

Title: Ga clustering and Ga-H interaction in virgin and hydrogenated InGaN/GaN nanostructures addressed via Ga K-edge diffraction anomalous fine structure spectroscopy

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Nitride semiconductors have fundamental properties that make them useful in several applied contexts. In particular, indium-gallium nitride ( $\text{In}_x\text{Ga}_{1-x}\text{N}$ ) alloys have enormous potential for solar energy harvesting and efficient lighting, thanks to their direct band gaps spanning the spectrum from near-infrared to near-ultraviolet. While the Ga-rich region of this material system has been widely investigated and exploited in technology, the same is not true for the In-rich region, which is characterized by huge, unintentional n-type conductivity. One of the possible causes of n-type background conductivity is hydrogen contamination. The behaviour of H in  $\text{In}_x\text{Ga}_{1-x}\text{N}$  is not trivial since it has been shown that H behaves as a donor in InN and as an amphoteric impurity in GaN. We showed that  $\text{In}_x\text{Ga}_{1-x}\text{N}$  epilayers deliberately hydrogenated via low energy ions are characterized by a reversible blue-shift of the photoluminescence emission peak after hydrogenation by an amount which monotonically decreases with decreasing  $x$  and vanishes for  $x \sim 0.49$ . This blue-shift is accompanied by a remarkable broadening of the interatomic distance distribution in the cation sublattice, as evident in the Fourier transforms (FT) of In K-edge EXAFS spectra. Both effects are understandable under the hypothesis of formation of specific In-H complexes in which four H atoms screen the effect the crystal potential has on the In cation, virtually isolating it from its environment. The genesis of these “solitary cations” brings about an increase of the fundamental band-gap energy.

Nonetheless, until today it has been still an open question whether the Ga local environment is affected by hydrogenation and whether “solitary” Ga may form; in fact the presence of a GaN buffer layer in the epitaxial InGaN(25 nm)/GaN(160 nm)/AlN/sapphire template used hinders access to such information by EXAFS. In this work, we present Diffraction Anomalous Fine-structure Spectroscopy (DAFS) data taken at the Ga K-edge and using the (0002) crystal plane reflection on series of virgin and hydrogenated InGaN epilayers. DAFS couples chemical and crystallographic selectivity and allows us to address the environment of Ga atoms in the InGaN epilayer, which XRD peak can be separated from the one of the buffer. DAFS has been performed at the new SIRIUS beamline of SOLEIL.

From quantitative analysis of DAFS we find that 1) deviation from cation random distribution in form of Ga clustering is present in most InGaN samples (both virgin and hydrogenated); 2) there is no big broadening of the second shell distance distribution in hydrogenated samples differently from what observed by In K-edge EXAFS, however, 3) for the samples expected to lay in the solitary cation regime the second shell differs from the one of the ternary alloy, possibly due to perturbation of the cation sublattice consequent to the formation of the In-H complexes.

We conclude that the observed Ga clustering is an important phenomenon to be taken into account for technological applications since it may affect the emission properties of the alloys. As for the effects of hydrogenation, our results suggest that formation of Ga-H complex is

improbable, however they confirm that modifications of the cation sublattice take place for certain hydrogenation doses and In concentrations. The understanding of the hydrogenation mechanisms is important in the perspective of using it as a novel route for tuneable, postgrowth band-gap engineering.