Structure of interfaces in GaN/AlN and Ge/Si multilayered heterosystems by XAFS spectroscopy

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Abstract. III-nitride heterostructures in the form of multilayered quantum wells (MQWs) or quantum dots (QDs) and interacting Ge QDs (“quantum molecules”) are promising candidates for high-speed intersubband (ISB) optical devices relying on the quantum confinement of electrons. Microstructural parameters (interatomic distances, coordination numbers, and Debye–Waller factors) were determined by means of EXAFS spectroscopy based on the Synchrotron Radiation, and the relationship between the variations in these parameters and the morphology of superlattices and symmetric assembles of QDs were established. The EXAFS technique has been used to study the local structure of thin hexagonal GaN/AlN MQWs grown by ammonia MBE at different temperatures. It is shown that the heterointerface intermixing leads to a decrease in the Ga–Al interatomic distance and the Ga–Ga coordination number in MQWs. The degree of intermixing in the boundary layers rises from 30% to 40% with increase of the growth temperature from 795 to 895 °C. It was found that in the first phase of quantum molecules growth Ge atoms concentration is 25%. With further growth (deposition of the base layers) Ge concentration increases up to 35–45%, depending on the temperature (from 610 to 550 °C) of deposition.

1. Introduction

III-nitride heterostructures in the form of multilayered quantum wells (MQWs) or quantum dots (QDs) are promising candidates for high-speed intersubband (ISB) optical devices relying on the quantum confinement of electrons [1].

MQWs serve as base materials for light emitting devices operating in ultraviolet spectral region, high-speed infrared intersubband optical modulators and infrared photodetectors [2, 3]. Short-period MQWs is utilized for replacement of a conventional AlGaN barrier in AlGaN/GaN heterostructures for high-electron mobility transistors to increase a two-dimensional electron
density [4]. An abruptness and a flatness of heterointerface are very important parameters to achieve high performance of these optoelectronic devices. It is well known that the optical properties of GaN/AlN QWs are strongly affected by arrangement of heterointerfaces, in its turn the arrangement of heterointerfaces strongly depend on growth techniques used to fabricate QWs as well as growth conditions [5]. Optimal growth conditions for GaN and AlN layers are rather different and have been well studied, the GaN layers are usually grown at a lower temperature and a higher active nitrogen flux than the AlN layers. However, it is difficult to change the growth conditions between the very thin GaN well and the AlN barrier layers. In the [6] was obtained conclusion that the optimal growth conditions for GaN/AlGaN MQWs fabricated by metal organic chemical vapor deposition are close to that for GaN layers, but to the best of our knowledge the effect of growth conditions on the arrangement of heterointerfaces in MQWs was not studied yet. The systems with interacting QDs—“quantum molecules” (in particular, GeSi nanorings, or quantum rings—QRs) have attracted much attention both as ground for studying coupling and energy transfer processes between “artificial atoms” and a new systems, which substantially extend the range of possible applications of QDs [7]. This nanostructure is a symmetric assembly of four QDs bound by the central pit and has been suggested as a candidate structure for logic architecture based on quantum cellular automata [8]. Extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) spectroscopy, in particular, in high-energy-resolution fluorescence detection (HERFD) mode are the powerful tools allowing to determine local atomic and electronic parameters of nanosized systems and were used to characterize strain and diffusion in heterosystems with GaN/AlN thin film superlattices and SiGe nanorings by XAFS spectroscopy. Surface sensitive methods of EXAFS and XANES spectroscopy using small incident x-ray angle provide a unique possibility to study the local structure changes and electronic spectra peculiarities in the thin layers, nanoclusters [9, 10], three-dimensional systems of coupled dots [11] and superlattices [12].

The spectrum of states in the self-organizing nanoclusters may be largely influenced by the elastic deformation at the boundaries arising from a mismatch of the lattice parameters of the nanoclusters and the substrate (GaN/AlN, Ge/Si). The substantial mismatches cause significant changes in the local structure and consequently in energy spectrum by a magnitude of $\sim 0.1$ eV [13], which is comparable with the dimensional quantization energy. Therefore, interpretation peculiarities of nanosystems experimental energy spectra as well as design of elements with given electronic properties must take into account the variation in local structure, strain and diffusion in heterosystems containing vertically ordered arrays.

2. Experimental

Hexagonal [0001]-oriented GaN/AlN MQWs with 200 nm thick AlN buffer layer were grown by ammonia MBE on c plane sapphire substrates using a Riber CBE-32 machine. High purity ammonia was used as a source of active nitrogen, standard effusion cells were used as sources of group III metals. To minimize contamination the substrates were outgassed at about 600 °C during 12 hours in the loading dock with vacuum pressure near of $8.0 \times 10^{-8}$ Torr. Then, prior to growth the substrates were annealed at about 900 °C during 1 hour and subjected to 10 min long nitridation at 840 °C under ammonia flow of 25 sccm. The substrate temperature was controlled by an infrared pyrometer. The AlN buffer layer was grown at 920 °C under ammonia flux of 15 sccm. During the MQWs growth the ammonia flux were kept at 200 sccm, whereas the substrate temperature was chosen 795, 845 and 895 °C for samples A, B and C, respectively. Thickness of GaN well and AlN barrier was about of 1 nm, the number of period was 30. A reference GaN layer with thickness of about 17.5 nm was grown in the same growth conditions as the sample A. For preliminary characterization of the MQWs structures transmission electron microscopy (TEM) and photoluminescence (PL) measurements were performed.
Ge/Si structures with QRs was grown by molecular beam epitaxy (Riber SiVA-21), according [14]. After standard cleaning and in-situ oxide desorption, a 150 nm-thick Si buffer layer was deposited on Si(100) substrate. Then, three layers of vertically stacked SiGe QDs separated by a 20 nm Si spacer were successively grown at a substrate temperature of 700 °C. Each QD layer was formed by deposition of 7.5 monolayers (MLs) of Ge. The top QD layer was completed by the deposition of a 5 nm Si overlayer at 700 °C. The buried SiGe islands have the typical base width of 150–200 nm, height of 7–8 nm, and sidewall inclination angle of 12–14° (sample 1 in figure 1). Hereafter, such structures were used as templates for formation of closely spaced QDs (quantum rings) in the next 10 layers. For this purpose, 10 layers of 4 MLs Ge with Si of 10 nm overlayers were deposited over disklike SiGe nanomounds at a temperature of 600 °C, which was lower than that used to fabricate the templates (samples 2, 3 in figure 1). Sample 2 was further alloyed with antimony.

Of special value of EXAFS spectroscopy is possibility to find out microstructure parameters, such as partial coordination numbers for atoms absorbing x-ray quantum, interatomic distances and Debye–Waller factors. HERFD XANES spectroscopy make possible in some cases to evaluate position and quantity of free valence states [9] and to realize FEFF simulation with various nanocluster sizes and shape [15].

Some of the EXAFS spectra above GaK- and GeK-edges were measured at the VEPP-3 storage ring of the Budker Institute of Nuclear Physics (Novosibirsk, Russia). Beam-line was equipped with a Si(111) double-crystal monochromator. Absorption was measured via surface-sensitive fluorescence yield, which was detected by a photomultiplier with NaI scintillator. The x-ray beam was incident at 4° to the sample plane, the photodetector was mounted in horizontal plane in such a way to achieve the best signal-to-noise ratio. Total thickness of the studied samples was specially chosen to decrease reabsorption of fluorescence excited by x-rays inside the samples. To eliminate the reflections of the synchrotron radiation from the substrate, the sample was usually mounted on a turning table rotated with frequencies in the range of 10–15 Hz, however, quite good spectra for the some samples were obtained without rotation.
Table 1. Parameters of microstructures of GaN/AlN MQWs (A, B, C) and GaN (reference) obtained in the simulation process of EXAFS data. Here \(N(Ga)\), \(N(Al)\) are the average coordination numbers Ga–Ga and Ga–Al accordingly; \(R(N)\), \(R(Ga)\), \(R(Al)\) are the interatomic distances Ga–N, Ga–Ga, Ga–Al accordingly.

| Sample | \(N(Ga)\) | \(N(Al)\) | \(R(N)\) | \(R(Ga)\) | \(R(Al)\) |
|--------|-----------|-----------|----------|-----------|-----------|
| A      | 8.9       | 3.1       | 1.93     | 3.15      | 3.16      |
| B      | 8.6       | 3.4       | 1.93     | 3.15      | 3.16      |
| C      | 8.0       | 4.0       | 1.92     | 3.14      | 3.13      |
| GaN ref. | 12         |           |          | 1.95      | 3.17      |

Other part of the spectra was measured at the ESRF (Grenoble, France). HERFD-XANES and EXAFS experiments have been performed at 12K at the beamline ID26 or ID20 equipped by 5-analyzer x-ray emission spectrometer. The x-ray beam was incident at 1° to the sample plane without rotation. The following equipment was used: input-crystal Si(111), crystal-analyzer Si(220), three Si-mirrors with Rh coating. Recording of the spectra was carried out using a two-axis detector for 5 scans at once. Full resolution of equipment is 1.45 eV, size of beam spot—10 × 20 µm. The high energy resolution helped to reveal subtle changes in the structure of nanosystems.

3. Processing, interpretation of experimental results, discussion

To reveal local environment of Ga atom in the studied MQWs the experimental GaK \(k^2\chi(k)\) functions in the photoelectron wave-number range from 3.5 Å\(^{-1}\) to 13 Å\(^{-1}\) were fitted using a theoretical model for hexagonal GaN by iteration of the coordination number, the interatomic distance and the Debye–Waller factor. The model was constructed with the EXCURV-98 simulation tool. During fitting the EXAFS amplitude damping factor due to multi-electron effects \(S_0^2\) was taken equal 1.0, for all samples, in accordance with our results obtained for thick GaN film. Coordination numbers for nitrogen atoms in the first coordination shell of Ga atom \((N_N)\) were kept equal to 4, the coordination numbers for cations in the second coordination shell were fixed, whereas the numbers of Ga and Al atoms varied \((N_{Al} = 12 - N_{Ga})\).

To reveal local environment of Ge atom in the studied “quantum rings” the experimental GeK \(k^2\chi(k)\) functions in the photoelectron wave-number range from 3 Å\(^{-1}\) to 12 Å\(^{-1}\) were fitted by iteration of the coordination number, the interatomic distance and the Debye–Waller factor. The model was constructed also with the EXCURV-98 simulation tool, XAFS fit parameters were computed from the Fourier filtered in the region 1.2–2.7 Å experimental GeK \(k^2\chi(k)\) data. During the fitting the EXAFS amplitude damping factor due to multi-electron effects \(S_0^2\) was taken equal 1.3 for all samples, in accordance with our results obtained for bulk Ge. During the simulation Debye–Waller factor for Si and Ge was taken the same \((2\sigma^2 = 2\sigma_1^2 = 2\sigma_2^2)\), the sum of the coordination numbers of Si and Ge was set equal to 4 \((N_{Si} + N_{Ge} = 4)\) following a successful experience of our previous studies.

Figure 2a shows the \(k^2\)-weighted GaK EXAFS spectra \((k^2\chi(k))\) for MQWs structures together with a spectrum of the reference GaN layer. Figure 2b shows Fourier transform magnitude \(|F(R)|\) without phase shift corrections of \(k^2\chi(k)\) for GaK EXAFS of MQWs and GaN reference samples.

The fit yields the Ga–Ga, Ga–Al, and Ga–N interatomic distances, as well as the coordination numbers. The interatomic distances determination error in the fitting procedure has not exceeded 0.01 Å. The fitting results are presented in Table 1.
Figure 2. (a) Experimental $k^2$-weighted GaK EXAFS spectra for GaN/AlN MQWs structures and GaN film. (b) Fourier transform magnitude $|F(R)|$ without phase shift corrections of $k^2\chi(k)$ for GaK EXAFS of MQWs and GaN reference sample. Spectra denoted A, B and C correspond to MQWs samples grown at the substrate temperature 795, 845 and 895 °C, respectively. Spectrum marked as GaN relates to the reference GaN layer with thickness of about 17.5 nm grown at the temperature 795 °C.

One can see from the table 1 that the distance between Ga and N as well as Ga and Ga atoms in the MQWs samples is at about 0.02–0.03 Å lower than that in the GaN layer that can be due to elastic compression of thin GaN layers in MQWs. Moreover, these data obviously evidence that some intermixing at heterointerfaces takes place. It should be noted that Ga–Al interatomic distances are close to that in AlGaN alloys. Besides, the Ga–Ga and Ga–Al atoms become closer with increase of the growth temperature (see data for sample C) as it occurs in AlGaN alloys with increment of the aluminum fraction. It is seen also that the measured EXAFS spectra can be fitted fairly well assuming that number of Ga neighbours in a wurzite configuration is lower than that in bulk GaN at that part of the Ga atoms is replaced by the Al atoms. Consideration of the abrupt heterointerface shows that taking into account Al neighbors from the AlN layers only cannot explain the values of coordination numbers ascertained with accuracy of ±0.3. Indeed, the Ga–Ga coordination number in ideal QWs with thickness of 3 ML, 4 ML and 5 ML equals to 10.0, 10.5 and 10.8, respectively. To match with experimental data a part of the Ga atoms in the second shell should be replaced by the Al atoms. In addition, the value of the Ga-Al coordination number rises with increase of the growth temperature. According to our estimation for 3 ML thick QWs in the samples A, B and C an intermixing degree in the boundary layers reaches about 30%, 35% and 40%, respectively. It should be noted that the intermixing degree linearly increases with the temperature increment though one could expect an exponential growth.

The interatomic Ga–Ga distances $R(Ga)$ for samples with fewer layers and thin (80–150 nm) superlattices correspond to the substantial deformations and stresses (∼ 0.03 Å) indicated by our earlier results for GaN quantum dots in a AlN host [10, 11, 16].

Figure 3a shows the raw $k^2$-weighted GeK EXAFS spectra ($k^2\chi(k)$) for quantum rings structures together with a spectrum of the reference Ge bulk. Figure 3b shows Fourier transform
Figure 3. (a) Experimental $k^2$-weighted GeK EXAFS spectra $k^2 \chi(k)$ for quantum rings structures together with a spectrum of the reference Ge bulk. (b) Fourier transform magnitude $|F(R)|$ without phase shift corrections of $k^2 \chi(k)$ for GeK EXAFS for the same samples. Sample 1 consist of stack of strain-pattering templates; samples 2, 3 consist of columns of quantum rings over the stack grown at the temperature of 600 °C. Sample 2 was alloyed with Sb.

Table 2. Parameters of microstructures of GeSi QRs (1–3) and Ge bulk (reference) obtained in the simulation process of EXAFS data. Here $N(Si)$, $N(Ge)$ are the average coordination numbers Ge–Si and Ge–Ge accordingly; $R(Si)$, $R(Ge)$ are the interatomic distances Ge–Si, Ge–Ge accordingly.

| Sample | $N(Si)$ | $N(Ge)$ | $R(Si)$ | $R(Ge)$ |
|--------|---------|---------|---------|---------|
| 1      | 3.1     | 0.9     | 2.38    | 2.44    |
| 2      | 2.2     | 1.8     | 2.38    | 2.43    |
| 3      | 2.2     | 1.8     | 2.39    | 2.44    |
| Ge bulk | 4      |         | 2.45    |         |

The fit yields the Ge–Ge, Ge–Si interatomic distances, as well as the coordination numbers. The interatomic distances determination error in the fitting procedure has not exceeded 0.01 Å. The fitting results are presented in table 2.

It was found that in the first phase of growth Ge atoms concentration is ≈ 25%. With further growth (deposition of the base layers) Ge concentration increases up to 35–45%, depending on the temperature (610–550 °C) of deposition. It was established for the samples with stoichiometric formula Ge$_x$Si$_{1-x}$, 0.25 < $x$ < 0.45, that interatomic distances Ge–Ge and Ge–Si correspond to distances, defined in [17] for solid solutions and in [18] for quantum dots Ge/Si. It should be noted that alloying sample by Sb does not change the microstructure parameters (table 2).
4. Findings and conclusions

Microstructural parameters (interatomic distances, coordination numbers, and Debye–Waller factors) were determined by means of EXAFS spectroscopy, and the relationship between the variations in these parameters and the morphology of superlattices and symmetric assembles of QDs were established. The EXAFS technique has been used to study the local structure of thin hexagonal GaN/AlN MQWs grown by ammonia MBE at different temperatures. It is shown that the heterointerface intermixing leads to a decrease in the Ga–Al interatomic distance and the Ga–Ga coordination number in MQWs.

The degree of intermixing in the GaN/AlN boundary layers rises from 30 to 40% with increase of the growth temperature from 795 to 895 °C. The interatomic Ga–Ga distances $R(Ga)$ for samples with fewer layers and thin (80–150 nm) superlattices correspond to the more substantial deformations and stresses ($\sim 0.03 \text{\AA}$) indicated by our earlier results for GaN quantum dots in a AlN host [10, 11, 16]. It was found that in the first phase of growth Ge atoms concentration is $\approx 25\%$. With further growth (deposition of the base layers) Ge concentration increases up to 35–45%, depending on the temperature (610–550 °C) of deposition. It was established for the samples with stoichiometric formula $\text{Ge}_x\text{Si}_{1-x}$, $0.25 < x < 0.45$, that interatomic distances Ge–Ge and Ge–Si correspond to distances, defined in [17] for solid solutions and in [18] for quantum dots Ge/Si.

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