Microstructure of quantum dots ensembles by EXAFS spectroscopy

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Abstract. We investigate the microstructure of Ge/Si and GaN/AlN sandwiches containing vertically aligned QDs. The study establishes an influence of blocking layers (Si, AlN) thickness, number of QDs layers (Ge, GaN) in heterostructure and annealing temperature on the microstructure characteristics of systems with quantum dots.

1. Scientific background and aims

Two- and multi-layered quantum dots containing systems are important for many practical applications. Coherent two-level systems and quantum logic gates are suggested to serve as the building blocks of quantum information processing. Two vertically or laterally coupled quantum dots have been proposed as a basis for entangled quantum bit operations. In a simplified model of week tunneling and strong quantization, the electronic coupling between QDs brought close together appears as the formation of bonding and antibonding molecular type orbitals from the single dot states by an analogy with covalent bonds in natural molecules.

In the multi-layered dot structures, dots in the upper layers tend to grow on the buried ones or there is a vertical correlation in Ge/Si [1], InAs/GaAs [2] and GaN/AlN [3] systems. It has been shown by AFM (atomic force microscope) that islands undergo a transition from a broad size distribution in a single layer to intraplanar size equalization and rapid coarsening of the islands for systems with low enough layers’ thickness of barrier material [4], i.e. the average island’s size increases with the number of deposited layers in such multi-layered structures [4, 5]. However, the coarsening effect only occurs in the first several periods and is not evident afterwards. The coarsening for the vertically correlated dots is clearly observed for the first 6-7 dot layers. After that, the dots show no significant change in size. The increase in uniformity with the number of the periods (less than 20-30 periods) is observed.

Developments of techniques allowing the determination of spatial and electronic structural parameters on the surface or interfaces of materials will provide tools to control and verify the creation of structures containing nanoclusters with discrete electronic spectra. The creation of such systems can
be an important step in the pathway towards miniaturization and engineering for quantum computer systems.

Interpretation of QDs ensembles energy spectra must take into account the peculiarities of local structure of such formation, due to the strain field near the interfaces. Traditional X-ray structural analysis and electron diffraction are of limited application for studying the local structural changes of nanoclusters, due to the scantiness of long-range ordering in these systems. EXAFS spectroscopy provides a good possibility for solving such problems [6-10]. Of particular value of this method is possibility to determine partial coordination numbers for absorption atoms for receiving information concerning interphase diffusion and sizes of nanosystems.

So the Ge/Si and GaN/AlN quantum dots vertical alignment have been recently demonstrated [1-5]. The aim of this paper is quantitatively determination by EXAFS spectroscopy an influence of the thickness of the principal (Ge, GaN) and blocking layers (Si, AlN), number of QDs layers in "sandwich heterostructure" and some of the preparation conditions on the microstructure characteristics of system with QDs.

2. Experimental

Ge and GaN sandwich heterostructures (from 1 up to 30 monolayers) were prepared by molecular beam epitaxy (MBE) growing procedure with follow-up deposition of blocking Si or AlN layers with thickness from 30 up to 500 Å. EXAFS spectra of the GeK-, 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 ESRF (Grenoble, France). Both beamlines are equipped with a Si(111) double-crystal monochromator. All measurements were performed in the fluorescence detection mode. Contemporary experimental setup of the DUBBLE beamline described in [11] at length. In all experiments the samples were placed at a 3 degree angle relative to the incoming X-ray beam and the detector was mounted on a horizontal plane in such a way as to achieve the best signal to noise ratio.

The fitting procedure was carried out in the $k$-space region $\Delta k = 3 – 13 \, \text{Å}^{-1}$ with the help of the DLV EXCURV 98 program [12]. The EXAFS amplitude damping factor due to multi-electron effects $S_0^2$ was taken 0.8.

3. Ge/Si- systems

Single pseudomorphic Ge films have been deposited on Si(001) substrate up to the critical thickness of four monolayers. As a result of the following deposition, pyramid-like Ge islands have grown in Stranski-Krastanov mode [6, 7].

3.1 Samples

Samples were prepared by MBE growing procedure at ~ 300 °C with follow-up deposition of blocking Si layers at ~ 500 °C. Following samples were studied:

1) Samples containing different number of QDs layers in “sandwich heterostructure” (from 1 to 20) with constant effective thickness of every Ge-layer (5 monolayers (ML)) and thin (30 Å) blocking Si- layers (samples 1-4).

2) Two-layer samples Si/Ge/Ge/Si with constant effective thickness of Ge layers (5ML) and different thickness of thin blocking Si- layers: 20, 25, 30, 40 Å (samples 5-8).

3) Sample (stack) containing layers with continuously decreasing Ge- coverage in upper layers (from 6 to 3 ML) for obtaining more uniform sizes of Ge- clusters in accordance with the decrease in the Ge- wetting layer thickness in the upper layers of a multi-layered structure in accordance with [5] (sample 9). Structural transition from pseudomorphic Ge films to pyramid-like Ge islands was controlled by Reflection High Energy Electron Diffraction with the pattern changed from streaky to spotty.

4) Sample containing 8 Ge- layers with constant effective thickness of Ge layers (5ML) and thick (500 Å) blocking Si- layers (sample 10).
3.2 Results and discussion.

Experimental $k^2$- weighted GeK EXAFS spectra of samples 1-10 are shown in Figure 1. Figure 2 shows inverse Fourier transform of the filtered in the first shell region of R-space experimental GeK $k^2\chi(k)$ data for the sample 6.

As can be seen in Table 1, coordination number $N_{Ge}$ for the sample containing one Ge-layer is $\sim$1,1 (sample 1). The $N_{Ge}$ coordination number increase up to $\sim$1,6 – 2,0 for all two- and multi-layered samples with thin (~30 Å) blocking Si layers(samples 2-9), indicates the decrease of two-dimensional pseudomorphic Ge films thickness and increase of Ge-clusters sizes, in contrast with multi-layers samples with thicker Si films (500 Å), which have smaller coordination numbers ($N_{Ge} \sim$ 1,1) (sample 10). It was established, that $N_{Ge}$ coordination numbers and sizes of Ge-islands increase with the decrease of blocking Si-layers thickness (for samples from 8 to 5). The origin of such growth of Ge-islands sizes for this and similar cases is attributed to the better condition for preferential nucleation for samples with thin blocking Si layers due to an inhomogeneous strain field induced by buried dots. This result is in accordance with electron spectroscopy and electron diffraction results.

| №  | $m$ (ML) | $n$ | $d$, (Å) | $N_{Ge}$ | $N_{Si}$ | $R_{Ge}$, (Å) | $R_{Si}$, (Å) | $2\sigma_{Ge}^2$, (Å²) | $2\sigma_{Si}^2$, (Å²) | $F_{\text{EXAFS}}$ |
|----|----------|-----|---------|---------|---------|---------------|---------------|----------------|----------------|-------------|
| 1  | 5        | 1   | 30      | 1,1     | 2,9     | 2,41          | 2,39          | 0,004          | 0,004          | 0,9         |
| 2  | 5        | 3   | 30      | 1,6     | 2,4     | 2,42          | 2,39          | 0,006          | 0,006          | 2,9         |
| 3  | 5        | 10  | 30      | 1,8     | 2,2     | 2,42          | 2,37          | 0,006          | 0,006          | 2,7         |
| 4  | 5        | 20  | 30      | 1,8     | 2,2     | 2,43          | 2,38          | 0,009          | 0,008          | 1,1         |
| 5  | 5        | 2   | 20      | 2,0     | 2,0     | 2,42          | 2,36          | 0,005          | 0,005          | 2,5         |
| 6  | 5        | 2   | 25      | 1,9     | 2,1     | 2,42          | 2,36          | 0,005          | 0,005          | 1,6         |
| 7  | 5        | 2   | 30      | 1,8     | 2,2     | 2,42          | 2,37          | 0,005          | 0,007          | 2,3         |
| 8  | 5        | 2   | 40      | 1,7     | 2,3     | 2,42          | 2,37          | 0,005          | 0,005          | 2,6         |
| 9  | 5; 6; 4,9; 4,2; 3,5 | 4   | 30; 50; 30 | 1,9 | 2,1 | 2,42 | 2,39 | 0,009 | 0,008 | 1,4 |
| 10 | 5        | 8   | 500     | 1,1     | 2,9     | 2,43          | 2,39          | 0,013          | 0,008          | 1,8         |
It has been found that QDs are characterized by interatomic Ge-Ge ($R_{Ge}$) distances of ~ 2.42 Å, which is 0.03 Å less than that in bulk Ge in accordance with our previous results [6, 7, 10].

4. GaN/AlN systems

4.1 Samples

Samples were prepared by MBE GaN growing procedure on AlN substrate at ~ 560-650 °C with follow-up deposition of blocking AlN layers at ~ 1000-1100 °C. The epitaxial growth was carried out using Ga(Al) effusion cells and NH$_3$ as the active nitrogen source by the special low temperature procedure [13]. QDs formation was controlled by HR TEM and photoluminescence measurements [13, 14]. Following samples were studied:

1) Samples containing different number of monolayers (ML) (from 1 to 6) in single GaN layer (samples 1-4).
2) Samples containing different number of QDs layers in “sandwich heterostructure” (from 1 to 27) with constant effective thickness of every GaN-layer (5 ML) and enough thin (100 Å) blocking AlN- layers (samples 5-8).
3) Samples with constant effective thickness of GaN-layer (5ML) in structure with single GaN layer annealing in ammonia at different temperatures (samples 9-12).
4) Samples containing seven GaN layers with constant effective thickness of every GaN-layer (7ML) and different thickness of blocking AlN- layers (samples 13-14).

4.2 Results and discussion

Experimental $k^2$- weighted GaK EXAFS spectra and Fourier transform magnitude $|F(R)|$ without phase shift corrections for samples 1 - 14 and bulk GaN (see Table 2) are shown in Figure 3 and Figure 4, accordingly.

Figure 3. Experimental $k^2$- weighted GaK EXAFS spectra of samples 1-14 and bulk GaN (see Table 2)

Figure 4. Fourier transform magnitude $|F(R)|$ without phase shift corrections of $k^2\chi(k)$ for GaK EXAFS spectra of samples 1 - 14 and bulk GaN (see Table 2)

Figure 5 shows inverse Fourier transform of the filtered in the first two shell region of $R$-space experimental GaK $k^2\chi(k)$ data for the sample 8.
Inverse Fourier transform of the filtered in the first two shell region of $R$-space experimental Ga\textit{K}$\chi(k)$ data for the sample 8 (see Table 2) – solid line, and theoretical fit result - dashed line.

Table 2. EXAFS fit parameters computed from the Fourier filtered in the region 0.8 – 3.2 Å experimental Ga\textit{K}$\chi(k)$ data ($\Delta k$=3 – 13 Å$^{-1}$) measured at 293 K for the GaN/AlN samples with different number of GaN layers ($n$) and different thickness ($d$) of AlN spacer between them. $R_{Ga-N}$, $R_{Ga-Ga}$ and $R_{Ga-Al}$ are Ga-N, Ga-Ga and Ga-Al bond lengths; $\sigma^2_1$, $\sigma^2_2$ and $\sigma^2_3$ are the Debye-Waller factors for these bonds, ($m$) is effective thickness of GaN-layers (in ML), $T_{\text{ann}}$ – temperature of annealing in NH$_3$, $F_{\text{EXAFS}}$ - the goodness of fit index.

| $N_e$ | $m$ (ML) | $d$ (Å) | $T_{\text{ann}}$ | $N_{Ga}$ | $N_{Al}$ | $R_{Ga-N}$ (Å) | $R_{Ga-Ga}$ (Å) | $R_{Ga-Al}$ (Å) | $2\sigma^2_1$ (Å$^2$) | $2\sigma^2_2$ (Å$^2$) | $2\sigma^2_3$ (Å$^2$) | $F_{\text{EXAFS}}$ |
|-----|----------|--------|-----------------|--------|---------|--------------|-----------------|-----------------|----------------|----------------|----------------|---------------|
| 1   | 1        | 1      | 200             | -      | 3.8     | 8.2          | 1.949           | 3.150           | 3.130          | 0.011          | 0.010          | 0.015         | 1.9           |
| 2   | 1        | 1      | 200             | -      | 7.2     | 4.8          | 1.941           | 3.140           | 3.130          | 0.010          | 0.011          | 0.012         | 2.0           |
| 3   | 1        | 1      | 200             | -      | 10.5    | 1.5          | 1.938           | 3.140           | 3.130          | 0.010          | 0.012          | 0.010         | 1.7           |
| 4   | 1        | 1      | 200             | -      | 10.1    | 1.9          | 1.939           | 3.142           | 3.130          | 0.009          | 0.012          | 0.010         | 2.0           |
| 5   | 1        | 1      | 100             | -      | 8.7     | 3.3          | 1.942           | 3.145           | 3.130          | 0.010          | 0.013          | 0.011         | 1.7           |
| 6   | 1        | 1      | 100             | -      | 10.6    | 1.4          | 1.940           | 3.146           | 3.130          | 0.009          | 0.012          | 0.16          | 1.6           |
| 5   | 1        | 1      | 100             | -      | 10.3    | 1.7          | 1.943           | 3.148           | 3.130          | 0.011          | 0.013          | 0.007         | 1.5           |
| 8   | 1        | 27     | 100             | -      | 9.4     | 2.6          | 1.947           | 3.155           | 3.130          | 0.011          | 0.013          | 0.008         | 1.4           |
| 9   | 1        | 1      | -               | -      | 12      | -            | 1.950           | 3.167           | -              | 0.009          | 0.015          | -             | 1.8           |
| 10  | 1        | -      | 830             | -      | 12      | -            | 1.949           | 3.160           | -              | 0.010          | 0.014          | -             | 1.9           |
| 11  | 1        | -      | 890             | -      | 12      | -            | 1.953           | 3.166           | -              | 0.009          | 0.013          | -             | 1.4           |
| 12  | 1        | -      | 1100            | 3.6    | 8.4     | 1.927        | 3.147           | 3.120          | 0.004          | 0.011          | 0.011         | 3.1           |
| 13  | 7        | 7      | 100             | -      | 10.4    | -            | 1.949           | 3.17            | -              | 0.005          | 0.010          | -             | 4.0           |
| 14  | 7        | 7      | -70             | 11.5   | -       | -            | 1.946           | 3.17            | -              | 0.007          | 0.012          | -             | 3.1           |

The origin of the vertical correlation of GaN-islands and growth in their size are attributed to preferential nucleation due to an inhomogeneous strain field induced by buried dots (as noted above for Ge/Si - systems). However, the coarsening effect only occurs in the first several periods and is not evident afterwards (as well as for Ge/Si system). Decrease of $N_{Ga}$ coordination number in going from samples 6, 7 to multi-layer sample 8 (consist of 27 GaN layers) is very likely determined by the interface diffusion due to multiple heating during preparation. As can be seen in Table 2, samples 9-11...
consist of large-scale GaN-islands in AlN-matrix \((N_{Ga}=12)\). At the same time the value of \(N_{Ga}\) decreases dramatically after annealing at higher temperature (see Table 2, Figure 3, 4 for sample 12) because of interface diffusion. Special attention can be given to the fact, that \(N_{Ga}\) coordination numbers go up with the decrease of blocking AlN-layers thickness (from sample 13 to sample 14). The origin of such growth of GaN-islands sizes is attributed to the better condition for preferential nucleation for samples with thin blocking AlN-layers.

It has been found, that the first coordination shell \(R_{Ga-N}\) interatomic distance in GaN/AlN heterostructures is equal to 1,93 - 1,95Å, which is smaller compared to bulk crystalline GaN in accordance with our previous results \([8-10]\). For the second shell, \(R_{Ga-Ga}\) interatomic distances equal 3,14 – 3,17 Å has been found.

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6. References

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