Improvement of growing of Ge QDs by the method of liquid phase epitaxy

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Abstract. This paper reports on improvement of the technological conditions for nano-heteroepitaxial structures (NHES) growth with Ge quantum dots (QDs) by liquid phase epitaxial (LPE) method applying impulse cooling on the substrate (ICS) The physical and mathematic modeling of the processes of growth and the analysis of the thermodynamic status has been carried out to optimize the construction of the thermal unit, the located in it graphite cassette and of the thermal conditions. For the analysis the Solid Works Flow Simulation program is applied, which has a satisfactory accuracy of calculations of heat-transfer simulation. The analysis has revealed shortcomings in the construction of the equipment. Having in mind these results the equipment is reconstructed and new different elements of the thermal block are installed. Good agreement of the experimental and calculated temperature distribution in the process of NHES with Ge QDs growing is obtained. The grown Ge QDs have improved structure with homogeneous distribution and size and depth of the Quantum Wells. The experiments carried out show good reproducibility of the growing process confirming the correctness of the mathematic modeling.

1. Introduction
Currently the development of technologies for growing of semiconductor nano-heteroepitaxial structures (NHES) with quantum wells (QW) and quantum dots (QDs) becomes important for application in solar cells [1].

In this context, the development of methods for growing of NHES without "wetting" layers between QDs by the Stranski-Krastanow mechanism [2], the method of liquid phase epitaxy (LPE) applying impulse cooling of the substrate (ICS) [3,4], used in this work, is actual and very promising. For its application in the devices technologies it is necessary the obtained nanostructures to be without defects, to have highly homogeneous in size and homogenously distributed QWs and QDs. The process should assure high reproducibility of the properties of the nanostructures being grown on large diameter substrates.

In our previous attempts it was not always possible to obtain reproducible results using the existing experimental equipment for growing epitaxial NHES with QDs. This observation required
improvement of the construction of the working units of the equipment and optimization of the technological parameters of the process.

The main objective of this work has been focussed on scientific research for resolving the technical problems related to: development and manufacturing of essentially new working units of the equipment for growing NHES with Ge QDs by LPE method applying IC; optimization of thermal conditions of the process; reconstruction of the cassette and units of equipment by application the results of physical and mathematical modelling; development of the methodology of the thermal fields adjustments in LPE setup during the process of growth.

2. Experimental

From the previous study some disadvantages in the construction of the equipment and in the technological approaches of the processes that adversely affect the quality of the grown NHES with QDs by the method of LPE with ICS have been determinate [5-7]. The main shortcomings have been: poor reproducibility of the processes associated with the uncontrolled mixing of melt solution materials of different compositions and its uncontrolled removing from the substrate, which leads to deterioration of the quality of the grown material; unexpected changes in the thermal conditions of the process of growing related to shift of the position of the sliders of the working cassette relative to the stationary thermal field, which leads to uncontrolled change of temperature of the end surface of the heat absorber.

To overcome these (and other) shortcomings a new vertical type cylindrical drum cassette has been developed and manufactured. The diameter of the cassette is 90 mm and its length - 150 mm. Schematic diagram of the cassette (section along the length axis) is shown in figure 1.

In order to optimized the thermal conditions and the construction of the thermal units of the equipment and of located there graphite cassette, the physical and mathematical modelling of the processes of growing of NHES QDs by the method of LPE method with applied ICS have been carried, analysing the thermodynamic status. For the analysis the SolidWorks FlowSimulation program has been selected which has a satisfactory accuracy of calculations for simulation of heat-transfer process. For the modelling our experimental data obtained earlier [8] have been used and the boundary conditions for the mathematical model and to plane the performance of the work. For the modelling the difference in the temperatures on the area of the end of the heat absorber and the substrate, \( \Delta T_{HA-S} \) 4°C, has been used and kept close to this value in the experiments. The temperature

![Figure 1](image-url). Schematic cross section diagram of the cassette with the water cooled heat absorber used for growing NHES QDs by the method of LPE method with applied ICS. 1 - thermo-couple of the heat absorber, 2 - thermo-couple of the substrate, 3 - frame of the water-cooled heat absorber, 4 - corpus of the cassette, 5 - substrate, 6 - cylinder for the containers, 7 - containers for the holders with melt solution materials, 8 - melt solution materials, 9 - slippery thermo-couple.
in the working space, $T_{WS} = 425 \degree C$, have been used for the modelling and during the process of growing. In the modelling of the conditions of the process of growing a c-Si substrate with diameter of 52 mm has been considered in the analysis. In the experiment the Ge QDs have been grown on the same type substrate - c-Si wafer with 52 mm diameter and orientation (111). The process has been carried out in the $H_2$ flow. A low melt temperature metal – Sn, has been added in the melt solutions used for formation of the buffer and spacer layers. The experiments of growing of NHES QDs and theoretical foundations of the method of LPE with ISC have been described in our previous publications [5-7].

Applying the physical and mathematical modelling has led to establishment of the negative factors affecting the process of growing of NHES QDs: the presence of inhomogeneous thermal field on the area of cassette of 4$^\circ$C/cm axially and to 2$^\circ$C/cm radially; the presence of temperature gradient up to 20$^\circ$C/cm in the area of the working plane of the heat absorber; a high inertness of the process when the thermal conditions have changed; dependence of the quality, homogeneity in distribution of the Ge QDs; dependence of the reproducibility of the process of growth on the position of the heat absorber on the back side of the substrate. As a result of mathematical modelling and optimisation of the thermal units of the equipment and the design of the graphite cassette the shortcoming in the growing process have been eliminated and the construction of the equipment has been improved: materials with appropriated heat conductivity have been used for the heat absorber, new materials have been used for manufacturing of the cassette in order to obtain homogeneous heat field, new materials have been used for the new designed system of shields in the heating area around the Si substrate. From the analyse of the gas flow into the reactor it has been established homogeneous temperature distribution of the flow in the cross section of the reactor and the shortcomings in the construction of the gas supply in the input of the reactor have been pointed and overcame.

In order to establish the appropriated conditions for the process of growing according to the results of modelling the control of temperatures in the three-zones heater of the oven (with quasi-hermetic quartz reactor where the cassette is situated) has been carried out by different thermocouples disposed on different places: in the external side of the heat absorber in the “cold” zone, in the central area of the substrate and in the external side of the cassette in the “hot” zone. The temperatures have been measured to be 430$^\circ$ C, 460$^\circ$ C and 468$^\circ$ C, respectively. Using the slippery (moving) thermocouple (number 9 in figure 1) the temperature on the length of the cassette has been measured in direction from its external side to the substrate and the data have been used to obtain the temperature distribution on the surface of the cassette and in the different places of the oven unit of the equipment. The preliminary measurements have been carried out in the cases of vertical and horizontal positions of the cassette. As a result the negative influence of the gravitation effect on the temperature

![Figure 2](image-url)
distribution has been determinate and the corresponding changes in the construction have been made to minimise it. The difference between the temperature of the surface of the cylindrical cassette and in its centre has been measured to be not higher than 0.5°C in the case of both positions of the cassette. This result shows homogeneous temperature distribution which demonstrates the advisability of the taken construction changes. These conditions have been applied for carrying out the process of growing open Ge QDs on c-Si substrate according the procedure described earlier [5,6]. The surface morphology of the obtained samples has been studied by AFM microscope type CMM-2000 (proton-Zelenograd, Russia) with soft cantilevel tip MSCT (Veeco, USA).

2. Results and discussion

The results obtained from physical-mathematical modelling of the thermal processes applied the values of the measured temperatures on different units of the equipment are compared to the corresponding calculated data from the simulation using SolidWorks FlowSymulation programme.

Figure 2 shows the optimised construction of the heat absorber and the distribution of the measured temperatures (the experimental data) in colours on different places on it. At the right side in the figure 2 the colour legend of the temperatures is presented, as well. The temperatures at the working area of the end of the heat absorber are very homogeneously distributed (red-brown colour of the area 5). The calculated temperature distribution along the radius of the working area of the edge of the heat absorber which has a contact with the substrate (having a circular shape) is displayed in figure 3. It is seen (curve 2—calculated) that the temperature field along the diameter (respectively along the radius) of the working area of the heat absorber is distributed homogeneously and the difference in the temperature along the radius does not exceed 0.07°C. The average temperature on the working area of the heat absorber is 417.66°C which coincides with the corresponding measured temperature distribution presented in figure 2. It has to be noted that the rate of the cooling water has been kept at 60 l/h, and its average temperature has been 26°C. The measured temperature distribution along the radius of the head absorber (between its periphery and its centre) (figure 2, curve 1) has larger deviation - ΔT = 0.2°C, compared to the calculated one which is 0.1°C. This slight difference could be explained by the accuracy of the measurement by the thermocouples and the temperature gauges. Actually, the experimental measurements have been performed with an accuracy of 0.1°C.

Figure 4 demonstrates the calculated (curves 2) and the experimental (curves 1) temperature distribution on the diameter of the Si substrate (with diameter d= 52 mm). In figure 5 the calculated distribution of the temperatures over the working surface of the Si substrate (d = 52 mm) is shown in colour. It is observed that the average measured temperature of the working surface of the substrate is

![Temperature distribution on the diameter (respectively on the radius) of the working area of the end of the heat absorber using flow of cooling water with rate 60 l/h and temperature 26°C. Curve 1 - experimental data, curve 2 - calculated data.](image1.png)

![Temperature distribution on the diameter (respectively on the radius) of the Si substrate at average temperature in the working zone T_{WZ} = 425°C. Curve 1 - experimental data, curve 2 - calculated data.](image2.png)
the temperature distribution measured over the working surface of the substrate is homogeneous and the difference in the temperatures is very small, 0.22°C (between L = 0 mm and L = 26 mm) and 0.26°C (between L = 26 and L = 52 mm). The experimental data (figure 4, curves 1) and calculated values of temperature shown in figure 4 (curve 2) and in figure 5 coincide very well. The small difference between the experimental and calculated temperatures (0.1°C) could be associated with accuracy of the measurement by the corresponding devices. Also, the difference could be due to the fact that the calculations have been performed without taking into account the gravity component in the horizontal arrangement of the cassette, while the experimental measurements have been carried out in its vertical version arrangement. It should be noted that, as shown in figure 2 and figure 5, the average temperature difference between the working area of the end surface of the heat absorber (figure 2) and the substrate (figure 5) is measured to be ΔT_{HAS} = 4.19°C which is very close to the value used in the modelling - 4.0°C, as pointed earlier.

Figure 5. Scheme of the substrate with the calculated temperatures. The average temperature in the working zone $T_{WZ} = 425°C$ and on the end surface of the heat sink $T_{HS} = 417.66°C$. The temperature colour legend is shown in the left side. 1 - frame of the heat sink, 2 - working area of the substrate, 3 - corpus of the cassette, 4 – drum for containers, 5 – container for the ware with the melt solutions, 6 – moving thermocouple.

421.85°C, the temperature distribution measured over the working surface of the substrate is homogeneous and the difference in the temperatures is very small, 0.22°C (between L = 0 mm and L = 26 mm) and 0.26°C (between L = 26 and L = 52 mm). The experimental data (figure 4, curves 1) and calculated values of temperature shown in figure 4 (curve 2) and in figure 5 coincide very well. The small difference between the experimental and calculated temperatures (0.1°C) could be associated with accuracy of the measurement by the corresponding devices. Also, the difference could be due to the fact that the calculations have been performed without taking into account the gravity component in the horizontal arrangement of the cassette, while the experimental measurements have been carried out in its vertical version arrangement. It should be noted that, as shown in figure 2 and figure 5, the average temperature difference between the working area of the end surface of the heat absorber (figure 2) and the substrate (figure 5) is measured to be $\Delta T_{HAS} = 4.19°C$ which is very close to the value used in the modelling - 4.0°C, as pointed earlier.

Figure 6. Temperature distribution on the diameter of the Si substrate at its overlapping with the end of the heat absorber and the melt solution, the average temperature in the working zone $T_{WZ} = 425°C$. Curve 1 - experimental data, curve 2 – calculated data.

Figure 7. Temperature distribution on the length of the cassette (axial direction) at average temperature in the working zone $T_{WZ} = 425°C$. Curve 1 - experimental data, curve 2 – calculated data.
Figure 6 shows the distribution of temperature along the radius of the Si substrate at the average temperature in the working zone is $T_{wz} = 425$°C when the substrate is aligned in the heat absorber and is put into contact with the melt solution. As can be seen from figure 6 the temperature profile is very smooth. The elimination of the shortcomings due to the asymmetric arrangement of the units in the construction of the cassette has resulted in very good temperatures inhomogeneity on the substrate. Some mismatches of experimental and theoretical curve in figure 6 can be caused not only by the factors described above, but also by the presence of some constructive special features during the process of measurement (the setting of the measuring thermocouple in the quartz capillary).

The calculated and the measured temperature profiles along the length of the cassette are demonstrated in figure 7. Both curves correlate well with each other. The shifts in the temperatures is due to the fact that the experimental data are measured with a sliding thermocouple located in the quartz capillary, which in its turn is located in the through hole made on the axis of the graphite cassette (number 4 in figure 2) which lead to the some difference (about 0.30° C) in the calculated and measured data. The calculated values have been obtained in the case of the graphite cassette without a through hole and the thermocouple without quartz and metal housing which could explain the difference.

According to the theoretical calculation in the prevailing part of the cassette length (L is between 30 – 130 mm, figure 7) the distribution of the temperature has linear character with difference in the temperatures on the substrate and on the area at the end of the heat sink < 0.1° C. Only at the areas of the cassette where the opening for the thermocouple (L is between 0 and 20 mm, figure 9).

Figure 8. AFM surface view (a), three dimensional image (b) and profile (c) of the Ge QDs on the Si buffer layer on (111) Si substrate obtained after modernization of the equipment. The marker in(a) corresponds to 100 nm.

Figure 9. AFM surface view (a), three dimensional image (b) and profile (c) of the Ge QDs on the Si buffer layer on (111) Si substrate obtained before modernization of the equipment. The marker in (a) corresponds to 100 nm.
figure 7) is situated there is small deviation from the linear curve probably caused by the difference in the thermo-conductivity of the materials: the substrate, melt solution, graphite cassette and the gas in the reactor camera. The temperature gradient in the linear part of the experimental data - 0.14°C is a little bit higher than in the calculated temperature distribution (0.1°C) which could be due to the gravitational effect, as discussed earlier, and it is suitable for the realization of the process. As a result, non-uniformity of the thermal field in the working area of the cassette in the axial direction is reduced to 0.3°C/cm and radial direction - to about 0.1°C/cm. In the working area the presence of the negative temperature gradient is reduced to 1°C/cm on a very large area of the end surface of the heat absorber.

In the figure 8 the AFM pictures of the open Ge QDs grown on buffer layer obtained on Si substrate (111) orientation at application of 1 cooling impulse after the modernization and optimization of equipment are shown. The Si substrate has been treated according the methods as described earlier in [5-7]. From the figure 8 b the sizes of the Ge QDs are determinate to be: the diameter is 30 nm and the height -5 nm. It is seen that the maximum difference in the size of the QDs is less that 20%. The surface roughness is < 1Å. The density of the grown Ge QDs is calculated to be $2.10^{10}$ cm$^{-2}$.

For the comparison the corresponding AFM pictures of the Ge QDs grown before the described above improvement and optimisation of the equipment are shown in figure 9. The Ge QDs are grown at the same conditions as those presented in figure 8. The diameter of the grown Ge GDs is in the range of 40-60 nm, and height is about 8-10 nm size. The difference in size of the Ge QDs and the surface roughness are higher and the density of their distribution is lower, less than $1.10^{10}$ cm$^{-2}$, compared to the structures grown in the optimized equipment.

4. Conclusion

The analyses of the results of physical-mathematical modelling of the thermal processes of the NHES growing of Ge QDs by the method of LPE with applying ICS have shown shortcomings in the constructed and used equipment. Applying the results of the thermodynamic analyse using the programme SolidWorks FlowSymulation the equipment for QDs growing has been reconstructed and improved. A new working cassette has been reconstructed and materials with appropriated thermal conductivities have been applied. The comparison of the result of the calculated and measured temperature distributions on the end of the heat absorber and on the substrate area has demonstrated good coincidence which confirms the correctness of the modernization of the equipment. The control experiments have been carried out and demonstrated better homogeneity in the surface distribution of the grown Ge QDs after optimisation of the construction of the equipment.

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