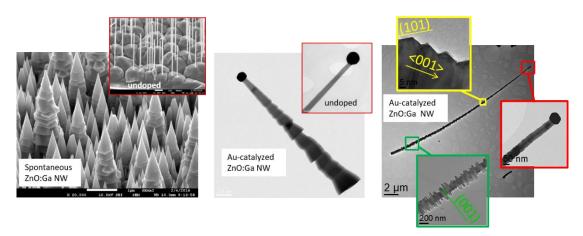


Figure: morphology of several Ga doped nanowires grown by MOCVD