Study of the morphology of Ge quantum dots grown by liquid phase epitaxy

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Abstract. This paper reports the results of a study of the morphology of Ge quantum dots (QDs) grown by liquid-phase epitaxy on Si substrate with orientation (111) while applying pulsed cooling of the substrate. The morphology of the structures with QDs is studied by atomic force microscopy. The QDs are grown by applying a different number of cooling pulses – 1, 3, 5 and 10, with a difference in the temperature between the substrate and the heat absorber $\Delta T_D = 5$ °C. The effect is studied of the different technological conditions on the size of the Ge QDs and the density of their distribution.

1. Introduction

Recently, the study of nano-heteroepitaxial structures with quantum size objects, such as quantum dots (QDs), have attracted the interest of many research teams due to their potential for application in optoelectronic devices with improved properties. The Ge quantum dots are regarded as promising materials [1,2]. They could be used as infrared detectors and third-generation solar cells. Based on theoretical calculations, it has been shown that application of Ge QDs in Si based solar cells increases their efficiency up to 53 % [3,4]. It should be noted that the maximal efficiency of the available commercial Si-based solar cells is 22 %.

It has been reported that the application of InAs QDs in the matrix of GaAs grown by MBE and MOCVD did not result in formation of high-efficiency solar cells as has been expected – the application of the QDs resulted in a decrease of the quantum efficiency and of the solar cells efficiency [5]. The authors attributed this result to the presence of stress in the “wetting” layers of the narrow gap material between the QDs where the centers responsible for the carriers’ recombination channels without light emission are created [5].

In this work, liquid phase epitaxy (LPE) in the regime of pulsed cooling (PC) of the Si substrate is applied to deposit Ge QDs arrays without an elastic tense "wetting” layer in between QDs, thus ensuring conditions for their formation close to the equilibrium and growth of structures with reduced carrier recombination [6]. The aim is to study the influence of the technological parameters during the liquid-phase epitaxy (LPE) on the Ge QDs size, namely, the number of the applied cooling pulses, on

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the surface morphology of nano-hetero-epitaxial structures with “open” QDs. Atomic force microscopy (AFM) is applied to study the surface morphology.

2. Experimental
Growing of Ge “open” quantum dots on a buffer Si layer formed on a Si substrate with (111) orientation is performed by LPE with application of cooling pulses [6,7] and an original technological scheme. The process of growing presented by the diagram in figure 1 consists of two stages - formation of the buffer layer and growing of Ge QDs.

Special equipment for growing multilayer NHJ structures with a horizontal supplier was constructed.

The formation of the buffer layer on the Si substrate consists of deposition of Sn, homogenization of a saturated melt solution of Si+Sn alloy heated to a temperature of 700°C and cooling down to 400°C in order to grow a thin Si layer. The Sn is removed by a specially designed device in the cassette used for growing the QDs. The second stage of the process is growing QDs by applying cooling pulses. A heat sink with temperature, $T_{HS}$, which is lower than the temperature of the substrate, $T$, by $\Delta T = T - T_{HS}$ is placed on the back surface of the substrate. Growing NHE structures with QDs with a surface density $< 10^{11}$ cm$^{-2}$ of the narrow-gap material Ge on a substrate of the wider band gap material single crystal Si [5] is performed at a temperature of the oven of 600 °C in an atmosphere of highly purified hydrogen. The difference in the temperatures of the substrate and the heat sink is $\Delta T = 5$ °C. After a certain time, which depends on the duration of the cooling pulse $\tau = 10^{-3} \div 10^{-1}$ sec, the heat sink assumes the temperature of the substrate and a nanolayer with QDs arrays crystallizes on the front surface of the substrate [8]. Due to the different lattice constants of the substrate material (Si) and the QDs material (Ge), in the initial stage a continuous "wetting" layer by the Stranski-Krastanov’s mechanism is formed. As the thickness of the growing layer increases, periodic stresses appear at the interface with the substrate. During the growing process, the formation of the Ge QDs takes place in the sites with minimum mechanical stress, i.e. in the positions with a perfect structure [9]. Different structures are prepared by applying different numbers of “cooling” pulses – 1, 3, 5 and 10. The number of pulses determines the different size of the objects grown. According to the theoretical considerations, the diameter and the height of the QDs should increase with the number of cooling pulses [10, 11]. The density of the crystallized QDs under optimum conditions is limited mainly by the period of the perfect crystalline structure in the interface. The residual Sn on the structures grown is removed by a water solution of HNO$_3$. The possible presence of Sn after the removal is checked by X-ray fluorescent analysis.

The surface morphology of the samples prepared is studied by a CMM-2000 AFM (Proton—Zelenograd, Russia) with a soft cantilever tip MSCT (Veeco, USA).

3. Results and discussion
Figure 2 presents AFM images of the Ge QDs grown by applying 1 “cooling” pulse. The results show that the QDs have a diameter of about 20 nm and a height of about 5 nm. The deviation in the size is $< 20 \%$. The mean surface roughness is $< 1$ Å. In this case, the QDs are very small and do not have a well-defined shape. A similar picture is observed in the case of applying 3 cooling pulses (not shown here); however the QDs have grown with a larger size – the diameter is about 60 nm and the height is 10 nm with a deviation $< 30\%$. 

![Figure 1. Schematic diagram of the processes of growing a buffer Si layer and Ge "open" QDs on a Si substrate with Sn solution hot fusion.](image-url)
Figure 2. AFM images of the samples with Ge QDs grown on a (111) Si substrate with a buffer Si layer grown after application of 1 “cooling” pulse ((a) and (b)) and the profile of the QDs (c). The marker in (a) corresponds to 100 nm.

Figure 3. AFM images of the samples with Ge QDs on a (111) Si substrate with a buffer Si layer grown after application of 5 “cooling” pulses ((a) and (b)) and the profile of the QDs (c). The marker in (a) corresponds to 100 nm.
The AFM images of the substrate surface with Ge QDs grown by applying 5 cooling pulses are shown in figure 3. The QDs have a much larger size, namely, a diameter of 190 nm and a height of 70 nm. The deviation in the size values is < 35%. It has to be noted that after applying 5 cooling pulses the Ge QDs have grown in a pyramidal-like shape with a density of $2 \times 10^{10}$ cm$^{-2}$.

As seen from the AFM images shown in figure 4 of the samples with Ge QDs grown after applying of 10 cooling pulses, the QDs have increased further in size – their diameter is 245 nm, the height is 150 nm with a deviation < 35%. The pyramidal-like Ge QDs distribution is less dense than that in the previous cases – the density of their surface distribution has decreased from $2 \times 10^{10}$ cm$^{-2}$ to $1.5 \times 10^{10}$ cm$^{-2}$.

The data obtained from the AFM measurements are summarized in table 1.

The increase observed in the size of the Ge QDs with the increase of the number of cooling pulses is in accordance with the theoretical considerations [10,11] and the experimental data reported by other authors as well [9].

![AFM images](image)

**Figure 4.** AFM images of the samples with Ge QDs grown on a (111) Si substrate with a buffer Si layer grown after application of 10 “cooling” pulses (a and b) and the profile of the QDs (c). The marker in (a) corresponds to 100 nm.

**Table 1.** Data obtained by AFM measurement of “open” Ge QDs grown on a buffer Si layer formed on a c-Si substrate with (111) crystalline orientation.

| Sample No. | Number of pulses | Average diameter, nm | Average height, nm | Average deviation in the QDs diameter, nm | Density of the QDs distribution, $\times 10^{10}$ cm$^{-2}$ |
|------------|------------------|----------------------|-------------------|-----------------------------------------|-------------------------------------------------|
| 1          | 1                | 25                   | 5                 | 20                                      | 2,0                                             |
| 2          | 3                | 62                   | 10                | 30                                      | 2,0                                             |
| 3          | 5                | 196                  | 69                | 35                                      | 2,0                                             |
| 4          | 10               | 245                  | 150               | 35                                      | 1,0                                             |
4. Conclusions

Ge QDs were grown from a molten solution on a Si substrate by LPE while applying cooling pulses. The study by AFM of the structural properties of the grown structures after applying different number of cooling pulses revealed the morphology, the surface roughness, the linear dimensions of quantum dots and their density. It was observed that the surface morphology with Ge quantum dots changed with the number of cooling pulses – the QDs size and their height increased. The density of their surface distribution on the substrate decreased after the application of 10 pulses; however, a significant increase was observed of their size, while the deviation in the size remained the same as after application of 5 pulses. As the number of pulses was increased to 5, the Ge QDs shape changed from a drop-like to a pyramidal-like one. The observed increase in the size and the changes in the shape of the Ge QDs correlated with the theoretical considerations reported earlier [10,11]. Work is in progress to apply LPE to grow nano-heteroepitaxial strictures with Ge QDs on Si substrates in view of highly efficient low-cost solar cells and other optoelectronics application.

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