Diffraction anomalous fine structure of forbidden reflection of super-ordered GaInP

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We used DAFS to probe super-ordered domains in InGaP/GaAs epitaxial growth. The sample was lattice matched InGaP epitaxially grown on GaAs with a substrate miscut angle of 6 degrees with respect to the (001) direction. InGaP epi-layer exhibited (111)-type alloy ordering, of alternating InP and GaP -like planes and giving rise to a (-5/2,5/2,-5/2) Bragg peak reflection which becomes allowed. Structural data can be extracted, at the same time, for the surroundings of Gallium in the bulk and in the epi-layer from allowed reflections, while the forbidden reflection gives structural details around Gallium in the ordered domains. Difference with the bulk InGaP Fourier transform confirms the symmetry selectivity of chosen reflections for the super-ordered domains.

Keywords: DAFS, Domains, Super-ordering, Semiconductors.

1. Introduction

DAFS is a structural spectroscopic technique suitable to investigate the crystalline structure of domains embedded in a matrix chemically not distinguishable. It is well known that important optical and electronic properties as birefringence and dichroism, (Zhang *et al.*) are resulting from arrangement of super-ordered domains with uniaxial symmetry, segregated in the solid matrix.
Evident difficulties have been found to structurally characterize domains, which are, by definition, a small percentage of the main system, with a different space organization and present same problems as "dilute systems".
We used DAFS to select, as in EXAFS, a chemical species as the absorber (Gallium K-edge, in our case) and, at one time, to select the domain contribution to the Bragg spectrum. In the system under study Gallium is present in the substrate as GaAs and in the epi-layer as InGaP with the same zinc-blende structure. The epi-layer domains of InGaP have the super-ordered structure (Alagna *et al.*), and the zinc-blende cell is doubled along the c axis. Hence the forbidden h/2 k/2 l/2 reflection becomes allowed and it is possible to deduct size and crystalline quality of the domains in the epi-layer, where two possibilities may coexist : common (111)-type long range ordering of InP and GaP alternating planes and local ordering with $(InP)_2$ and $(GaP)_1$ planes (Liu *et al.*).
The DAFS of these extra peak bears short range information around the Gallium, within the epi-layer super-ordered domains, and it is possible to extract EXAFS-like structural information (Proietti *et al.* 1998), giving details for Gallium bond distances.

2. Experimental

Nominally lattice matched $In_{1-x}Ga_xP/GaAs$ (x=0.51) hetero-epitaxial epi-layers were grown by Low Pressure Metalorganic Chemical Vapour Deposition technique using TMGa, TMIn, AsH_3 and PH_3, as source materials on GaAs substrate with miscut angle of 6 degrees off the (001) direction. The resulting surface plane is deviated toward the (011) direction.
High Resolution X-Ray Diffraction and Trasmission Electron Microscopy measurements describe sample with very high quality layers and thickness uniformity. When super-ordering is present in the cationic sublattice of group (III) along the (111) direction, the c axis is doubled and additional spots are present in the diffraction pattern corresponding to h/2, k/2, l/2 Miller indices. This reflection, that becomes partially allowed only if super-ordered domains are formed during the growth process, has been used in the DAFS study (Francesio *et al*. 1996)
Spectra have been collected at BM01 beamline at ESRF (Fr), downstream of a bending magnet, using an unfocussed beam, four circle diffractometer, monochromator and integrated software. The mounting geometry was such that the diffracted beam was collected with polarization perpendicular to (001) growth direction.
In the $\theta/2\theta$ scan two Bragg peaks, respectively for the GaAs substrate and for the InGaP epi-layer, are recorded for each allowed reflection. Driving the monochromator between λ =1.21149 Å and λ =0.91219 Å, across the Gallium K-edge, with a wavelength step of 0.0002 Å Intensity variation of each peak is recorded giving rise to two DAFS spectra, selectively due to Gallium in the substrate and Gallium in the epi-layer
An extensive range of data has been collected in order to study the reliability of data with noise level compatible to structural parameters extraction. Five scans have been accumulated for both allowed and forbidden reflection
More than one allowed reflection has been recorded to check both the intensity of the reflection, that allows to obtain a good signal to noise ratio, and the percentage of DAFS signal with respect to the edge jump, which is typically more relevant for partially allowed reflections, being connected to the backscattering factor of the absorbing atom.
The typical (004) gave an intense signal (10^4 cps, in the pre-edge region) and the (044), chosen to have a different polarization geometry, had similar intensity.
The DAFS spectrum of the "forbidden" has been recorded using the (-5/2, 5/2, -5/2) reflection. Only one of the four possible reflections is present, indicating that super-ordered domains are formed only on the (-11-1) plane (in our geometry). The intensity, of the order of 10^3 cps, and the large variation of intensity with the energy, allowed us to obtain good data in a range sufficient to perform satisfactory data analysis.

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3. Results and Discussion

The experimental extracted DAFS spectra, for the allowed (044) and the forbidden (-5/2, 5/2, -5/2) are reported in Figure 1.
The two DAFS spectra from 044 reflection (substrate and epi-layer) are respectively reported in Figure 1a and b, while in 1c is the spectrum due to the forbidden reflection.
In the EXAFS-like analysis phase and amplitude corrections as illustrated in Proietti *et al*. (1998) have been taken into account. The analysis has been checked with the DAFS spectrum of the well known structure of GaAs and GaP..
The spectra have been checked for reproducibility and noise level in the wide collected range with satisfactory result, but only part of the range has been used in present data analysis. While experimental data extending to higher energies would increase

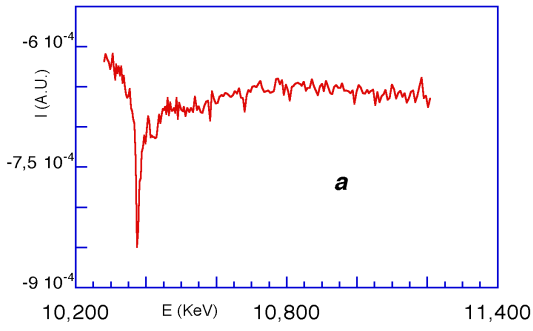

Figure 1a.. Raw DAFS spectrum of InGaP epi-layer, from the allowed (044) reflection

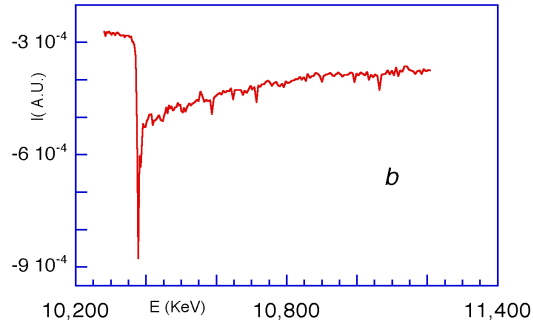

Figure 1b. Raw DAFS spectrum of GaAs substrate, from the allowed (044) reflection.

the precision on bond lengths, we have to consider that an averaged distance will be weighted towards the shorter distance because of the $1/r^2$ dependence inherent in the EXAFS theory. In our case this is of relevant importance for the forbidden reflection and we had to keep the same analysis range between known and unknown systems to avoid unwanted numerical effects affecting bond lengths precision of the unknown system under study.

The first attempt to extract bond distances and coordination numbers has been tested on the substrate peak, being GaAs extensively studied with EXAFS, and on the well known GaP. We used bulk GaP as standard. In the k range examined, between 4 and 12 $Å^{-1}$ and with R range between 2 and 5 Å, is available an over-exceeding number of independent points necessary to fit three shells both in GaAs and in GaP, and a sufficient number of independent points to fit the unknown system. Here we report the extracted data for GaP.

The bond lengths and the coordination numbers used (and not refined) in the fit for the known systems are those reported in the literature. Central atom and backscattering phaseshifts have been calculated ab initio, while E_0 has been fitted together with Debye-Waller type factors and cross section for inelastic scattering. Typical bond lengths of 2.38 Å for Gallium-Phosphorus, 3.89 Å for Gallium-Gallium and 4.56 Å for Gallium-Phosphorus 2nd

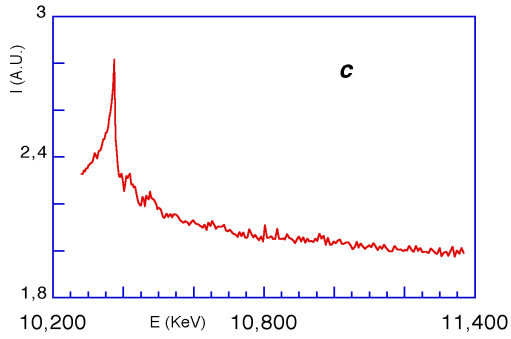

Figure 1c. Raw DAFS spectrum of InGaP super-ordered domains in the InGaP epi-layer, from the forbidden (-5/2, 5/2, -5/2) reflection

nearest neighbours have been satisfactory used to reproduce the experimental spectrum.

Once obtained satisfactory fit for GaP, the Indium has been considered fitting the InGaP epi-layer contribution from (044) allowed reflection. In this respect we have to notice that within the epi-layer there are the super-ordered domains, but they do not interfere with the epi-layer characterisation, being the (044) peak to be ascribed to the zinc blende arrangement only.

All the parameters used to simulate the GaP data have been transferred to the epi-layer spectrum, taking into account the appropriate phase for Indium and no attempt has been made to vary coordination numbers, while the Debye-Waller type factors have been kept as similar as possible to an ideal situation.

The simulation of the experimental data is fully satisfactory taking into account the literature crystallographic distances only, with errors estimated between 0.01 Å for first neighbours to a 0.1 Å for third nearest neighbours.

The best fit of the allowed reflection, to which InGaP contributes with zinc blende structure, was achieved with 4 Phosphorus at 2.40 Å, 6 Indium at 3.93 Å, 6 Gallium at 3.93 Å and 12 Phosphorus at 4.60 Å.

Once obtained the fit for the allowed reflection, the same parameters and phaseshifts have been transferred to the fit of the forbidden (–5/2, 5/2, -5/2) reflection, which has identical chemical composition.

For the DAFS data from the forbidden (–5/2, 5/2, -5/2) reflection of InGaP, and hence directly related to the super-ordered domains only, the best simulation (reported in Figure 2) has been obtained using: 4 Gallium-Phosphorus 2.42 Å, 6 Gallium-Gallium 3.91 Å, 6 Gallium-Indium 3.96 Å 6 Gallium-Phosphorus 4.57 Å 6 Gallium-Phosphorus 4.59 Å. The distant Phosphorus splitting is due to the presence of two distinct sets of second neighbours, i.e. Gallium and Indium.

The unusually long Gallium-Phosphorus in first shell is due to the measure polarisation, due to the fact that we are collecting contribution along the (110) direction. The same distance had been already reported by Tabor-Morris *et al* (1993) in a polarised EXAFS study, where contributions from ordered and super-ordered domains of the epi-layer were mixed together.

Ozolins and Zunger (1998) also theoretically predicted the parallel to (-11-1) direction Gallium-Phosphorus distance as 2.43Å.

But the very striking point is the appearance, besides the first shell of Phosphorus at 2.42 Å, of a new and unexpected Gallium-Indium distance at 3.01 Å.

This distance matches perfectly that theoretically predicted by Froyen and Zunger (1991) for fully relaxed near-surface

reconstructed structures for neutral InGaP/GaAs. The final minimum energy surface geometry presents indeed a buckled and tilted dimer with a cation-cation long distance of ca. 3 Å.
The contribution is in the same position as seen previously by Tabor-Morris *et a.l.* for the same system, but, in our case, is very clearly originated from the super-ordered domains only because the DAFS spectrum from the forbidden reflection is isolating the contribution from the domains, and is not describing the averaged epi-layer structure.

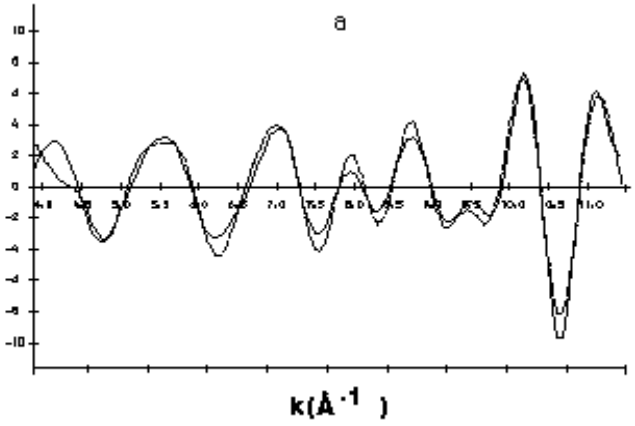

Figure 2a. Extracted DAFS spectrum from the forbidden (-5/2, 5/2, -5/2) reflection from the super-ordered InGaP domain in the epi-layer. . Super-ordered monolayers only contribute to present experimental DAFS spectrum (solid line) and calculated (broken line) due to the diffraction geometry (see text).

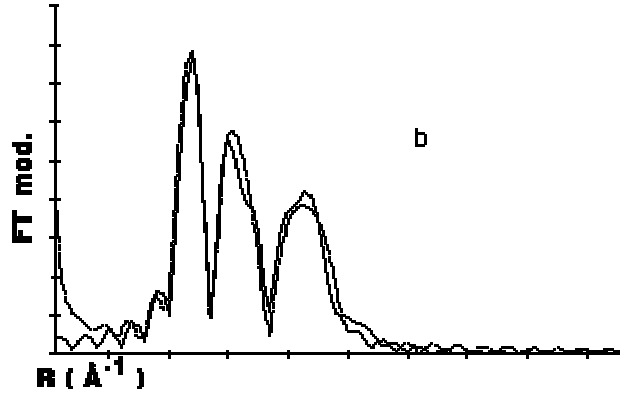

Figure 2b. Fourier Transform (solid line) and relative fit (broken line) for DAFS spectrum from forbidden reflection. Radial distances in FT are phase corrected. Super-ordered monolayers only contribute to present data. See text for discussion about the 3 Å peak

4. Conclusions

Data analysis of the obtained experimental raw data of forbidden -5/2 5/2 -5/2 reflection, allows to obtain structural information around the Gallium in the super-ordered domains with two main important findings : *i*) theoretical results indicating the existence of surface dimers driving the growth of super-ordered domains are confirmed as indicated by Froyen & Zunger (1991) ; *ii*) a long Gallium - Phosphorus bond (2.42 Å) as predicted by Ozolins & Zunger (1998) is identified .

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