Quantum dots microstructure by XAFS spectroscopy: GaN/AlN system depending on preparation conditions

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Abstract. GaK EXAFS spectra of GaN/AlN heterostructures were measured. Microstructure parameters of GaN/AlN heterosystems with discrete electronic spectra largely influenced by the elastic deformation at the boundaries of the nanoclusters and substrate was detected by the direct method. The local structure parameters determined by EXAFS spectroscopy are linked to preparation conditions and nanostructures morphology and adequate models are suggested and discussed.

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1. Introduction

We have used EXAFS (Extended X-ray Absorption Fine Structure) [1,2] spectroscopy to study structural peculiarities of materials containing GaN/AlN heterostructures depending on the preparation conditions.

The phenomenon of "self-organization" in the process of heteroepitaxial semiconductor system growth allows fabrication of dense, extended, well-ordered structures containing islands of uniform shape and size. In semiconductor nanostructures, with spontaneously ordered inclusions of a narrower band gap material within a broader bandgap matrix, the limiting case of the dimensional quantization is realized. Zero-dimensional quantization exist within a certain interval of microinclusion sizes with the formation of so-called quantum dots (QDs) which are characterized by discrete electronic spectra.

In recent studies it was shown that at a certain thickness of the epitaxial film on substrate: Ge/Si [6,7] or AlB/AlAs (InAs/AlAs [8] and GaN/AlN [9]) in the electronic spectra of the heterostructures features appeared which were associated with the zero-dimensional density of the states. These features are due to the dimensional quantization of the hole spectrum in the Ge, GaN, InAs islands appearing during disturbed two-dimensional growth.

The spectrum of states in the self-organizing nanostructures may be largely influenced by the elastic deformation at the boundaries arising from a mismatch of the lattice parameters of the nanocluster and substrate. In the GaN/AlN system the lattice mismatch amounts to 2%. This will cause changes in the local structure: local distortions of the symmetry, changes in the valence angles and interatomic distances. Such structural changes may change the energy spectrum by a magnitude of the order of 0.1 eV.

Local structural changes in thin layers and nanostructures are not detectable by traditional X-ray structural analysis or electron diffraction, due to the absence of long-range ordering. EXAFS spectroscopy provides a unique possibility for solving such problems [1,2,10]. This experimental technique allows determination of parameters regarding the local environment of atoms and electronic parameters of nanoclusters. In particular, our previous experiments using GeK XAFS showed that Ge QDs are characterized by interatomic Ge-Ge distances of 2.41Å which is 0.04 Å less than in bulk Ge [11-13].
2. Experimental

EXAFS spectra of the GaK-edges were measured at the VEPP-3 storage ring of the Budker Institute of Nuclear Physics (Novosibirsk, Russia) and at the DUBBLE beamline of the European Synchrotron Radiation Facility (Grenoble, France). Both beamlines are equipped with a Si(111) double-crystal monochromator. A 1300 mm long silicon mirror, with a 1.5 Å rms roughness and 1.5 microrad slope error, was used to reduce the higher harmonic content of the primary beam and to focus the beam in the vertical direction at the DUBBLE beamline. The calculated reduction factor for the higher harmonics is about 1000. All measurements were performed in the fluorescence detection mode. The C-TRAIN detector[14-15] with XSPRESS processing electronics [16] was used at the DUBBLE beamline. In all experiments the samples were placed under an angle of 3 degrees relative to the incoming X-ray beam and the detector was mounted in horizontal plane in such a way to achieve the best signal to noise ratio.

The spectra have been measured on GaN/AlN heterostructures which contain GaN two-dimensional layers or nanoclusters on AlN substrates. These samples have been produced using molecular beam epitaxy (MBE) on (0001) sapphire substrate. The sample 1 consist of 20 layers with each an effective thickness of 4 GaN monolayers, sample 2 consist of 15 layers with each an effective thickness of 5 GaN monolayers. These layers are separated by AlN layers with a thickness of about 100 Å. The GaN monolayer thickness is equivalent to 2.5 Å (on average). The samples 3-6 consist of 1 GaN layer with each an effective thickness from 2 to 5 GaN monolayers. These layers are covered by AlN protective layers with a thickness of about 100 Å.

Ga atoms local arrangement in these systems have been determined using the fitting procedure in the EXCURV92 program [17] of Fourier filtered experimental data (figure1). Fits to data have been made for \( \chi(k)k^2 \) in the photoelectron wave-number range from 3Å\(^{-1}\) to 12.5Å\(^{-1}\) using GaK EXAFS experimental data which were Fourier filtered in the regions 1.0Å<R<3.3Å for the first (N) and the second (Ga) coordination shells. The interatomic distances determination error in the fitting procedure has not exceeded 0.01 Å.

3. Results and discussion

GaK EXAFS data for bulk crystalline material have been analysed to determine the amplitude damping factor caused by multi-electron effects - \( S_0^2 \) and the energy threshold value - \( E_0 \). The interatomic
distances $R_{Ga-N} = 1.951 \ \text{Å}$ and $R_{Ga-Ga} = 3.186 \ \text{Å}$ determined in [18] as far as coordination numbers $N_{Ga-N} = 4$ and $N_{Ga-Ga} = 12$ have been fixed in the fitting procedure. The obtained values for $S_0^2 = 0.8$ and $E_0 = 10.7$ eV have been fixed in the subsequent analysis of GaN/AlN heterostructure containing quantum dots. Figure 2 shows experimental $k^2$-weighted GaK EXAFS spectrum for bulk crystalline GaN and for GaN/AlN heterostructures. Values of the respective Fourier transform modules, which do not take into account phase shifts are presented in the figure 3.

![Figure 2](image1.png)

Figure 2. Experimental $k^2$-weighted GaK EXAFS spectrum ($\chi(k)k^2$) for bulk crystalline GaN and for GaN/AlN heterostructures.

![Figure 3](image2.png)

Figure 3. Fourier transform modules of $\chi(k)k^2$ GaK EXAFS without phase shift: for bulk crystalline GaN and for GaN/AlN heterostructures. The respective peaks are marked by the shell numbers and types of surrounding atoms in accordance with [18].
Obviously, the last picture reflects qualitative structural changes since the phase-shift corrections can not be done simultaneously for the various types of surrounding atoms since interference effects perturb the peaks amplitudes. Nevertheless, some observations can be made.

As can be seen in the figure 3, starting from the second coordination shell (2Ga), the peaks amplitudes for the GaN/AlN heterostructure are appreciably lower compared to these for the bulk GaN, indicating a decrease of Ga atoms in corresponding shells. This effect increased when moving from Sample 1 to Sample 6. All peaks corresponding to the higher shells exhibit some shape changes and shifts to lower distances. This is caused by some compression as a result the structural mismatch between the GaN clusters and the AlN substrate.

It should be mentioned that in the figure 3 peaks corresponding to up to the fourth coordination shell and for 8Ga coordination shell are well reproduced for bulk GaN and GaN heterostructures and correlate well with model calculations, while for the 6Ga shell the corresponding peak amplitude for GaN heterostructures decreased considerably in comparison with bulk GaN and in comparison with model calculations. This can be explained by multiple scattering effects, which have not been taken into account in the present calculations.

Our multi-shell model calculations have demonstrated that contributions from nitrogen atoms to the spectra is small starting from the third shell and it is reasonable do not take them into account during the fitting procedure. Results of fitting procedure are shown in the Table 1.

Table 1. Structure parameters of bulk GaN [18] and parameters obtained by fitting procedure for $k^2$-weighted GaK EXAFS spectrum of bulk crystalline GaN and GaN/AlN heterostructures. $R_1(\text{Å})$, $R_2(\text{Å})$ – interatomic distances Ga-N and Ga-Ga, correspondingly; $N_1$, $N_2$ – coordination numbers of N and Ga by Ga; $\sigma_1^2$, $\sigma_2^2$ – Debye-Waller factors ($\text{Å}^2$).

| Sample | $R_1 \pm 0.01\text{Å}$ Ga-N | $\sigma_1^2 \pm 0.001\text{Å}^2$ Ga-N | $N_1$ Ga-N | $R \pm 0.01\text{Å}$ Ga-Ga | $\sigma_2^2 \pm 0.001\text{Å}^2$ Ga-Ga | $N_2 \pm 0.3$ Ga-Ga |
|--------|------------------|------------------|---------|------------------|------------------|---------|
| GaN -bulk | 1.95 | 0.007 | 4 | 3.18 | 0.006 | 12 |
| 1 | 1.93 | 0.005 | 4 | 3.13 | 0.006 | 10.7 |
| 2 | 1.93 | 0.004 | 4 | 3.15 | 0.006 | 8.7 |
| 3 | 1.94 | 0.004 | 4 | 3.16 | 0.006 | 7.4 |
| 4 | 1.94 | 0.005 | 4 | 3.16 | 0.005 | 5.9 |
| 5 | 1.94 | 0.004 | 4 | 3.15 | 0.005 | 6.2 |
| 6 | 1.97 | 0.015 | 3 | 3.15 | 0.006 | 4.1 |

As a result the Debye-Waller factors have been determined for the first ($\sigma^2 = 0.007 \text{Å}^2$) and the second ($\sigma^2 = 0.006 \text{Å}^2$) shells of Ga in bulk GaN.

The goodness of fit is defined by the fit index $F$ [17] which equal to values near 2.0. As a result of fitting procedure it has been found that in the GaN/AlN heterosystems the first Ga-N interatomic distances $R_1 = 1.93 \text{Å} - 1.94 \text{Å}$, i.e. 0.02 Å smaller than in crystalline GaN. The Debye-Waller factor for this shell is $\sigma^2 = 0.004 \text{Å}^2 - 0.005 \text{Å}^2$, which is also smaller than in crystalline GaN ($\sigma^2 = 0.007\text{Å}^2$). For the second Ga-Ga shell the fitting procedure gives for heterosystems interatomic distance $R_{Ga-Ga} = 3.13 - 3.16 \text{Å}$ which is 0.04 Å smaller than in crystalline GaN. The Debye-Waller factor for this shell is the same for all samples. Evident decreasing of interatomic distances in going from bulk GaN to GaN/AlN heterosystem caused by the elastic deformation at the boundaries arising from a mismatch of the lattice parameters ($\sim 2\%$) of the AlN substrate (lattice constant $d = 3.11 \text{Å}$) and deposited GaN (lattice constant $d = 3.18 \text{Å}$). Decrease of Debye-Wallers factors of Samples 1-5 for the first coordination shell is evidence of strain increase in heterosistems and high ordering of N atoms in Ga surroundings.
Special attention must be given to anomalous behavior of structural parameters of Sample 6. Stochiometric conditions of MBE deposition were not realized for this sample. GaN deposition was fulfilled under nitrogen deficit. This condition corresponds to coordination number near 3 of N by Ga. Only this model with three nitrogen atoms and one gallium atom in the first shell of Ga gives good fitting with physically reasonable parameters and with fit index F equal to values near 2.0. High value of Debye-Waller factor for Samples 6 (0.015 Å²) can be explained in this case by static disordering of atoms in first shell of Ga.

Attempts to modify the model by adding Al atoms from the AlN substrate and the separating layers in order to construct a second shell for Ga atoms were made. However, in most cases this leads to an anomalous big value of the Debye-Waller factor for the Ga-Al shell. This indicates that there is a negligible contribution of the Ga-Al signal to the spectrum. Therefore we can not determine the Ga-Al interatomic distance and coordination number correctly. This can be explained by large structural disordering (distortions) in the second and higher coordination shells of Ga, especially in the AlN separation layers and substrate. The lattice spacing constants mismatch between the GaN thin film and the AlN substrate may be a reason for such a disordering.

Table 2 presents estimation of average Ga-Ga coordination numbers for simple two-dimensional model in comparison with result of experiment fitting depend of effective thickness of GaN film. Table 2. Parameters of samples preparation (T substrate - temperature of AlN- substrate under GaN- deposition, ML number - effective thickness in monolayers of GaN film) and Ga-Ga coordination numbers from two-dimensional model estimations (left column) and from the fitting procedure (right column).

| Sample | T substrate, °C | ML number | \(N_{Ga-Ga}\) two-dimensional model estimation | \(N_{Ga-Ga}\) fitting of experiment | Comment |
|--------|----------------|-----------|-----------------------------------------------|-----------------------------------|---------|
| 1      | 600            | 4         | 10.5                                          | 10.7 ± 0.3                        | two-dimensional layers |
| 2      | 400            | 5         | 10.8                                          | 8.7 ± 0.3                         | three-dimensional nanoclusters |
| 3      | 400            | 5         | 10.8                                          | 7.4 ± 0.3                         | three-dimensional nanoclusters |
| 4      | 400            | 3         | 10                                             | 5.9 ± 0.3                         | small three-dimensional nanoclusters |
| 5      | 500            | 2-3       | 9-10                                          | 6.8 ± 0.3                         | small three-dimensional nanoclusters |
| 6      | 400            | 5         | 10.8                                          | 4.1 ± 0.3                         | compound with distortion of stectiometry |

As can be seen in Table 1, the simple two-dimensional model gives good agreement with experiment fitting for Sample 1 only, which was prepared at the substantially higher temperature (600 °C). This sample has the highest decrease of interatomic distances \(R_{Ga-N}\) caused by essential contribution of strained GaN located close to interface. Remaining Samples 2-5 consist of three-dimensional clusters GaN. Estimation of the average size of GaN clusters in Sample 2 from Transmission Electron Microscopy (TEM) results gives \(d = 50 \, \text{Å}, h = 20 \, \text{Å}\). Remaining Samples 3-5 consist of smaller GaN clusters, in particular Samples 4, 5 with smaller effective thickness of GaN layer (2-3 ML). We can focus attention on some increase average size of GaN clusters by increase of temperature of GaN deposition from 400 °C to 500 °C (in transition from Sample 4 to Sample 5).

4. Conclusion
It has been found that the first shell \(R_{Ga-N}\) interatomic distance in heterostructure GaN/AlN is equal to \(~1.93 \, \text{Å}\), which is 0.02 Å smaller compared to crystalline GaN. For the second Ga-Ga shell an interatomic distance \(R_{Ga-Ga} \sim 3.14 \, \text{Å}\) was found, which is 0.04 Å smaller than in crystalline GaN. The coordination number \(N_{Ga-Ga}\) was found to be from 5.9 to 10.7. It was established that heterostructure contains three-dimensional islands or two-dimensional thin films depending of temperature of AlN- substrate during GaN- deposition. Our results suggest that average size of GaN clusters and elastic strains and deformations depend of preparation conditions, such as temperature of AlN- substrate and time of deposition, or effective thickness of GaN film.
The microstructure parameters of GaN/AlN heterosystems with discrete electronic spectra largely influenced by the elastic deformation at the boundaries arising from a mismatch of the lattice parameters of the nanoclusters and substrate was detected by the direct method showing that EXAFS spectroscopy is very perspective tool to study materials containing nanostructures.

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