Structural properties of Ge/Si(001) nano-islands and AlGaN nanowires by Diffraction Anomalous Fine Structure and Multiwavelength Anomalous Diffraction

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Abstract. In this paper, we show that combining Multiwavelength Anomalous Diffraction (MAD) and Diffraction Anomalous Fine Structure (DAFS) spectroscopy, in grazing incidence geometry, allows to obtain structural properties (strain and composition) of semiconductor nanostructures. We report results obtained on dome-shaped Ge nano-islands grown on Si(001) surfaces and AlGaN nanowires grown on Si(100). It is shown that, in the case of sharp interfaces, MAD alone can not determine the mean Ge content in the region of the substrate-island interface and needs to be combined with Extented-DAFS measurements.

1. Introduction

The knowledge of strain, chemical composition, interface quality, atomic ordering, i.e. structural properties at the long and short range scales, are of great importance to understand the growth mechanisms as well as the electronic and optical properties of hetero and nanostructures [1]. Strain is closely related to composition, shape and aspect ratio of the nanostructures, and on the mutual stress which nanostructures, substrate and the matrix apply to each other.

X-ray diffraction is known to be a powerful tool for measuring strain fields and correlations [2]. On one side, X-ray Multiwavelength Anomalous Diffraction (MAD) allows to extract the scattering amplitude of the resonant and non resonant atoms. On the other side, X-ray Diffraction Anomalous Fine Structure (DAFS) spectroscopy allows to determine the local environment, as X-ray Absorption Fine Structure (XAFS) does, of resonant atoms located in an iso-strain volume selected by diffraction (spatial selectivity). The combination of both is a very powerful approach to disentangle strain and composition. MAD records the diffracted intensity in the reciprocal space at several energies close to the energy of an absorption edge. DAFS records the diffracted intensity, at fixed scattering vector Q value in the reciprocal space, as a function of energy below and above an absorption edge, over an extended range, up to 1000eV, with
small energy steps (1 to 4 eV). The Extended DAFS spectrum (EDAFS, oscillations above the edge) provides the chemical and electronic selectivity [3, 4, 5]. Both DAFS and MAD are non-destructive methods, which provide a statistical structural information, complementary to the very local imaging given by microscopy, and they can be applied also to the case of encapsulated nanostructures.

A major improvement of the DAFS spectroscopy is to perform the experiment in grazing incidence geometry (GIMAD and GIDAFS), to reduce the scattering contribution of the substrate, allowing to focus on the nanoobjects structural properties. In the past few years, grazing incidence MAD and DAFS have been applied to materials of great technological interest as semiconductors nanostructures, for instance InAs/InP(001) quantum wires [6, 7], GaN/AlN(001) quantum dots [8, 9, 10], GeSi(001) [11]. A recent review can be found in Ref. [12], chapters 10 and 11.

In this paper we focus on the results of our most recent work combining MAD and DAFS in grazing incidence to study Ge/Si(001) nano-islands and AlGaN nanowires. GeSi alloys have been widely studied, from the beginning of semiconductor research, on one side for device applications and integration on Si-based technology [13, 14], and on the other, as a model system for semiconductor alloys. Its composition has been experimentally studied by various techniques such as energy-filtering transmission electron microscopy, electron tomography using Z-contrast imaging in scanning TEM [15, 16], x-ray energy dispersive spectrometry [17], anomalous x-ray diffraction [18] and by combining selective wet chemical etching with atomic force microscopy [19]. A strong effect of Ge-Si intermixing giving different composition profiles [20, 21, 22] has been reported. Despite the wide knowledge acquired in the SiGe/Si system, there are still open questions concerning the interplay between the strain, the intermixing and their relations with the shape of the islands. These questions will be investigated in this paper. We will show that grazing-incidence multiwavelength anomalous diffraction (GIMAD) combined with GIDAFS can be exploited to determine the mean Ge content even in the difficult region of the substrate-island interface and gather statistically significant information to correlate island composition with strain and morphology.

2. Ge/Si(001) nano-islands

2.1. Samples

We present in the following some results on Ge nano-islands grown on flat (nominal) Si(001) by Molecular Beam Epitaxy (MBE). GIDAFS measurements have been performed for samples grown under different conditions. Two different samples ($D_1$ and $D_2$) have been studied. The main growth parameters are summarized in Tab. 1. We show the Atomic Force Microscopy (AFM) images of samples $D_1$ and $D_2$ in Fig. 1. The islands exhibit dome shape. At the end of the growth, a capping was deposited at low temperature (50°C), on sample $D_2$. No capping layer was deposited on sample $D_1$.

| Sample                        | $D_1$ | $D_2$ |
|-------------------------------|-------|-------|
| Growth temperature (°C)       | 650   | 750   |
| Ge depositions (MLs)          | 5.5   | ~7    |
| Ge growth rate (nm/s)         | 0.003 | 0.0038|
| Average dome diameter / height (nm) | 80 / 19 | 140 / 35 |
| Si capping layer              | no    | 2 nm grown at 50°C |
2.2. Grazing Incidence Multiwavelength Anomalous Diffraction

MAD and DAFS measurements in Grazing Incidence were performed at beamline BM02 at the ESRF according to the experimental scheme described in previous papers [10, 26]. A linear gas-detector (Vantec-1, Bruker) was used to record the scattered intensity. Grazing Incidence \( h \)-scans, i.e. scans along surface in-plane direction \(< h00 \rangle\), were performed at 12 energies across the Ge \( K \)-edge (11103 eV) and close to the in-plane Si(400) Bragg reflections. They were performed at an incident angle \( \alpha_i = 0.1^\circ \) below the critical angle for total external reflection, \( \alpha_c = 0.163^\circ \) at 11 keV. The scattered intensity was integrated over the exit angle \( \alpha_f \) in the range of 0 to about 1.5\(^\circ\). The modulus of the Ge and Si structure factors \((|F_{Ge}|, |F_{Si}|)\) and the phase difference \( \varphi_{Si} - \varphi_{Ge} \) were recovered as a function of the reciprocal lattice unit \( h \), \( F_{Ge, Si}(h) = |F_{Ge, Si}(h)| e^{i\varphi_{Ge, Si}(h)} \) being the Ge and Si structure factors.

The composition profile, as a function of \( h \), is obtained in a straightforward way by using the following formula:

\[
\frac{|F_{Ge}|}{|F_{Si}|} \approx \frac{x_{Ge} f_{Ge}^0}{1-x_{Ge} f_{Si}^0}, \quad \text{where } f_{Ge}^0 \text{ (resp. } f_{Si}^0) \text{ are the Ge (resp. Si) Thomson scattering and } x_{Ge} \text{ the Ge concentration. In the frame of the Iso-Strain Scattering method [27] , } \alpha_f \text{-scans allow to relate } h \text{ to the height } z \text{ above the Si surface of an iso-strain region of the quantum dots (QDs). The Miller indexes } (h, k, l) \text{ are expressed in reciprocal lattice units (r.l.u.) of Si. Figures 2a) and b) show the square root of the scattered intensity at 11.053 keV } (\sqrt{I_{exp}}), \text{ the modulus of Ge and Si structure factors, as well as the Ge content, as a function of } h \text{ and } z, \text{ for samples } D_1 \text{ and } D_2. \text{ Figures 2a) and b) show a steep increase of } x_{Ge} \text{ for } h \text{ in the range of 3.97 to 3.99. This can be a real Ge composition gradient but, in the case of a sharp interface, it could also be the result of Si substrate contribution to the scattered intensity (see section 2.4). Considering the Ge concentration for } h \text{ lower than 3.97, the results clearly show a strong intermixing phenomenon leading to an island composition of about 60\% Ge (resp. 50\%Ge), for sample } D_1 \text{ (resp. } D_2) \text{ together with a slight linear increase of Ge concentration below } h=3.97. \text{ The maximum of } |F_{Ge}| \text{ is positioned at } h=3.935 \text{ (resp. } h=3.96) \text{ for sample } D_1 \text{ (resp. } D_2) \text{, meaning that the domes grown on the } D_2 \text{ sample are more strained than those grown on } D_1.

Figure 3 shows the DAFS spectra for sample \( D_1 \) measured at 3 different \( h \) values, corresponding to iso-strain regions in the dots located at 3 different heights \( z \) above the Si surface. For each spectrum, a best fit was obtained by refining \( \beta_{SiGe} = \frac{|F_{Ge}|}{|F_{Si}|} \) and \( \varphi_{Si} - \varphi_{Ge} \) in the following relation:

\[
I_{exp} \propto D(E) \times \left[ \left( \cos(\varphi_{Si} - \varphi_{Ge}) + \beta_{SiGe} \left(1 + \frac{f_{Ge}'}{f_{Ge}^0}\right) \right)^2 + \left( \sin(\varphi_{Si} - \varphi_{Ge}) + \beta_{SiGe} \frac{f_{Ge}'}{f_{Ge}^0} \right)^2 \right] \tag{1}
\]

where \( D(E) \) is the detection efficiency. The EDAFS oscillations above the edge that show up in the fit curve originate from the experimental anomalous scattering factor \( f_{Ge}' \) and \( f_{Ge}^0 \) of bulk Ge and clearly do not fit the experimental oscillations. From the \( \beta_{SiGe} \) values, the Ge contents \( x_{Ge} \) are equal to 0.62±0.01, 0.65±0.01 and 0.69±0.01, for \( h=3.939, 3.959 \) and 3.979, respectively, in good agreement with the MAD results. The corresponding phase differences \( \varphi_{Si} - \varphi_{Ge} \) are

![Figure 1. 1x1µm² AFM images of samples (a) D₁ and (b) D₂.](image-url)
equal to \(-0.61\), \(-0.965\) and \(-0.765\) rad, respectively. In case of a homogeneous random alloy we should expect a phase difference close to zero since Si and Ge atoms fill in a random way equivalent crystallographic sites. The most straightforward explanations for producing non zero phase difference are the following. First, the scattering contribution of strained Si substrate beneath the QD is not negligible for \(h\) values close to Si substrate reciprocal lattice unit (\(h=4\), for instance), thus not only the homogeneous random alloy is probed but also the upper region of substrate which produces non zero phase difference (for \(l\) different of 0). Second, this can be explained by the presence of steady out of plane Ge concentration gradient, however, in the present case MAD (and EDAFS oscillations, see 2.3) do not reveal such a gradient. Note that the phase difference is a model-free parameter, that is related to the Ge and Si spatial distribution and therefore could help a lot to unveil this important aspect of the QD morphology.

2.3. Grazing Incidence Diffraction Anomalous Fine Structure

We report EDAFS measurements performed on two samples grown in slightly different conditions, as reported in section 2.2. Figure 4 shows the background-subtracted EDAFS spectrum for one of the samples, \(D_1\), together with the corresponding best fit curves. We show, for sample \(D_1\), three experimental EDAFS spectra recorded at three different Q vector values. They are defined by \(h = 3.939\), \(h = 3.959\), and \(h = 3.979\). In such a way, according to the iso-strain method, a different region is selected along the vertical axis \(z\). The corresponding \(z\) values are approximately \(z = 3nm\), \(z = 6nm\) and \(z = 9nm\), respectively. Slight changes are observed among the raw spectra, suggesting that compositional changes as a function of \(z\) must not be large. Indeed, as shown in the numerous classic papers on GeSi alloys, the spectrum shape depends strongly on the relative Ge/Si composition due to the well known change in
the backscattering amplitude of nearest neighbor atom, when switching from one specie to the other. This is also illustrated by the EDAFS atomistic simulations that we report further in section 2.4. We performed quantitative analysis to determine both composition and interatomic distances. The analysis was limited to the nearest neighbor contribution due to the limited $k$ range (2.6-10 Å) and the S/N ratio of the EDAFS spectra. Theoretical phases and amplitudes were calculated using the Feff8.02 code [28], taking into account polarization and potential self-consistency for a sphere of 0.6 nm radius. Amplitude and phase corrections, deduced from fitting of the smooth part of the raw DAFS spectrum, have been applied. This allows us to analyze the EDAFS spectrum just as an EXAFS spectrum, according to the analysis scheme described in [5]. Fitting of theory to experiment has been performed by means of the Ifeffit code [29] implemented by the Artemis package [30].

![Figure 4](image)

From top to bottom: raw EDAFS spectra (triangles) and best fit curves (solid lines) for sample $D_1$ recorded at three different $h$ values, 3.939, 3.959 and 3.979. Curves are shifted for sake of clarity.

The best fit results are shown in table 2. The total coordination number, $N = N_{\text{Ge}} + N_{\text{Si}}$, has been fixed to 4. As expected for sample $D_1$ due to the overall spectra shape, the Ge content slightly increases from the base to the dome core, ranging from $x=0.54$ to $x=0.6$, showing that the composition change at the nano-islands/substrate interface is quite abrupt, and the Ge concentration stays almost constant as a function of $z$. This is in agreement with MAD results, except near the Si Bragg peak corresponding to substrate-island interface region (at $h = 3.979$ for instance). In this region, the Ge content deduced from MAD is lower than the one deduced from EDAFS oscillations due to the scattering contribution of strained Si substrate beneath the QDs. For sample $D_2$, that has been grown at higher substrate temperature, a stronger change in composition is observed, $x$ values range from $x=0.4$ to $x=0.52$. This is also in agreement with MAD results. Regarding interatomic distances, we observe a decrease of both Ge-Si and Ge-Ge bond lengths from the core to the dome-substrate interface. It can be associated to strain relaxation along $z$. Nevertheless, it has to be noted that due to the reduced fit $k$-range, errors are consistent (ranging from 0.02 to 0.03 Å).

2.4. Structural Modelling

We have performed atomistic calculations to model the GeSi islands. The aim is to improve the interpretation of GIMAD and GIDAFS experiment by investigating important issues as the effect of a gradient in the chemical composition on the experimental spectra, getting a detailed theoretical description of the local environment as a function of $h$ (or $z$), estimating the real-space resolution of the experiments. We have calculated the equilibrium atomic structure for islands with a height of 9.6 nm and radius 30 nm, that is with an aspect ratio of 0.16. These islands dimensions are similar to those investigated by other groups [31, 32]. In our models we have approximated the island surface as a rounded surface, neglecting, as a first step, the typical facets of this kind of nanostructures [33]. In order to obtain the minimum energy configuration.
Table 2. EDAFS best fit results for samples $D_1$ and $D_2$. Error bars on interatomic distances range from ± 0.01 to 0.03 Å. Debye-Waller factors values range from 3 to 7x10$^{-3}$ Å$^2$. Error bars on $x_{Ge}$ are of about 0.05. The correction factors, i.e. the values of the phase difference $\phi_0 - \phi_{Ge}$ and the scale factor $S_D$ have been obtained from fit of the smooth part of DAFS spectrum [5] ($\phi_0$ (resp. $\phi_{Ge}$) is the phase of the total structure factor $F_0$ (resp. Ge structure factor $F_{Ge}$)).

| Sample | $h$ | $x_{Ge}$ (Å) | $R_{Ge-Ge}$ (Å) | $R_{Ge-Si}$ (Å) | $\phi_0 - \phi_{Ge}$ (rad) | $S_D$ |
|--------|-----|--------------|-----------------|-----------------|----------------------------|------|
| $D_1$  | 3.979 | 0.54 | 2.41 | 2.40 | -2.18 | 5.5 |
|        | 3.959 | 0.57 | 2.42 | 2.40 | -1.57 | 3.3 |
|        | 3.939 | 0.6  | 2.44 | 2.41 | -1.57 | 3.2 |
| $D_2$  | 3.984 | 0.40 | 2.41 | 2.39 | -2.3  | 4.0 |
|        | 3.972 | 0.48 | 2.45 | 2.40 | -1.63 | 4.0 |
|        | 3.949 | 0.6  | 2.44 | 2.41 | -1.57 | 3.1 |

we start with all the atoms located in the atomic positions of bulk relaxed silicon. We minimize the system potential energy by means of classical molecular dynamics simulation carried out by means of LAMMPS code [35, 36], a molecular dynamics code specially designed for parallel computation, which makes feasible to manage systems with a large number of particles. The minimization consists in three steps: cooling down the system from 10 to 1 K during 2 ps, a subsequent cooling from 1 to 0.1 K during 2 ps more, and eventually we let the system reaching the minimum energy at 0.1 K, which implies about 8 ps more. The equation of motions were integrated using a time step $\Delta t = 3$ fs. To describe the interactions between atoms we have employed the Tersoff potential [37]. As the real size of the substrate can be considered infinite, to take into account this fact we have applied periodic boundary conditions to its lateral dimensions (x,y). Along z direction, we keep fixed during all the simulation the atomic positions of the deeper layer of silicon atoms as explained in the following. A similar procedure, which managed 2 million of atoms, was employed to model InAs/GaAs square nanomesas [38]. Calculations were carried out using 8 AMD Opteron 2.4 GHz machines. Minimization was completed after 3 days of computation.

One important factor that determines the atomic structure of the island is its interaction with the substrate. An important question arises: how much substrate must be included in the model? In principle the size of the substrate must be large enough to allow the island to relax as much as possible, but this could require too long computational times. As the relaxation degree of the island depends essentially on its aspect ratio [34], we have performed several tests for smaller islands, varying the size of the substrate (width and depth) to determine the effect of the substrate size on the relaxation of the island. We have found that the relaxation degree of the island depends basically on substrate depth and only slightly on substrate width. In principle relaxation equilibrium is completely achieved for a substrate depth equal to three times the island height. We found that a good trade-off between calculation times and relaxation degree is a depth of about twice the island height. Hence we have introduced in our simulations a substrate with width and depth of 124 and 22 nm respectively. The system we modelled contains about 18 millions atom, of which 17 million correspond to the substrate.

To investigate the composition gradient issue, we have calculated the atomic structure for islands with two different chemical composition profiles $C_1$ and $C_2$, shown in Figure 5. $C_2$ is the profile commonly found in most MAD results, which consists of a Si-rich base with a stabilization of the composition at 40-50 Å above the substrate [31]. $C_1$ represents instead an abrupt composition profile at the interface. Reciprocal space composition corresponds, according to the iso-strain method, to real space composition, as it is possible, in the case of free standing
3. EDAFS Calculations

EDAFS oscillations are described by the following expression

\[ \chi_Q = \sum_i^{N_{Ge}} \left[ \cos(\phi_0 - \phi_{Ge})\omega_i' \chi_i' + \sin(\phi_0 - \phi_{Ge})\omega_i'' \chi_i'' \right] \] (2)

where \( i \) identifies resonant atoms, \( N_{Ge} \) is the total number of resonant (anomalous) atoms, \( \omega' \) and \( \omega'' \) are the crystallographic weights, \( \chi' \) and \( \chi'' \) the real and imaginary parts of the EDAFS, and \( \phi_0 \) (resp. \( \phi_{Ge} \)) the phase of the total structure factor \( F_0 \) (resp. Ge structure factor \( F_{Ge} \)).

In our models the number of resonant atoms is very large. Hence to calculate EDAFS we have to resort to a weighted averaged based procedure. We divide the island into \( N_b \) blocks (slices) of height \( h \sim 10 \text{Å} \). After this division we can rewrite EDAFS as

\[ \chi_Q = \cos(\phi_0 - \phi_{Ge}) \sum_i^{N_b} \sum_j^{N_i} \omega_{ij} \chi_{ij}' + \sin(\phi_0 - \phi_{Ge}) \sum_i^{N_b} \sum_j^{N_i} \omega_{ij}'' \chi_{ij}'' \] (3)

Now subscript \( i \) identifies blocks, subscript \( j \) resonant atoms and \( N_i \) is the number of resonant atoms in block \( i \). The latter equation can be rewritten as

\[ \chi_Q = \cos(\phi_0 - \phi_{Ge}) \sum_i^{N_b} N_i \bar{\omega}_{i} \chi_i' + \sin(\phi_0 - \phi_{Ge}) \sum_i^{N_b} N_i \bar{\omega}_{i}'' \chi_i'' \] (4)

where \( \bar{\omega}_{i} \chi_i' \) and \( \bar{\omega}_{i}'' \chi_i'' \) are block averages. To calculate these averages we select randomly a certain number atoms of each block, and calculate EDAFS. We increase the number of atoms until convergence is reached (for about 80 atoms). As we divide the island in 10 blocks, we estimate EDAFS from 800 atoms selected randomly from about 300000 resonant atoms. Each individual EDAFS was calculated by Feff8.2 code \([39, 40]\) inside a 8Å radius sphere. Self-consistent calculation of scattering potentials was performed. EDAFS spectra for models \( C_1 \) and \( C_2 \) are shown in figure 6 for several \( h \) values. We observe that the shape changes are much stronger for \( C_2 \) due to the smooth variation of Si concentration. Indeed the spectrum shape at low-\( k \) values depends strongly on the composition of the next nearest shell, since back scattering amplitudes of Ge and Si are very different from each other. If we compare with EDAFS oscillations of sample \( D_1 \) we can say that model \( C_2 \) describes much better the experiment.
An important aspect that we wanted to quantify by atomistic simulations, is the MAD and EDAFS spatial resolution issue. Once a realistic cluster is obtained, according to the method described above, one can calculate, as shown in Figure 6, EDAFS and MAD (not shown), compare it to the experiment, and select the model that is closer to it. Nevertheless, the information content of this kind of simulation is richer. We can wonder for example how large is the region of the sample, in the real space, contributing to EDAFS at a given $h$ value. This is indeed represented mathematically by the crystallographic weights in equation (2), which gives the weight of any scattering path contributing to $\chi_Q$. Knowing the individual atomic positions in the cluster, they can be calculated, providing a kind of EDAFS spatial resolution. We found that EDAFS is essentially $\chi'$-like, and that the width of the Gaussian shape weights is of about 20 Å. Another interesting issue, of the same kind, is how realistic is the raising, or gradient, of Ge content at the interface substrate-dome given by MAD. Once diffraction (MAD) is calculated for the cluster, (not shown here for space limitations), one can, applying MAD formalism, deduce the concentration profile corresponding to that theoretical MAD spectrum. The same model profile used to generate the cluster should be found if information is not lost on the way. As we can observe in Figure 7, this is the case for model $C_2$, characterized by a smooth concentration profile. For model $C_1$ instead, which is more abrupt, information is lost, and an artificial smoother gradient is found. This shows that one must be careful about MAD results on concentration profiles that can look smoother than in reality. This happens in the case of a sharp interface: the pure Si region of the substrate is more strained by the island and its contribution to diffraction in reciprocal space is larger. This can be seen by MAD as a higher Si concentration at the dome base. This proves that realistic simulations, including as much substrate region as needed, is of fundamental importance, providing a deeper and more reliable data interpretation.

**Figure 6.** Extended DAFS calculated as a function of reciprocal unit $h$ for models $C_1$ and $C_2$.

**Figure 7.** Ge concentration extracted back from the simulated MAD of models $C_1$ and $C_2$. 
4. AlGaN nanowires

III-Nitride semiconductor materials are of major importance for blue and UV light emission applications, although their ultimate potentialities are still plagued by the high density of dislocations \((10^7 - 10^{10} \text{ cm}^{-2})\) and other structural defects which result from the lack of lattice-adapted substrates. By contrast, GaN nanowires (NWs) exhibit an exceptional crystalline quality [41, 42], which makes them serious candidates for fabricating high efficiency III-N NWs-based devices. Actually, it has already been demonstrated that GaN/InGaN/GaN and AlGaN/GaN/AlGaN NW heterostructures can be successfully grown to achieve light emitting diodes (LEDs) in the visible [43, 44] and UV [45] range, respectively. Whereas growth of NWs by metal organic chemical vapor deposition (MOCVD) generally requires the use of metallic catalysts, with the eventual risk of metal contamination, one advantage of molecular beam epitaxy (MBE) is to permit the growth of high quality, stacking fault-free, GaN NWs without using any external catalysts. It has been established that GaN NW growth is mostly driven by in-plane Ga diffusion towards NW base, followed by a diffusion on their side and, finally, incorporation on top, provided that growth temperature is high enough [46, 47, 48, 49]. As surface adatom diffusion in the basal plane as well as along the \((1-100)\) walls of NWs [49, 50, 51] is critical, it is expected that growth of ternary (InGaN or AlGaN) NWs will be strongly dependent on the difference in diffusion of different adatom species. In particular, in the case of AlGaN NWs, the question raises of predicting/controlling their composition, due to the fast diffusion of Ga compared to Al. It is the goal of this preliminary study to provide insight on the growth mechanism of AlGaN NWs and to clarify in particular the issue of a possible composition gradient related to the different diffusion length of Al and GaN adatoms.

4.1. Samples

The sample (figure 8) was grown by PAMBE, catalyst-free, in standard nitrogen-rich conditions. The nominal Al content in the fluxes was 40%. A 3-4 nm AlN buffer layer was deposited onto the substrate to improve wire orientation [46]. To compensate for the reduced adatom mobility of Al compared to Ga, an In flux equivalent to 0.4 ML/s (in (0001) InN growth units) was supplied [49], and growth temperature was 862°C, i.e higher than that of In-assisted GaN nanocolumns. Figure 8 shows 1 micron long AlGaN nanowires whose base is embedded in a rough 20nm thick AlGaN layer. The question is twofold : what is the Al content in the wires and is there any Al/Ga concentration gradient?

Figure 8. Scanning Electron Microscopy of AlGaN nanowires grown on Si(111).

4.2. Grazing Incidence Multiwavelength Anomalous Diffraction

MAD and DAFS measurements were performed at beamline BM02 at the ESRF. A linear gas-detector (Vantec-1, Bruker) was used to record the scattered intensity. MAD 2D maps were measured at 12 energies across the Ga K-edge (10367eV), close to the specular GaN(105) and AlN(105) Bragg reflections. The x-ray beam linear polarisation was perpendicular to the diffraction vector and was oriented 65° with respect to the [0001] direction. The modulus of anomalous (resp. non anomalous) structure factors \(|F_{Ga,Al+N}|\) and the phase difference \(\varphi_{Al+N} - \varphi_{Ga}\) were recovered as a function of the reciprocal lattice unit \(h,l (F_{Ga,Al+N}(hkl) = |F_{Ga,Al+N}(hkl)|e^{i\varphi_{Ga,Al+N}(hkl)})\). Figures 9 and 10 show 2D maps in the reciprocal space representing the modulus of anomalous and non anomalous structure factors.
It also shows the positions of relaxed GaN and AlN (105) reflections. At first glance, there are two scattering spots, one centered at \( h = 1.02, l = 5.05 \) and the other, centered at \( h = 1.03, l = 5.12 \), i.e. very close to the relaxed AlGaN line, which connects the relaxed GaN and AlN (105) reflections. The former corresponds to a Ga rich AlGaN whereas the latter corresponds to an Al rich AlGaN. For obtaining the Al content, DAFS spectra were measured at these two positions \((h = 1.03, l = 5.05)\) and \((h = 1.03, l = 5.12)\).

**Figure 9.** 2D experimental map of the Ga scattering amplitude or the modulus of the Ga partial structure factor \( F_{Ga} \).

**Figure 10.** 2D experimental map of the Al and N scattering amplitude or the modulus of the partial structure factors \((F_{Al}+F_{N})\).

Figure 11 shows the integrated intensity variation as a function of the energy, measured by the linear detector. Fitting of the DAFS cusps, assuming an AlGaN compounds with the wurzite structure, give an Al content of 0.7 (resp. 0.23) for \( h = 1.03, l = 5.12 \) (resp. \( h = 1.03, l = 5.05 \)). An Al content of 0.23 is consistent with the cathodoluminescence of the wires, therefore one can safely attribute the scattered intensity at \( h = 1.03, l = 5.05 \) to the wires. A close inspection of Figures 9 and 10 shows that the Ga and the Al+N structure factors of the Al rich spot do not superpose, whereas those of the Ga rich spot do superpose. This means that a composition gradient exists in the 2D AlGaN layer that grows in between of the wires.

**Figure 11.** DAFS spectra measured at \( h = 1.03, l = 5.12 \) and \( h = 1.03, l = 5.05 \) \((k = 0)\).

**Figure 12.** Ga K-edge EDAFS oscillations for GaAlN nanowires at \( h = 1.03, l = 5.12 \) and \( h = 1.03, l = 5.05 \) \((k = 0)\), together with the corresponding best fit curves.
4.3. Grazing Incidence Diffraction Anomalous Fine Structure

Figure 12 shows the background subtracted EDAFS oscillations together with the corresponding best fit curves. Best fit results are summarized in Table 3. The difference between the two spectra is quite remarkable, either in the raw $\chi(k)$ and FT spectra. It is due to the change in the local Ga environment related to the change in composition of the two different regions of the nanocolumn selected by diffraction. The sample is much more Al-rich at $l = 5.12$. Quantitative results have been obtained by least square fitting of raw $\chi(k)$ using Iffeffit code implemented by Artemis package. Theoretical phases and amplitudes were generated by means of Feff8.2 code. DAFS corrections to phases and amplitudes have been applied according to a first order $\chi$ approximation analysis scheme as described in reference [5]. They are deduced by fitting of the smooth part of the DAFS spectrum. Polarization of the x-ray beam has been taken into account considering that in the experimental diffraction conditions the vector was nearly parallel to the sample surface (about 20°). Fits have been performed imposing hexagonal symmetry and taking into account single and multiple (three atoms) scattering paths up to a distance of about 4.5 Å from central Ga absorber. The Al content varies from $x = 0.1$ at $l = 5.05$ to $x = 0.45$ at $l = 5.12$. Interatomic distances are coherent with composition although the $c/a$ ratio shows that strain is not completely relaxed.

| Sample          | Bulk GaN | Bulk AlN | nanowires $l=5.05$ | nanowires $l=5.12$ |
|-----------------|----------|----------|---------------------|---------------------|
| $R(Ga-N)$ (Å)   | 1.947    | -        | 1.94                | 1.93                |
| $R(Ga-Ga)_{op}$ (Å) | -        | -        | 3.15                | 3.13                |
| $R(Ga-Ga)_{inp}$ (Å) | 3.189    | -        | 3.17                | 3.14                |
| $R(Ga-Al)_{op}$ (Å) | -    | 3.11     | 3.12(fix)           | 3.12                |
| $R(Ga-Al)_{inp}$ (Å) | -    | -        | 3.12(fix)           | 3.12                |
| $c$ (Å)         | 5.186    | 4.982    | 5.18                | 5.10                |
| $x_{Al}$        | 0        | 1        | 0.1                 | 0.45                |
| $c/a$           | 1.626    | 1.6      | 1.64                | 1.62                |

5. Conclusion

In summary, we have demonstrated that the combination of x-ray Multiwalength Anomalous Diffraction (MAD), x-ray Diffraction Anomalous Fine Structure (DAFS) spectroscopy together with Molecular Dynamics simulations is a very powerful approach to determine structural properties, as strain and composition, of nanostructures.

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