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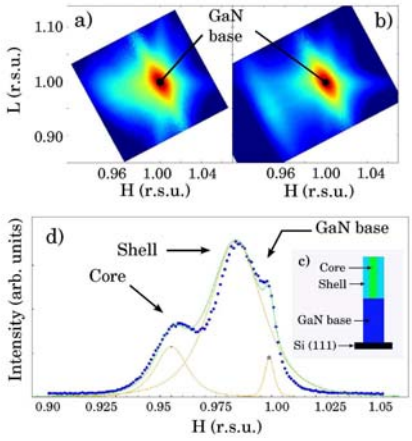
Report:

We studied the local atomic structure of InGaN Nanowires (NWs) grown by Molecular Beam Epitaxy (MBE) onto a GaN base. The NWs have different morphologies depending on the growth conditions: homogeneous In distribution (*sample 1*) or core-shell structure (*sample 2*) in which an In-enriched region forms spontaneously along the NWs axis. Different optical properties correspond to the different morphologies, i.e. the PL spectra as a function of temperature of the core–shell sample exhibit a typical S-shape feature characteristic of carriers localization that is not the case for the homogeneous NWS. Localization of holes has been demonstrated experimentally by Chichibu *et al.*[1], who proposed a hole localization process, associated with atomic condensates of In-N. Such a mechanism could be associated to a deviation from InGaN alloy randomness and to the hypothetical formation of In-N-In chains or InN clusters of a few In atoms. To date, only two experimental observations at the atomic scale consistent with a kind of weak phase separation or In aggregation have been found [2-4]. In this project we have performed EXAFS experiments at the In K-edge to study the local atomic environment of the In atoms and to investigate the existence of these phenomena.



The samples were characterized by X-ray diffraction (XRD) and Multiwavelength Anomalous Diffraction (MAD). Fig.1, shows Reciprocal Space Maps of the two samples and an *hkl* scan together with a scheme of the core-shell sample (see rep. HS4168). XRD measurements provided average lattice parameters and and MAD provided the In content in the different regions of the samples. EXAFS spectra of *sample 1* and *sample 2* were recorded at the In K-edge (27940 eV), at room temperature, in fluorescence mode at beamline BM30B. The spectra were recorded by orienting the sample surface nearly parallel to the incident beam (incidence angle equal to about 5º) and perpendicular to it (incidence angle equal to about 85º). In such a way the X-ray photons polarization vector ε was nearly perpendicular and parallel to the sample surface, respectively. The background subtracted EXAFS spectra are shown in Fig. 2. The reason for measuring EXAFS with parallel and

perpendicular polarisation is to exploit the strong anisotropy of the EXAFS probe at the K-edge. Simultaneous fitting of spectra obtained with parallel and perpendicular polarization allows us to determine the *a* and *c* lattice parameters and the In/Ga ratio, i.e. In concentration, in-plane and out-of-plane, and to detect the presence of lattice deformations due to strain and of anisotropies in composition produced by deviations from random atomic distribution in the alloy. The EXAFS signals were calculated for a cluster of InN composed by 50 atoms, with a radius of 5.70 Å. To include Ga atoms we calculated the same cluster substituting all the In atoms, but the central absorber, with Ga.

Sample	*d(In-N)* (Å)	d_{in} (In-In) (Å)	d_{in} (In-Ga) (Å)	d_{out} (In-In) (Å)	d_{out} (In-Ga) (Å)	*c* (Å)	$\alpha_{In,in}$ %	$\alpha_{In,out}$ %
Sample 1	2.11 ±0.01	3.31 ±0.02	3.28 ±0.02	3.26 ±0.02	3.25 ±0.02	5.29±0.02	31 ±4	21±3
Sample 2	2.13 ±0.01	3.39 ±0.02	3.34 ±0.02	3.35 ±0.02	3.33 ±0.02	5.45±0.03	54 ±8	44±4
GaN bulk	1.95	3.18 (Ga-Ga)	-	3.18 (Ga-Ga)	-	5.189	-	
InN bulk	2.15	3.54	-	3.54	-	5.708	-	

In the fit procedure the scattering paths of both clusters, involving In(Ga) as scatterers, were included and weighted by a factor *x* for In and (1 −*x*) for Ga. In such a way *x* is refined and represents the In concentration. Theoretical amplitudes and phase shifts were calculated *ab-initio* by FEFF8[5] code taking into account the beam polarization vector, *ε*, directed along the [110] and [001] crystallographic directions, corresponding to the parallel and perpendicular orientations with respect to the (0001) surface plane. The fit results are shown in the Table. Further details about the data analysis are reported in a forthcoming paper[6].

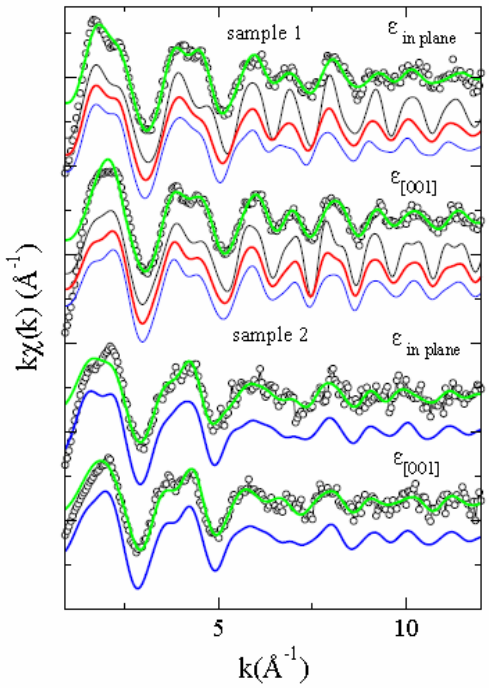


Fig.2: Experimental EXAFS spectra (open symbols) with in-plane and out-of-plane ([001]) X-ray beam polarizations, at In *K* edge, for self-organized core-shell nanowires (*sample 1*, upper panel) and homogeneous nanowires (*sample 2*, lower panel). They are compared to best fit curves (green solid lines) and to simulated EXAFS spectra (solid lines shifted downwards). The latter correspond, for *sample 1*, to structural models relaxed by *ab initio* calculations for different In content, from upper to lower curve : 6% In random distribution (black curve), 33% In random distribution (blue curve). The red curve is the linear combination of the black and blue curves taking into account the core/shell volume ratio (1/2.5). For *Sample 2*, simulated EXAFS spectra correspond to In random distribution (blue curve).

Best fit curves are shown as green lines in Fig.2. For *sample 1* we find an anisotropy in the In for the two polarization directions. It is equal to 21% for the out-of-plane polarisation and 31% for the in-plane polarization. Nevertheless, the EXAFS average In concentration is (0.31+0.21)/2 = 0.26 that is very close to the value calculated with the In concentrations found by MAD knowing the core/shell volume ratio (1/2.5) and assuming a random distribution. The anisotropic behaviour in the distribution of In-In pairs in the II coordination shell could suggest a tendency to In clustering in the growth plane and to In short range ordering in the growth direction. Unfortunately, as we cannot disentangle the shell and core contributions by EXAFS we cannot go further in detail concerning SRO in the core and shell separately.

Regarding *sample 2*, first, we find that the out-of-plane In concentration in II shell (44%) is equal, within the experimental errors, to the average value found by MAD (46%), showing that the out-of plane In distribution is random. Second, the in-plane In concentration is higher (54%) than the MAD value of 46% as for *sample 1* for but the effect is much weaker and, considering the lower S/N ratio leading to large we cannot state that a clear anisotropy is observed for *sample 2*.

Regarding interatomic distances, for *sample 1*, the d(In-N) value is close to the value for bulk InN, as expected for III-V semiconductors, in which bond distances do not follow the Vegard's law and stay close to the values of the correspondent binary compounds. The In-Ga(In) distances corresponding to the NNN atoms are quite close to each other and close to the values foreseen by the Vegard's law for alloys, as observed by other authors for InGaN[2-4]. In addition, they are smaller in the growth direction (out-of-plane) than in the growth plane (in-plane). They are also smaller than the values corresponding to the relaxed alloy. This is in agreement with the presence of *c*-matching with the Ga enriched shell region, as shown by RSM. Regarding *sample 2* the values found for *a* and *c* are quite close to the value foreseen by the Vegard's law, in agreement with the relaxed nature of this sample as observed by RSM (Reciprocal Space Mapping).

These results are consistent with previous XANES results at the In L_3 edge also reported in the forthcoming paper cited above[5]. For a thorough interpretation of the XAFS results we performed *ab-initio* simulations of L_{III} and *K* edges for a random

In distribution model. The input parameters of the structural model were the lattice parameters and compositions measured by diffraction. For *sample 1* we generated two structural models to represent the core and the shell and for *sample 2*, that is homogeneous, we generated only one model. Initially the atoms were located in the crystallographic sites of a perfect wurtzite structure, with a random distribution of In/Ga atoms. We used a 4 × 4 × 4 supercell (256 atoms). Then we performed an *ab initio* energy minimization, at constant volume, to relax the atomic positions. The calculations were carried out using the Vienna *ab initio* Simulation Package (VASP)[7]. Figure 2 shows the results of the structure relaxation for a random distribution with 33% (core, *Sample 1*) and 46% In contents (*Sample 2*).

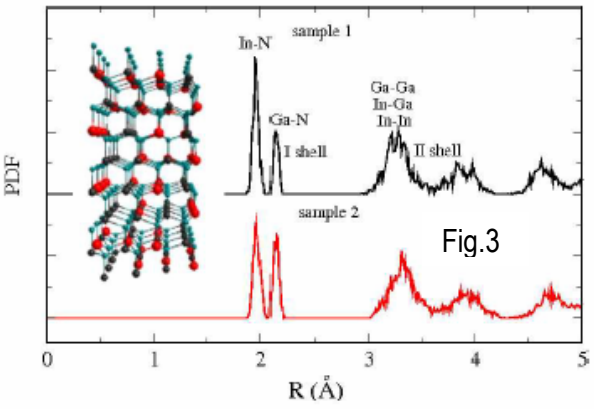


Fig.3

Then, with this structural model we performed *ab initio* calculations of both XANES at Indium *LIII* edge by using the FDMNES code[8] and EXAFS at In K-edge by using theoretical amplitudes and phase shifts generated by the FEFF8[5] code. EXAFS spectra were calculated for each In absorber in the supercell, considering the neighbours atoms belonging to a 5Å radius sphere, and averaging out all the contributions. The results are shown in Fig. 2. The experimental [001]-polarised EXAFS spectrum of *sample 1* is qualitatively well reproduced by the linear combination of EXAFS spectra corresponding to 6%and 33% In random distribution and taking into account the core/shell volume ratio. Instead, in the case of the *in-plane*-polarised XAFS the spectrum shape is not very well reproduced by the same linear combination, especially in the range from 3 Å−1 to 4 Å−1 where the simulation shows a different shape compared with experiment that corresponds to an In content lower than the experimental one. This is in agreement with the anisotropy of In concentration detected by polarised XAFS best fit results which give 31% in-plane and 21% out-of-plane with respect to 25% (random case). More details about the Short Range Order could be obtained from the EDAFS[9] (Extended Diffraction Anomalous Fine Structure) oscillations to be measured at the core and shell positions in the reciprocal space and at the In- and Ga K-edges. Regarding *sample 2*, in which the mismatch strain is fully relaxed, the experimental XAFS spectra are well reproduced by the random distribution model.

Our results show that XAFS and MAD data can be interpreted in a coherent way providing evidence of an anisotropic In distribution in InGaN core/shell nanowires. That is, there exists more In-In pairs in-plane than out-of-plane with respect to the random distribution. We also observe that this takes place in *sample 1* which has a strained In enriched core and barely not in *sample 2* which is homogeneous and relaxed. Therefore, the driving force for the anisotropic distribution could be the presence of mismatch strain along the *c*-axis due to the formation of the Ga enriched shell region. The *c* mismatch strain is in turn due to the peculiar growth mechanism of the core-shell nanowires during which the In enriched core and the Ga enriched shell are spontaneously formed and grow simultaneously[10]. Our findings are in agreement with the results of Ref.4 in which the authors found an anisotropic In distribution in the In second shell coordination. In that case the number of In In pairs was higher than what expected for a random In distribution, for the out-of-plane polarisation direction. Interestingly, the samples of Ref.4 were planar epilayers of InGaN/GaN with in-plane compressive strain and outof- plane tensile strain. In our case we find an anisotropy of opposite sign but also, the strain is opposite compared with Ref.4. Indeed the In-rich core is compressed in the growth direction by the Ga-rich shell. It would point to a tendency of In to condensate in the direction of tensile strain. Also in our case the sample showing this feature of In condensation shows a higher PL efficiency, as for the anisotropic sample of Ref.4. Although the true nature of localisation in InGaN is still under debate, it is worth pointing out that our results are in agreement with the existence of In-N-In atomic condensates which have been hypothesized to explain the defect-insensitive emission probability of InGaN materials[1].

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