N-incorporation in MOVPE-grown GaNAs/GaAs planar and nanowire structures using tertiarybutyl-hydrazine

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Dilute nitride III-V compounds (III-N-As) are candidates for application to high efficiency *intermediate bandgap solar cells* (IBSCs). Doping of group-III arsenides and phosphides crystals with nitrogen (N) atoms, in substitution of group-V atoms, leads to the introduction of N-impurity localized states and the formation of an intermediate band-gap at energies below that of the host material CB edge.[1] Theoretical calculations have shown that ideal IBSCs based on III-N-V compounds with N concentrations in the 1−3 % range can achieve efficiencies above 60% under concentrated solar power irradiation.[2] Demonstration of the key operating principle of a IBSC has been reported for GaNAs-based heterostructures grown by plasma-assisted MBE and MOVPE. We recently proposed[3] nanowire-IBSCs based on III-N-V compounds as promising systems to overcome many of the limitations encountered so far in planar heterostructured IBSCs; indeed, the combination of IBSC functionality with the unique physical properties associated with core-multishell nanowires-based devices would effectively allow photovoltaic cells with unprecedentedly high conversion efficiencies, simpler junction geometry, and low materials usage.[4]

N-incorporation into GaNAs during MOVPE depends on specific combinations of N-precursor, reactor fluid-dynamics and crystal orientation. In this work we use *tertiary-butyl-hydrazine* ($^{t}BuN_2H_3$) as N precursor, as its relatively weak tertiarybutyl-N bond makes it less stable with respect to other N-precursors, allowing growth temperatures <560°C. Trimetyl-gallium (Me_3Ga) and tertiarybutyl-arsine ($^{t}BuAsH_2$) were used as Ga and As precursors.

Planar GaNAs/GaAs epitaxial samples were grown on (100)-, (111)B- and (110)GaAs substrates. The latter two orientations relate respectively, to the substrate orientation employed for the VLS self-assembling of III-V nanowires, and the sidewall orientation of GaAs nanowires over which GaNAs shells are overgrown. Samples were grown under different As:Ga and N:As precursor ratios in the vapor. GaAs-GaNAs core-shell nanowires were grown by Au-catalyzed (VLS) self-assembly[5] on (111)BGaAs substrates in the form of dense nanowire arrays.

Planar and nanowire samples were characterized by high resolution XRD (HRXRD) and photoluminescence (PL) to determine the heterostructure elastic strain and N content (x) of GaN_xAs_{1-x} layers/shells. For each sample both symmetric and a-

symmetric HRXRD reflections were measured, and the experimental patterns were compared with simulations performed using the dynamical diffraction theory (Fig. 1a). (100)-oriented epilayers were pseudomorphic (i.e., unrelaxed with respect to the underlying GaAs substrate), with a N composition x in the range 0.23−0.58%, increasing with the N:As precursors ratio in the vapor. No diffraction peaks ascribable to a GaNAs alloy could be detected instead, for samples grown on (111)B substrates, indicating negligible N-incorporation (x<0.01%) for (111)B-oriented epilayers. 7K PL confirmed the formation of the GaNAs intermediate gap (Fig. 1b) in quantitative agreement with N-compositions, as determined by HRXRD.

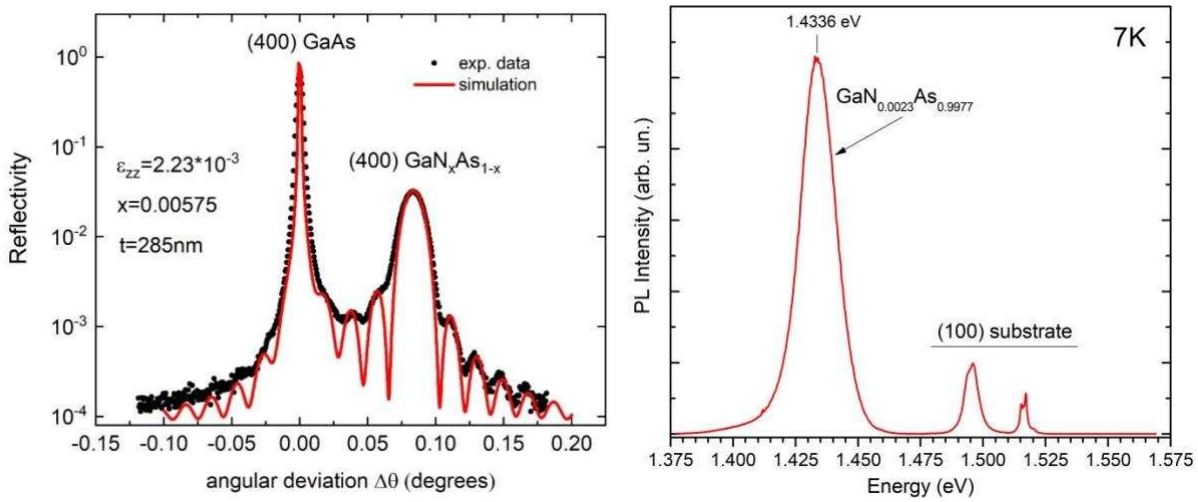

Figure 1: Experimental (black dots) and simulated (red curve) HRXRD pattern of a GaN_xAs_{1-x}/(100)GaAs (x=0.575%) sample (a); 7K PL spectrum of a GaN_xAs_{1-x}/(100)GaAs (x=0.23%) sample (b).

Present results allowed to determine the solid-vapor distribution curve for Nincorporation in GaNAs using $^tBuN_2H_3$ and compare with recent data in the literature.[6] Axial strain and N-content in GaAs-GaNAs core-shell nanowires were finally, determined based on the heavy- and light-hole free-exciton blue-shift of GaAs in the nanowire PL spectra, as induced by the GaAs-GaNAs lattice mismatch.

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