Grazing Incidence Diffraction Anomalous Fine Structure (DAFS) study of InAs-InP buried Quantum Wires

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We apply x-ray anomalous diffraction in grazing incidence and X ray absorption spectroscopy to the study of encapsulated semiconductors nanostructures. We study InAs Quantum Wires grown by Molecular Beam Epitaxy onto InP(001) substrates. The x-ray energy is tuned across the absorption As K-edge making diffraction chemically selective, as absorption, to get direct information on composition. *hkl*-scans close to the (442) Bragg reflection of InP at several energies above and below the As k-edge, allow to extract the partial structure factor $F_{A=As}$ of the As atoms. Quantitative analysis of the oscillatory extended region above the edge give information on composition and out-of-plane strain of the wires. The absorption and diffraction results are compared giving further insight giving different views of the As local environment.

I. GIDAFS MEASUREMENTS

Grazing incidence Anomalous diffraction (experiment HS2641) at the As K-edge (11.867 keV) was performed at the French Collaborating Research Group beamline BM2. The grazing incidence geometry allows to optimize the interaction of the X-ray beam with the sample minimizing the substrate contribution. In a previous experiment we studied a sample labelled CP1276 [1], the results have been published in reference [2], for comparison we report on experiment carried out with another sample labelled I3701, grown under different experimental conditions.

II. DATA ANALYSIS

A. hkl-scans and As partial structure factor

We performed l-scans (h=k=3.98, $l\in$[1.6-2.3]), at several energies (12) close to the As K-edge, taking advantage of the As anomalous variation to identify As contribution in reciprocal space. In figure 1a) the square root intensity $\sqrt{I_{obs}}$ curves are compared for the two samples to F_T, the complex structure factor of phase φ_T that includes the overall contribution of non anomalous atoms and the Thomson scattering of all anomalous atoms, and to $F_{A=As}$, the complex structure factor of phase φ_A that includes the Thomson scattering of all anomalous atoms. F_T and F_A are extracted according to the Multi-wavelength Anomalous Diffraction (MAD) principles [2, 3].

One can see that the F_A profile is quite different for the two samples. For sample CP1276 the F_A contribution is quite symmetric and shows a defined maximum at l=1.9. Assuming that the size effect dominates on the F_A shape we deduced from the Full Width at Half Maximum of $F_{A=As}$, that the QWrs height average value is about 2.54nm, that is close to the value measured by TEM.

For this sample we performed FDM, in our previous study [2], calculations to obtain theoretical strain maps based on a periodical 2D structure coherently grown on the InP substrate according to biaxial elastic strain. The FDM simulations reproduce well the F_A shape and maximum position with an ε_{zz}= 6.1% showing that the wires are partially relaxed in the (001) direction with respect to pseudomorphic case (ε_{zz}= 6.7%). In case of sample I3701 the extraction of F_A gives more complex results. The F_A shape is no longer symmetric and we cannot actually see a well defined maximum. It also shows a kind of satellite feature and a minimum coinciding with the F_T minimum. This suggests a more complex morphology and, likely, the coexistence of different As environments, due, for example, to a less abrupt InAs/InP interface even leading to some As diffusion inside the capping. This issue is treated below by quantitative analysis of GIDAFS (and EXAFS) oscillations.

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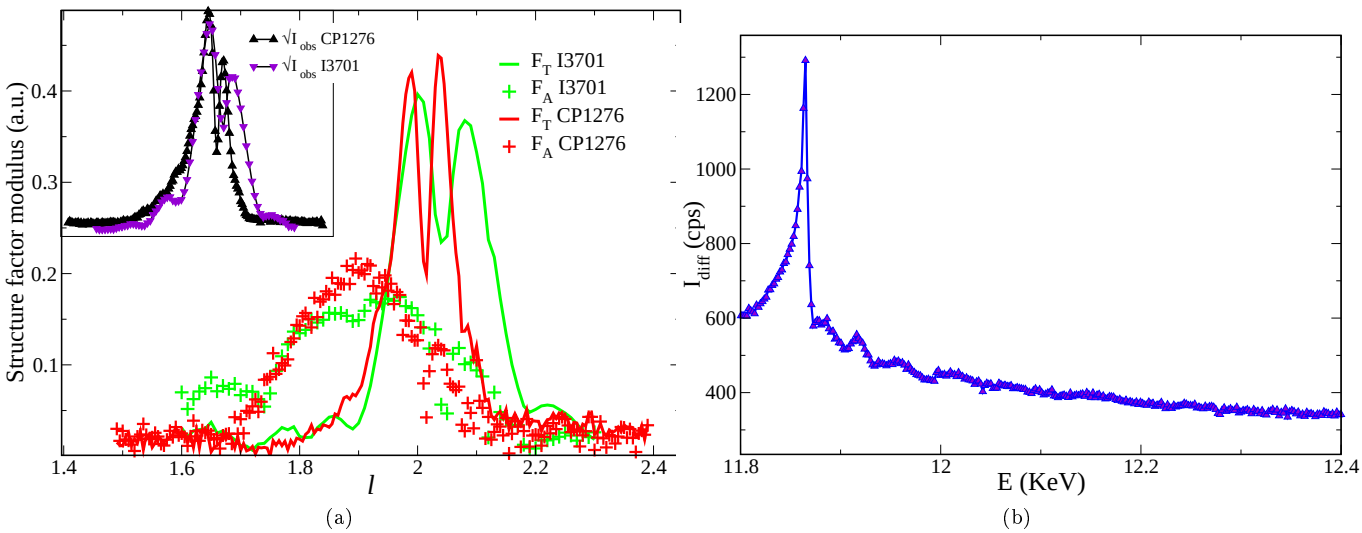

Figure 1: a) Partial structure factors F_T and $F_{A=As}$ for samples CP1276 (inset) and I3701 b) I3701 GIDAFS spectrum at the As K-edge

B. DAFS oscillations

Further information about composition and strain can be achieved by quantitative analysis of the DAFS oscillations, showing up in the extended region after the absorption edge. We show in figure 1b) the I3701 GIDAFS spectrum measured at h=k=3.98, l=1.85. The fine structure after the edge is related to the As local environment. The DAFS measurements are quite challenging in grazing incidence and in addition, we measured the signal coming from an extremely thin epilayer (2ML equivalent thickness). Nevertheless, the signal-to-noise ratio could have been higher and the energy (k) range extended, without difficulties experienced with the monochromator 2cd crystal. The data analysis was performed according to the standard criteria and available codes for Extented X-ray Absorption Fine Structure [4, 5]. The DAFS oscillations has been analysed by fitting the theoretical signal to the experiment by means of the IFEFFIT code [6]. The DAFS measurement, for the (442) Bragg reflection, is carried out with the beam polarization vector forming angle of 23° with the normal to the sample surface, that is close to the perpendicular geometry used for EXAFS. We used the same phase and amplitudes as for the $\varepsilon_\perp$EXAFS spectra, estimating that errors on amplitudes due to the $\cos^2(\overrightarrow{\varepsilon}\cdot\overrightarrow{r})$ factor are negligible compared to the experimental errors, and we refere in the following to the DAFS spectra as $\varepsilon_\perp$spectra. Theoretical phase and amplitudes have been calculated for a bulk InAs cluster by the FEFF8 code [7], with the incident photon polarization parallel to the [001] direction (i.e. perpendicular to the surface). We also calculated theoretical phases and amplitudes for an InP cluster in which one of the P atoms was substituted by an As absorber. This was done to investigate the presence of P atoms, as Next Nearest Neighbours (NNN), in the local As absorbers environment. This is a crucial point in the fit procedure since it gives the QWrs composition at the atomic scale.

The parameters that were allowed to vary and the fit results are reported in Table I I. The scattering paths that we found to be relevant were : the Nearest Neighbour (NN) $As-In_I$ path, the NNN paths $As-As_{II}$ and $As-P_{II}$ and the three legs multiple scattering (MS) paths $As_{abs}-In_I-As_{II}$ and $As_{abs}-In_I-P_{II}$. We refined the interatomic distances of the single scattring paths, the Debye-Waller factors, the photoelectron energy origin (e0) and the P concentration (x). The path lengths for the MS paths were expressed as a function of the NN and NNN distances. Figure **??** shows the comparison of the DAFS spectrum with the best fit theoretical curve.

III. RESULTS

The DAFS results are summarized in Table I and compared with EXAFS. An interesting comparison is shown in figure 2 where the EDAFS signal for the two samples together with the best fit curves are plotted. We see that the two spectra show differences beyond the noise level. This makes a difference with respect to the EXAFS measurements exhibit very similar features. We also observe a difference in the fit parameters. The As-As and As-P distances for sample CP1276, 4.30 and 4.20Å respectively, are much more apart from each other than for sample I3701 (4.22 and 4.19Å). We also see a shift in the As-In distance that shows to be longer than for EXAFS. We have to notice that

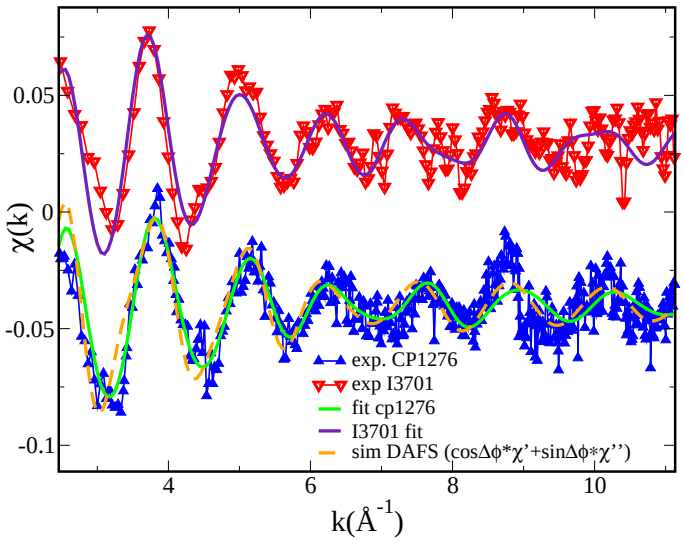

Figure 2: Extended DAFS spectra and best fit curves for samples CP1276 and I3701.

Sample→	***InAs***	***InAs/InP***	***CP1276***	***CP1276***	***I3701***	***I3701***
paths (Å)↓	***Bulk***	***(pseud.)***	***(EXAFS $\varepsilon_\perp$&$\varepsilon_{//}$)***	***(DAFS $\varepsilon_\perp$ only)***	***(EXAFS$\varepsilon_\perp$&$\varepsilon_{//}$)***	***(DAFS $\varepsilon_\perp$ only)***
As_{abs}-In_I	2,632	2,60	2,593±0,003	2,57±0,02	2,593±0,003	2,63±0,02
(As_{abs}-As_{II})$_{//}$	4,284	4,29	4,16±0.06	-	4,15±0.06	-
(As_{abs}-As_{II})$_\perp$	4,284	4,15	4,23±0,04	4,30±0,04	4,25±0,04	4,22±0,04
(As_{abs}-P_{II})$_{//}$	-	-	4,19±0,07	-	4,15±0,07	-
(As_{abs}-P_{II})$_\perp$	-	-	4,17±0,03	4,20±0,06	4,18±0,03	4,19±0,06
As_{abs}-In_I-As_{II}	4,765	5,26	4,71	4,72	4,72	4,73
As_{abs}-In_I-P_{II}	-	-	4,66	4,66	4,66	4,68
(As_{abs}-In_{III})$_{//}$	5,023	4,87	4,88±0.03	-	4,87±0.03	-
(As_{abs}-In_{III})$_\perp$	5,023	5.16	4,93±0.06	-	4,94±0.06	-
$\%P_{//}$			0,3±0,1	-	0,4±0,1	-
$\%P_\perp$			0,5±0,1	0,4±0,2	0,6±0,1	0,4±0,3
S_D	-	-	-	0.5	-	0.6

Table I: EDAFS and EXAFS best fit values for interatomic distances, Debye-Waller factors and P concentration (x) obtained by IFEFFIT mimimization using theoretical fitting standards provided by FEFF8 code. The amplitude and phase correction factors have been obtained by cristallographic analysis of the DAFS lineshape.

the S/N ratio is not as good as that of EXAFS spectra, it does not allow III shell analysis and gives larger errors on II shell distances. In the case of sample CP1276, we find a higher As-As distance and a lower P concentration with respect to the correspondent EXAFS values. We observe in fact an $As-As_\perp$ distance, 4.30Å that is close to the bulk (4.28Å) or tetragonally strained (4.29Å) values. This discrepancy can be attributed due to the different selectivities of the two techniques. EXAFS is chemically selective, DAFS instead, is chemically and spatially selective. We can state that in this case we are probing, by the two techniques, different regions in the sample : the As atoms belonging to the wires in case of DAFS and all the As atoms, wires, interface, capping..., in case of EXAFS. The values found support our previous findings of pure InAs wires with a small As/P intermixing at the interface.

The difference between the EXAFS and DAFS data for sample CP1276 is well illustrated in fig. 2 where the EDAFS best fit (solid line) is compared with the EDAFS calculated (dashed line) from the EXAFS best fit [5]. The two curves are clearly different, out of the DAFS measurement noise.

In case of sample I3701 the $(As-As)_\perp$ and $(As-P)_\perp$ distances found are closer to each other and more similar to the values typical of strained InAsP alloys. Nevertheless, the short $(As-As)_{//}$ and $(As-P)_{//}$ distances measured by EXAFS (4.1Å) shows the existence of a strained region of InAs matched to InP. The shorter $(As-As)_\perp$ distance seen both by EXAFS and DAFS could be an average between the tetragonal value of 4.29Åand the strained alloy distance of about 4.20Å. Therefore this result suggests a stronger As/P intermixing mechanism at interface for sample I3701

compared with CP1276. We must note that that in any case for both samples a phenomenon of interdiffusion As/P is detected. The comparison between EXAFS and DAFS suggests a different mechanism: a slight P diffusion through the capping volume for sample CP1276 and a more intense P diffusion at interface for sample I3701.

IV. CONCLUSIONS

In this work we pursue the study of InAs QWrs by means of GIDAFS spectrocopie. We compare two different sample grown by MBE in different growth conditions with the aim to elucidate, on one side the material properties in terms of strain and composition, and on the other side to exploit ultimate application of diffraction for the study of a challenging system as small size embedded nanostructures. We make use of grazing incidence to optimize the interaction of the x-ray beam with the nanostructure, we perform anomalous reciprocal space mapping to identify the different contribution to diffuse scattering, hkl scans to recover, in a model-free way, the structure factor of the anomalous As atoms, we record continuous energy scans, at a chosen Q value, to analyse quantitatively both the edge region and the extended region above the edge. In this way we fully profit of the spatial and chemical selectivity of diffraction.

In addition we performed EXAFS measurements which give an overall average view of the As local environment. The comparison between EXAFS and DAFS is quite interesting, showing that different atomic environments can be detected. We observe the coexistence of different As local environments : a strained pure InAs phase inside the wires and an interface region the weight and shape of which change depending on growth conditions: for sample CP1276 it looks to be sharper whereas for sample I3701 a wider interface region with an As gradient spreading out in the InP capping layer seems to be more likely.

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