Microstructure and morphology of 2D arrays of Ge quantum dots in a Si/Al$_2$O$_3$ matrix

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Abstract. The paper presents the results of the microstructure and morphology study of two-dimensional Ge QD arrays in a Si/Al$_2$O$_3$ matrix formed by annealing multilayer periodic structures with Ge nanolayers in a Si/Al$_2$O$_3$ matrix. The distinctive features of samples in the series are the location and thickness of the Si barrier layers between Ge and aluminium oxide matrix. X-ray reflectometry and diffractometry and transmission electron microscopy studies have shown that large Ge$_x$Si$_{1-x}$ nanocrystallites are formed and the multilayer structure is destroyed after annealing of the multilayer sample Al$_2$O$_3$/Ge without Si. It was found that the presence of Si barrier layers in multilayer Al$_2$O$_3$/Si/Ge structures reduces the interdiffusion of Al and Ge, but Ge$_1$,Si$_{x}$ nanocrystallites are formed as a result of Si and Ge interdiffusion. Thus, the introduction of Si barrier layer into the Al$_2$O$_3$/Ge structure allowed obtaining of two-dimensional arrays of Ge$_{1-x}$Si$_x$ nanocrystallites with the penetration of Si up to 0.64.

1. Introduction
The SiGe nanocrystallites (quantum dots, QD) embedded in a wide bandgap matrix are very promising for applications in photovoltaic [1, 2] and memory devices [3, 4]. It was previously shown theoretically and confirmed experimentally that in structures with Si$_{1-x}$Ge$_x$ nanocrystallites up to 10 nm in size, the effective band gap can be controlled by changing not only the QD sizes, but also their composition [5]. The Al$_2$O$_3$ wide bandgap matrix is attractive since it possesses a high thermodynamic stability and larger permittivity as compared with Si or Ge oxide. So, special efforts of the technologists were aimed at self-assembled growth of Si$_{1-x}$Ge$_x$ nanocrystallites in aluminum oxide matrix [6]. The first results on the experimental obtaining of multilayer (ML) periodic structures with Ge nanolayers in a Si/Al$_2$O$_3$ matrix and formation of SiGe QD two-dimensional (2D) arrays are presented in [7, 8]. In these papers Si is used as a barrier layer between Ge and the aluminium oxide matrix with strong oxygen-metal bond. However, it was shown in [9] that after annealing, both germanium and silicon QDs are formed in such structures, the size and quantity of which are determined by the layer thickness and annealing temperature.

The aim of this work is to study the microstructure and morphology of Ge nanocrystallites 2D arrays in a Si/Al$_2$O$_3$ matrix formed by annealing at 900 °C of ML periodic structures with Al$_2$O$_3$/Si/Ge/Si nanolayers. It was expected that the introduction of double Si barrier layers would allow more precise control of the size and composition of formed QDs.

2. Experimental methods
In this work, ML Al$_2$O$_3$/Si/Ge/Si periodic structures obtained on a Si (001) substrate by electron beam
evaporation in vacuum are studied. The samples series under study included four sets of nanolayers periods Al$_2$O$_3$/Ge, Al$_2$O$_3$/Ge/Si and Al$_2$O$_3$/Si/Ge/Si with different thickness of the Si barrier layers (table 1). These periods in the samples were repeated up to 24 times. The thicknesses of Ge nanolayers and dielectric Al$_2$O$_3$ layers were formed the same and amounted to 3 and 5 nm, respectively, while the thickness of the Si barrier nanolayers was 0 nm (sample TX6 - Al$_2$O$_3$/Ge), 1 nm (samples TX5 and TX7 - Al$_2$O$_3$/Ge/Si and Al$_2$O$_3$/Si/Ge/Si) and 2 nm (sample TX8 - Al$_2$O$_3$/Si/Ge/Si).

The morphology and microstructure of 2D arrays of QD Ge in the Si/Al$_2$O$_3$ matrix before (samples are labeled as TX5_ini, TX6_ini, TX7_ini, TX8_ini) and after annealing in vacuum at 900 °C (samples TX5_ann, TX6_ann, TX7_ann, TX8_ann) were studied by X-ray reflectometry (XRR) and diffractometry (XRD) and transmission electron microscopy (TEM).

XRR curves were registered in symmetric $\theta$-2$\theta$ scan mode using parallel beam of monochromatic Cu-K$_\alpha$ radiation by means of High-resolution X-ray diffractometer D8 Discover (Bruker AXS, Germany) designed in horizontal Bragg-Brentano geometry and equipped with semiconductor PSD LYNXEYE working in point-detector 0D mode. Primary 4-bounce channel cut (220) Ge monochromator was used for monochromatization of the radiation of the Bruker rotating Cu anode. The parallel beam of the X-rays was obtained by means of a Göbel mirror.

Registration of X-ray diffraction (XRD) patterns was performed in symmetric $\theta$-2$\theta$ scan mode by means of powder X-ray diffractometer D2 PHASER (Bruker AXS, Germany) designed in vertical Bragg-Brentano geometry and equipped with semiconductor 1D position-sensitive detector (PSD) LYNXEYE with opening angle of 5°. Cu-K$_\alpha$ radiation of the Bruker X-ray tube with Cu anode monochromatized by Ni filter was used. During the measurements, the sample was rotated around the sample holder axis coinciding with the axis of the goniometer to reduce the influence of the possible effect of preferential orientation of crystallites. Additional measurements were carried out to evaluate the detector zero shift and displacement corrections for use in further analysis. For that, the samples were placed in the NaCl powder, so that its surface coincided with the surface of the powder. The $2\theta$ Bragg angle positions of NaCl reflections were preliminary calibrated using X-ray powder standard Si640d (NIST, USA).

X-ray phase analysis was carried out by means of program EVA (Bruker, Germany) using Powder Diffraction File-2 (PDF-2) (International Centre for Diffraction Data (ICDD 2014), USA). The unit cell parameters of the phases were calculated from the observed Bragg angles $2\theta$ and their Miller indices by means of crystallography-oriented least square technique realized in program CelSiZ [10]. The XRD reflections of all observed phases were checked for the microstrain broadening since their contribution can significantly affect the determined crystallite size. To verify and evaluate average crystallite sizes $D_{XRD}$ and microstrain values $\varepsilon$ method of Size-Strain Plot (SSP) for the reflections of pseudo-Voigt (pV) type realized in program $\varepsilon$izeCr [11] was used. According to $\varepsilon$izeCr procedures in the absence of microstrain contribution ($\varepsilon = 0$), confirmed by SSP, the individual value of $D_{XRD}$ is calculated using the Scherrer equation for each reflection and the average value of $D_{XRD}$ is obtained by least square method.

ML structures with QDs were also studied using a JEOL JEM 2100F transmission electron microscope with an accelerating voltage of 200 kV in the diffraction contrast and high resolution modes. Samples for the study were prepared in the cross section geometry in accordance with the standard procedure, with preliminary mechanical thinning and further polishing by Ar$^+$ ions beam with energy of 4 keV.

3. Results
The XRR patterns of all investigated samples are shown in figure 1(a). The XRR curves obtained from as-prepared samples show an interference pattern typical for periodic multilayer structures: they include narrow intense peaks up to the fourth order corresponding to the layer period (ML Bragg peaks), thickness oscillations corresponding to the total film thickness, and broad maxima arising due to the presence of a “cap” layer on the structure surface (figure 1(a), black curves). Annealing leads to significant changes in the morphology of the ML structure, this is manifested in interference patterns.
So, interference is practically not observed on the XRR curve of the TX6_ann sample, which indicates a disruption of the ML uniformity up to their complete intermixing (figure 1, red dashed curve).

It should be noted that the changes in XRR patterns due to annealing of samples with Si barrier layers are the more significant, the higher the Si content in the sample (TX5, TX7, and TX8). Thus, in comparison with TX5_ann, in the XRR pattern for the TX5_ann sample, a change in the intensity of the ML Bragg maxima is observed, while their positions and half-widths differ slightly. Notice that thicknesses oscillations are still observed. This indicates the appearance of some inhomogeneity in the layers while maintaining the planarity of the interfaces [12].

Note that the observed changes in the XRR patterns for sample TX7 and TX5 before and after annealing are mainly the same: despite a slight decrease in the intensity of ML Bragg peaks, they are still observed up to $\theta \approx 4^\circ$. This behavior probably also reflects the formation of some inhomogeneity in the layers after annealing at 900 °C.

For the TX8_ann sample, we found the destroying of the ML structure after annealing reflected by disappearance of the most ML Bragg peaks in the XRR curve. The morphology changes of the TX8_ann and TX6_ann samples are analogous: annealing leads to a disruption of the uniformity of all nanolayers. The observed broad maxima in the XRR picture of the TX8_ann sample correspond to interference on the upper “cap” layer; changes in the structure morphology are not so significant in comparison with the TX6_ann sample.

### Table 1. Sample description and obtained experimental data.

| Sample No | Layers on Si(001) substrate | XRD | TEM |
|-----------|-----------------------------|-----|-----|
| TX5_ann   | [16x(5nm Al$_2$O$_3$/3nm Ge/1nm Si)]$^a$ | Ge$^b$ | a (Å) c (Å) | Ge | 6-10 |
| TX6_ann   | [24x(5nm Al$_2$O$_3$/3nm Ge)]$^i$ | Al$_6$Ge$_5$ | 64(40)$^i$ | Al$_6$Ge$_5$ | 10-12 |
| TX7_ann   | [24x(5nm Al$_2$O$_3$/1nm Si/3nm Ge/1nm Si)]$^i$ | Al$_6$Ge$_5$ | 3.2(4)$^c$ | SiGe, Al$_6$Ge$_5$ | 2-3 |
| TX8_ann   | [24x(5nm Al$_2$O$_3$/2nm Si/3nm Ge/2nm Si)]$^i$ | Al$_6$Ge$_5$ | 5.3(9)$^c$ | SiGe, Al$_6$Ge$_5$ | 2-3 |

$a$ covered by 8 nm top Al$_2$O$_3$ layer; $^b$ according to PDF-2 card 00-004-0545, a = 5.6576 Å, space group $Fd-3m$ (227); $^c$ calculated by SSP technique. For the sample TX5_ann in case of $s = 0$, $D_{XRD} = 21.3(6)$ nm; $^d$ according to the observed value of the unit cell parameter and assuming linear Vegard’s law, Ge phase contains 6.5(7) %, 48(1) % and 64(1) % of Si (a = 5.4301 Å, space group $Fd-3m$ (227), PDF-2 card 00-005-0565) in the samples TX5_ann, TX7_ann and TX8_ann, respectively; $^e$ according to PDF-2 card 00-050-1269, $a = 11.45$ Å, $c = 11.67$ Å, space group $R-3c$ (167); $^f$ in case of bimodal distribution, $D_{XRD} = 95(31)$ nm and 32(3) nm.

The XRD patterns of annealed samples are shown at figure 1(b). The results of unit cell parameters and crystallite size-microstrain values calculations are presented in table 1.

There is no reflections of Ge oxides were found in the all samples investigated. In the samples TX6_ann, TX7_ann and TX8_ann annealed at 900 °C the reflections of Al$_6$Ge$_5$ were clearly detected. In the TX7_ann and TX8_ann samples with double barrier Si layers of 1-2 nm thickness in the initial composition (MLs Al$_2$O$_3$/Si/Ge/Si, table 1) the observed two reflections are very wide. One of these reflections can also be attributed to the Ge phase. The crystallite sizes $D_{XRD}$ of Al$_6$Ge$_5$/Ge in the TX7_ann and TX8_ann are small, about 3-5 nm (table 1). In the TX6_ann sample (ML Al$_2$O$_3$/Ge without Si barrier layers) reflections of Al$_6$Ge$_5$ are much stronger and narrower. Two new Al$_6$Ge$_5$ reflections appear in the TX6_ann XRD pattern (figure 1(b)), whereas Ge phase is not detected.
Taking into account all the reflections observed for the TX6_ann Al$_x$Ge$_{3-x}$ phase, $D_{XRD} = 64(40)$ nm value is obtained. Assuming that the large estimated standard deviation of $D_{XRD}$ is the result of the bimodal distribution of $D_{XRD}$ in the TX6_ann sample, the crystallite sizes of $D_{XRD} = 95(31)$ nm and 32(3) nm were obtained.

![Figure 1. XRR curves of the as-prepared and 900 °C-annealed samples (a) and part of XRD patterns of the samples after 900 °C annealing (b). The XRR curves and XRD patterns are moved vertically for better visualization.](image)

Different from other samples, the TX5_ann film with single Si barrier layer (ML Al$_{x}$O$_{3}$/Ge/Si, table 1) exhibits only rather narrow Ge reflections in the XRD pattern (figure 1(b)) resulting in a $D_{XRD}$ value of about 22 nm (22.36(6) nm in model with microstrain and 21.3(6) nm in the absence of them). For this sample the SSP (figure 2(a)) and Williamson-Hall Plot (WHP, not shown) gave a clear evidence of the microstrain in the Ge crystallites. For the Ge phase in TX7_ann and TX8_ann evaluation of $s$ cannot be performed due to only one Ge reflection observed. At the same time, WHP and SSP indicate the absence of microstrain ($s = 0$) in the crystallites of Al$_x$Ge$_{3-x}$ in TX6_ann, TX7_ann and TX8_ann, see an example of SSP in figure 2(b). The presence of microstrain in Ge crystallites may be due to the penetration of a small amount of Si into the Ge nanocrystallite structure. Assuming that instead of Ge phase the Ge$_{1-x}$Si$_x$ phase present in the samples, linear Vegard’s law results in $x = 0.065, 0.48(1)$ and 0.64(1) of Si for the TX5_ann, TX7_ann and TX8_ann, respectively.

TEM study showed that the samples after annealing have a ML structure containing alternating layers with bright and dark contrast (figure 3). In the images of sample TX6_ann without silicon the layers structure does not have a clear contrast, the layers are divided into separate nanocrystallites (figure 3(a)). However, in the images of sample TX7_ann (as well as in TX8_ann) with silicon the layer structure has an absolutely clear continuous contrast (figure 3(b)). If we take into account that Si and Al$_{x}$O$_{3}$ have a bright contrast in the image and the dark lines correspond to Ge layers, then the layers thickness of samples TX7_ann and TX8_ann measured by TEM images is in good agreement with technological data.

High resolution TEM studies of samples showed that after annealing the nanocrystallites surrounded by an amorphous Al$_x$O$_{3}$ matrix are observed in the structures (figure 4). In sample TX6_ann the observed nanocrystallites reached a size of 10-12 nm. The interplanar distances
measured in the high resolution TEM (HRTEM) images (figure 4(a)) were of the order of 6 Å, so it is probable that these nanocrystallites can be attributed to Al$_6$Ge$_5$, the presence of which is confirmed by the XRD method (table 1).

**Figure 2.** SSP ($k_{\text{Scherrer}} = 0.94$, $k_{\text{Stokes}} = 4$) for Ge (a) and Al$_6$Ge$_5$ (b) crystalline phase of the sample TX5$_{\text{ann}}$ (a) and TX6$_{\text{ann}}$ (b) annealed at 900 °C. $FWHM_{\text{corr}}$ is full width at half maximum corrected to instrumental broadening.

**Figure 3.** Bright field TEM images of the samples cross section (a) TX6$_{\text{ann}}$ and (b) TX7$_{\text{ann}}$ annealed at a temperature of 900 °C.

**Figure 4.** HRTEM images of nanocrystallites in (a) TX6$_{\text{ann}}$ and (b) TX8$_{\text{ann}}$ samples annealed at 900 °C.

In samples TX7$_{\text{ann}}$ and TX8$_{\text{ann}}$ nanocrystallites of elliptic shape with sizes of about 2-3 nm in thickness and 5-6 nm in length are detected. Note that in table 1 we have included only the thickness of nanocrystallites ($D_{\text{TEM}}$), since it is determined by XRD and is suitable for comparison. The
interplanar distances measured from the HRTEM images had values in the range of 3.1–3.3 Å, which corresponds to the interplanar spacings of Si, Ge or mixed Ge\textsubscript{1-x}Si\textsubscript{x} (figure 4(b)).

The diffraction pattern of the annealed samples also showed the presence of nanocrystallites with an arbitrary orientation in the amorphous matrix. On the samples diffraction a set of diffraction rings from polycrystalline inclusions is observed. Measurement of interplanar distances confirmed the presence of the Al\textsubscript{2}Ge\textsubscript{3} phase in the sample, which was previously observed by the XRD and HRTEM methods. In addition, the presence of Ge, Si and mixed SiGe nanocrystallites was detected in the TX7\_ann and TX8\_ann samples. Interestingly, the measurement of interplanar distance showed that in samples with a smaller thickness of Si layers, the silicon penetration in SiGe nanocrystallites is less and is about 10-20 % and 20-30 % in sample TX7\_ann and TX8\_ann, respectively. The values of interplanar distances calculated from electron diffraction patterns are consistent with the values obtained from the XRD data and measured in HRTEM images (table 1).

4. Discussion and Conclusion
The XRD results correlate with the XRR evolution (figure 1(a)). In the Si layer-free ML Al\textsubscript{2}O\textsubscript{3}/Ge (TX6 sample) there are no barriers for Al and Ge interdiffusion, resulting in formation of large Al\textsubscript{2}Ge\textsubscript{3} crystallites and destroying the ML structure after annealing reflected by disappearance of the most ML Bragg peaks in the XRR curve.

In the samples TX7\_ann and TX8\_ann with double barrier Si layers of 1-2 nm thickness (MLs Al\textsubscript{2}O\textsubscript{3}/Si/Ge/Si, table 1), the interdiffusion of Al and Ge is difficult. As a result the formed Al\textsubscript{2}Ge\textsubscript{3} and Ge crystallites are small with sizes of 3-5 nm comparable with the Ge layer thickness in the as-prepared ML. The formation of the 2D arrays of QD Ge does not significantly distort the ML structure and XRR curves of the TX7\_ann sample after 900 °C are the best.

However, with an excess of Si in the structure, as in the TX8\_ann sample, the formation of Si\textsubscript{1-x}Ge\textsubscript{x} nanocrystals is observed, where x varies over a wide range of values from 0 to 1, which reflects the destruction beginning of ML structure. As a result, we cannot talk about the formation of two-dimensional Ge QD arrays in this sample.

As can be seen in the table 1, the crystallite size $D_{\text{XRD}}$ determined by XRD is in a good agreement with the QD size obtained by TEM for the samples TX7\_ann and TX8\_ann, characterized by small $D_{\text{TEM}}$ values ~3-5 nm. At the same time, there is a large discrepancy between the XRD and TEM results for the TX6\_ann and TX5\_ann samples. While XRD gives the sizes $D_{\text{XRD}}$ of crystallites between 22 nm and 95 nm, TEM shows nanocrystallites size of 5-12 nm. Also in the sample TX5\_ann with single barrier Si layer (initial ML Al\textsubscript{2}O\textsubscript{3}/Ge/Si, table 1) no Al\textsubscript{2}Ge\textsubscript{3} reflections were detected.

To clear up this discrepancy a simple simulation of samples with large (22 nm and 95 nm) and small crystallites (3-5 nm) was performed. As shows on the figure 5 it is impossible to distinguish by XRD the reflections of the phases with a small $D$ in the presence of large ones in two cases, if the crystallites belong to the same phase or if the reflections of different phases overlap. An assumption can be made about bimodal distribution of the crystallites size – with large crystallites detected by the XRD and small crystallites observed by the TEM in the samples TX5\_ann (large Ge and small Ge and/or Al\textsubscript{2}Ge\textsubscript{3} crystallites) and TX6\_ann (large Al\textsubscript{2}Ge\textsubscript{3} and small Al\textsubscript{2}Ge\textsubscript{3} and/or Ge crystallites).

Thus, single Si barrier layer prevents a large interdiffusion of Al and Ge and leads to the formation of Ge crystallites with a small Si penetration and an intermediate size of ~22 nm, and also prevents the formation of large Al\textsubscript{2}Ge\textsubscript{3} nanocrystallites.

Summarizing it can be concluded that the role of the Si barrier layer is very important in the formation of 2D arrays of Ge QDs in a Si/Al\textsubscript{2}O\textsubscript{3} matrix by electron beam evaporation in vacuum. The introduction of a single Si barrier layer into the structure design allows to obtain of Ge\textsubscript{1-x}Si\textsubscript{x} nanocrystallites (the penetration of 6.5(7)% Si in the Ge structure). The structure design with double Si barrier layers makes it possible to control the size and composition of the formed SiGe QD.
Figure 5. Illustration of why XRD does not detect small crystallites in the presence of large (if all their XRD reflections are overlapping).

The data obtained will contribute to the optimization of the technology for producing SiGe quantum dots in an amorphous aluminium oxide matrix.

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