**REPUBLIC OF AZERBAIJAN**

*On the rights of the manuscript*

# ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

# PREPARATION AND ELECTRIC PROPERTIES OF COMPLEX-DOPED CRYSTALS OF Ge-Si <Ga, Sb, Ni> SOLID SOLUTIONS

Speciality: 2220.01– Semiconductor physics

Field of science: Physics

Applicant: **Elnara Maharram Islamzade**

**Baku -2021**

The work was performed at the Institute of Physics of the National Academy of Sciences of Azerbaijan in "Impurities in semiconductors" laboratory.

Scientific supervisor: Doctor of Physics-Mathematics Sciences, Professor
**Gusnu Khalil Azhdarov**

Official opponents: Corresponding Member of ANAS, Doctor of Physics-Mathematics Sciences, Professor
**Oktay Abil Samadov**

Honored Scientist, Doctor of Physics-Mathematics Sciences, Professor
**Eldar Mehrali Gojayev**

Doctor of Physical Sciences, Professor
**Mayil Masim Tagiyev**

Dissertation council ED 1.14 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Institute of Physics of National Academy of Sciences of Azerbaijan.

Chairman of the Dissertation Council: Active member of ANAS, Doctor of Physics-Mathematics Sciences, Professor
**Nazim Timur Mammadov**

Scientific Secretary of the Dissertation Council: Doctor of Physical Sciences, Associate Professor
**Rafiga Zabil Mehdiyeva**

Chairman of the scientific seminar: Doctor of Physics-Mathematics Sciences, Associate Professor
**Talat Rzagulu Mehdiyev**

## GENERAL DESCRIPTION OF WORK

**Relevance and degree of research of the topic.**

Classical system of continuous number of Si-Ge solid solutions which basic components are initial materials of electronic industry holds a superior position among the semiconducting solid solutions of applied significance.Scientific works being of priority in this trend are based on the possibilities of permanent change of fundamental parameters of the material and characteristics of electroactive impurities in it by elementary change of solid solution composition.

According to reference, the potential sphere of Si-Ge crystal wide use involves the creation of thermoelectric generators, graded detectors of infrared radiation, a great number of optoelectronic devices, substrates for epitaxy, solar elements, photo – and gamma-detectors and etc. It gives reasons for the works on producing high-quality crystals with given composition and controlled level of electroactive impurities, studying their electron properties as well.

Recently there has been made the considerable progress towards the production of Si Ge bulk crystals by methods of Czockralski, Bridgman, zone melting and their various modifications. A great number of works have been dedicated to investigation of semiconducting parameters and characteristics of Si-Ge crystals and their energy spectrum of small and deep impurity centers. High priority tasks related to regularities of changing the segregation of typical small impurities with the melting composition at solid solution crystallization are being investigated. Electron properties of Si-Ge doped crystals with quickly diffusible electroactive impurity content are as yet imperfectly understood. Particular interest to these materials is determined by the possibility of forming the additional electroactive complexes having a significant influence on electro transport properties of the material. From the other hand, the presence of quickly diffusible impurity in matrix gives a scope for precious control of crystal electron properties within a wide range by its thermal treatment at the appropriate temperatures.

The thesis has been made within the scope of Institute Physics

ANAS schemes of research works on production and investigation of Si-Ge solid solutions, complex –doped by typical small impurities and quickly diffusible atoms of deep centers.

In this thesis there have been solved complex problems on productions of $Ge_{1-x}Si_x$ ($0 \le x \le 0,15$) bulk crystals complex doped by small acceptor ( Ga) and donor ( Sb ) impurities and quickly diffusible atoms (Ni) as well as determination of main impurity state spectrum and characteristics of electro transport phenomena in materials under investigation. We note that the choice of Ni doubly charged acceptor impurity is due to its effective influence on electro transport properties of materials at issue and its tendency to the formation of various electroactive complexes with other impurities in matrix.

**Object and subject of research.**

The object of the study is complexly doped germanium-like Ge1-x – Six < Ga, Sb,Ni>( 0 < x < 0,15 ) crystals of solid solutions. The subject of the study is the development of various technologies for obtaining these crystals, as well as the study of their electro-physical properties.

**The aim and objectives of the study.**

Production of complex – doped crystals Ge<Ga, Sb, Ni > and $Ge_{1-x}Si_x$<Ga, Sb, Ni > with given composition (x) and concentration level of small (Ga, Sb) and deep ( Ni ) impurities. Determination of change peculiarities of main impurity state spectrum, electro transport characteristics and conditions of electroactive complex formation in thermotreated crystals of materials like these.

To achieve the above-mentioned aim in thesis the following tasks have been solved:

1. In Pfann approximation and representations of virtual medium model for binary systems to describe theoretically axial concentration distribution of main components ( for solid solutions ) and Ga, Sb impurities in Ge and Ge-Si crystals grown from melt by conservative and non-conservative methods.
2. To determine principal methods and technological parameters for producing $Ge_{1-x}Si_x$ < Ga, Sb > crystals ($0 \le x \le 0,30$) with given axial concentration distribution of components and

impurities.

3. To develop techniques of $Ge_{1-x}$ $Si_x$ < Ga, Sb > ( $0 \leq x \leq 0{,}30$ ) complex – doped crystal growth by traditional and up-dated Bridgman method, method of melt directed concentration supercoiling as well.
4. To develop techniques of high-temperature treatment and doping of Ni impurity by diffusion method followed by hardening.
5. By evidence of Hall coefficient temperature dependences and $Ge_{1-x}$ $Si_x$ < Ga , Sb , Ni > ( $0 \leq x \leq 0{,}15$ ) sample electro conductivity within T 77-350 K to determine the spectrum of main impurity states and ohmic mobilities of electrons and holes in crystals at different relationships of impurity concentrations and establish the influence of thermal treatment on these material characteristics.
6. To conduct analysis and interpretation of all obtained evidence set on growth and electron properties of Ge $_{1-x}$ $Si_x$ <Ga,Sb,Ni > complex-doped germanium –like crystals in terms of existing knowledge and theories in these leads.

**Research methods.**

In the thesis, an analysis and systematization of works related to the growth of Ge1-xSix ($0 \leq x \leq 0.15$) crystals by various methods was carried out. In the Pfann approximation and representations of the virtual environment model for binary systems, mathematical modeling of the concentration profiles of the main components and impurities in complex-alloyed Ge-Si <Ga, Sb> ($0 \leq x \leq 0.30$) crystals is carried out. Experimental methods (Hall measurements) were used to determine the electrical properties of $Ge_{1-x}Si_x$ <Ga, Sb, Ni> ($0 \leq x \leq 0.15$) samples grown by traditional and modernized Bridgman methods.

**Main scientific statements for defensing the thesis**.

Mathematical relationships on axial concentration distribution of components ( Ge , Si ) and impurities ( Ga, Sb ) in Ge $_{1-x}$ $Si_x$ ( $0 \leq x \leq 0.30$ ) obtained in Pfann approximation and within virtual medium model for binary systems describe adequately the evidence on crystals grown from the melt at rates < 5.5 mm/h.

Mathematical modelling of concentration profile of main components and impurities in Ge-Si crystals grown from the melt both conservative and non-conservative methods determines the optimum methods and technological parameters for producing the crystals with given properties.

The spectrum of main impurity states in $Ge_{1-x}Si_x$ <Ga,Sb,Ni> ( $0 \leq x \leq 0.15$ ) doped crystals at the temperature of its maximum solubility ( ~ 1150 K ) involves the set of appropriate spectra of each of doping elements in these materials.

Thermal treatment of Ge-Si <Ga, Sb , Ni > at ~ 1050-1080 K creates the additional deep acceptor complexes ( DAC ) with energy levels arranged below the first acceptor state of nickel in matrix. DAC activation energy rises with the silicon content in matrix according to the virtual crystal model for solid solutions. The most reliable model for the centers like these is the complex of $Ni_s Ga_s$ pair.

Sequential thermal treatment of crystals within T 770-1150 K controls precisely the electron properties of the material.

All the set of evidence on ohmic mobility of free charge carriers in $Ge_{1-x}$ - $Si_x$ < Ga, Sb, Ni > within T 77-300 K is described theoretically within additivity approximation of three main scattering mechanisms: on the phonons, alloy disorders and impurity ions.

**Scientific novelty of the research.**.

In Pfann approximation there have been solved mathematical problems in concentration distribution of ( Ga, Sb ) components and small impurities in Ge-Si solid solution ingots grown from melt by modified methods of Bridgman and zone melting, methods of directed concentration super cooling of melt and double feed, as well as in the dynamics of solid solution growth by hybrid method.

There have been developed techniques of production and controllable complex doping of $Ge_{1-x}Si_x$ ($0 \leq x \leq 0{,}30$ ) crystals with given composition ( x ) and concentration of above-mentioned impurities ( within $10^{15} - 10^{16}$ $sm^{-3}$ ) have been grown.

It is shown that the spectrum of main impurity states in Ni doped $Ge_{1-x}Si_x$ < Ga, Sb, Ni > ($0 \leq x \leq 0.15$) crystals by diffusion method at its maximum solubility temperature (~ 1150 K) involves the set of

appropriate spectra of each of doping elements in given materials.

It is established that Ga-Si < Ga ,Sb, Ni > crystal quenching at T 1050-1080 K induces the creation of additional acceptor centers in matrix with energy level arranged below the first Ni acceptor state. The most reliable model of centers like these is considered to be the complex of substituting atom pair of $Ni_s$ and $Ga_s$ - $Ni_s$ $Ga_s$ impurities or Ni interstitial atoms and $Ga_s$-$Ni_i$$Ga_s$ substituting atoms.

There has been established the possibility of precise control of electron and hole concentration and mobility in Ge<Ga, Sb, Ni> and Ge-Si<Ga, Sb, Ni > by their thermal treatment within T 770-1150 K.

Ohmic mobilities ot free charge carriers in $Ge_{1-x}$ $Si_x$ < Ga, Sb , Ni > ( $0 \le x \le 0{,}15$ ) within T 77-300 K are described adequately by the theory within the additivity approximation of three main mechanisms of electron and hole scattering in matrix: on the lattice vibrations, solid solution alloy disorder and ionized impurity centers.

**Theoretical and practical significance of the research.**

As noted above, the potential sphere of Si-Ge crystal use is extremely wide. In this thesis the developed techniques on the growth of $Ge_{1-x}$ $Si_x$ complex –doped bulk crystals with given compositions of concentration profiles of main components and impurities in matrix are perspective. Techniques like these can be used successfully in different centers of semi conductive material science and laboratory practice by growing doped crystals of solid solutions from melt both conservative and non-conservative methods. In this case optimum technological parameters for doped crystal growth with given parameters have been determined by appropriate modelling on the base of presented mathematical relationship in thesis.

The spectrum of main impurity states in $Ge_{1-x}$ $Si_x$ < Ga, Sb, Ni > ( $0 \le x \le 0.15$ ) shows the potential of using these crystals to create both graded and selective radiation detectors within infrared spectrum.

The influence of high –temperature treatment (500-1150 K) of complex doped crystals with quickly duffusible Ni impurity on the impurity state spectrum, effective concentration of impurities and mobility of free charge carriers in matrix offers scope to control preciously electric properties of semiconductor over a wide range.

**Approbation and application.** The main results of the thesis have been discussed at V International Scientific Conference "Crystallophysics of XXI century" ( Moscow , 2013 ) ; International Conference " Novel Semiconductor Materials and structures ( Baku 2013), VI International Conference "Crystallophysics and deformation behavior of perspective materials" (Moscow, 2015); International Conference "Modern Trends in Condenced Matter Physics", dedicated to the 100 $^{th}$ anniversary of Academician G.B. Abdulayev ( Baku 2018 ) .

Published scientific works: **The main materials of the thesis were published in 15 publications, of which 8 articles (3 of them in journals with an impact factor included in the SCI list) and 5 conference proceedings.**

**Structure, volume and main content of the thesis.**

The thesis comprises the introduction, 4 units, the results and reference of 135 names. The work contains 163 pages of text, with the total number of characters in the computer text equal to 160 357. The number of characters in the title page is 375, in the table of contents is 1932, in the introduction is 12 831, in the main content of the thesis is 120 466, in the results of the work is 2388. In the thesis included 42 figures and 3 tables.

## BRIEF SUBJECT – MATTER OF THESIS

**In introduction** after thesis topic justification there has been formulated the aim of investigations, scientific novelty and practical significance of obtained results as well as scientific statements for thesis. There have been briefly described the data being characteristic of thesis unit content.

**The first unit** reviews and analyzes principle reference data on fundamental semiconductive, structural and impurity characteristics of crystals of silicon, germanium and their solid solutions. There has been elucidated a number of works on the spectrum of main energy states of small and deep impurity centers in crystals at issue and state of theory in this lead. There have been presented and analyzed the data

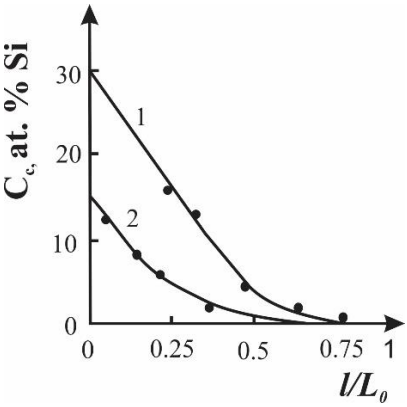
of the works on electrotransport properties of crystals, mobility and main mechanisms of electron and hole scattering in matrix as well.

**The second unit** given the brief characteristic of technology state on the growth of Ge-Si system solid solution bulk single crystals presents the data on producing and doping these crystals from the melt by conservative and non-conservative methods. Summarizing the brief review of the current state of the technology for growing crystals of solid solutions of the Ge-Si system from the melt, we can draw the following conclusion. The successes achieved in the last two to three decades make it possible to obtain Ge-Si single crystals with both variable and constant axial compositions in the entire continuous series of solid solutions. These capabilities of technology can fully meet the needs of scientific research in this material. However, the need to use low growth rates of the material required to ensure its single crystallinity and homogeneity leads to the extreme unprofitability of the production of solid solution ingots on an industrial scale. The solution to the problem is possible by fully automating the technology of growing Ge-Si single crystals based on crucible-free zone melting and Czochralski methods. In the case of using these methods, the possibility of achieving high temperature gradients at the crystallization front makes it possible to ensure the growth of perfect single crystals at significantly high rates of melt crystallization.

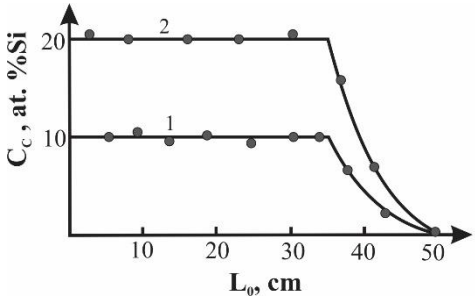
In present thesis $Ge_{1-x}Si_x$ ($0 \le x \le 0.30$) crystals have been grown using the silicon seed by Bridgman method; ingot melt feed of given composition by modified Bridgman method and method of directed concentration supercooling of the melt. Maximum length and diameter of crystals are 50 mm and 14 mm, respectively. The rate of ingot growth is 1-4 mm/h. In Fig.1 the characteristic curves of silicon concentration distribution ($C_c$) along Ge-Si two crystals grown by these methods are presented as an example. The experimental and theoretical data have been denoted by circles and solid lines respectively. Experimental values of $C_c$ are determined by measuring disk density ~ 1 mm in thickness cut out of various parts of Ge-Si solid solutions in the direction perpendicular to ingot crystallization axis.

We note that the density of Ge-Si density is sensitive enough to their composition because of great difference of Si (~2.33 g/cm $^{-3}$) and Ge ( ~ 5.33 g/cm $^{-3}$). By hydrostatic method each of disk density has been determined weighing them in the water and air. Theoretical curves by axial concentration distribution of components in all crystals grown by above - mentioned methods have been calculated on the base of relationships obtained in Pfann approximation. As it is seen from 1 A, B, C for all three methods of Ge-Si crystal growth the good agreement between theoretical and experimental values of $C_c$ along the ingot length has been taken place. The agreement like this is indicative of creating the conditions close to the phase equilibrium between the melt and growing crystal in the technological cycle process on the crystallization front. In fig.1 the data show the set potential of the three methods at issue to produce Ge-Si solid solution crystals of both homogeneous and changing compositions including linear change of component concentration along the matrix.

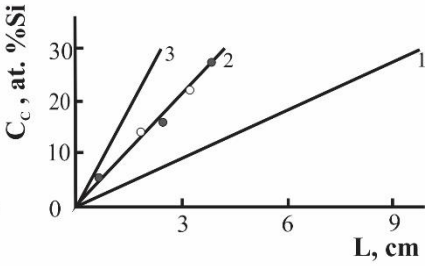
Small impurity centers have been introduced into crystals under investigation in their growth process from the melt. This process is assisted by sufficiently great solubility of these impurities in Ge-Si crystals at their melting temperatures ($10^{19}$ cm $^{-3}$ -10 cm $^{-3}$). The parameter determining the distribution and level of impurity concentration in crystals is the segregation coefficient. Equilibrium values of this parameter for Ga and Sb in Ge are 0.087 and 0.003, in Si are 0.008 and 0.023. Small values of this impurity parameter brings about the significant gradient of concentrations along the ingots grown from the melt by traditional methods. In Fig.2 there have been given characteristic evidence curves of Ga and Sb impurity concentration dependences along Ge-Si crystal length grown by modified Bridgman method at initial melt compositions and feeding ingots – $C_2^0$ = 1,7 at % and $C_f$ = 10 at % Si, respectively (Fig.1 1 (B)). We note that impurities (Ga, Sb) as an alloying composition are embedded in crucible over the seed along with Ge and Si feeds. Impurity concentrations in grown ingots are determined according to Hall measurement sample data made of different parts of crystals.




(A)




(B)




(C)

Fig.1. Concentration distribution of Si along the length of two Ge-Si crystals grown by traditional Bridgman method (A); modified Bridgman method Ge-Si feeding (B) and method of directed concentration supercooling of melt (C). Circles are experimental data, solid lines are theoretical data, calculated in Pfann approximation. (A) are the curves 1,2 corresponding to the crystals grown from melt with initial compositions $Ge_{0.93}Si_{0.07}$ and $Ge_{0.973}Si_{0.027}$, respectively. Total crystal length $L_0 = 40$ mm. (B) curves 1,2 are the use of $Ge_{0.90}Si_{0.20}$ feeding, respectively. (C) direct lines 1,2,3 are in agreement with gradients T in melt equal to $\partial T / \partial L$ = 10,23 and 40 K/cm, respectively.

Theoretical problem in axial distribution of impurity concentrations in Ge-Si ingots has been solved in Pfann approximation and within the model of virtual medium for two –component systems. In this case the following relations are true at the first and second stages of crystal

$$C_c^{im} = C_1^{im} K^f_{im} = C_1^{0,im} K^{F_{im}^{l}} {}^{-yk\,f}{}_{im} \quad (1)$$

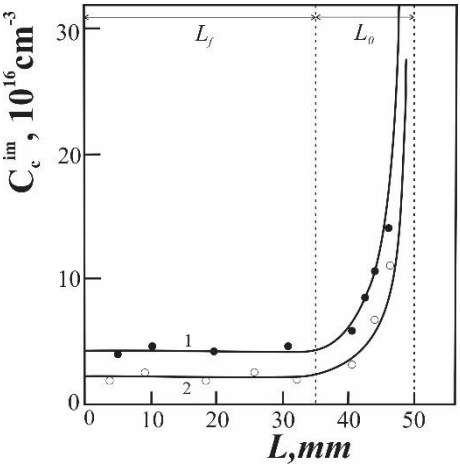
$$C_c^{im} = C_1^{im} K^x_{im} = C\, C_1^{0,im} K^{X_{im}}_{im} (1-y)^{K_{im}^{x}\,-1} \quad (2)$$

growth respectively (see Fig.1 (B)). In ( 1 ) and ( 2 ) there have been put the following symbols: $C_c^{im}$ is the impurity concentration in crystallized ingot; $C_1^{0,im}$,$C_l^{im}$ are impurity concentrations in melt at initial and current moments of melt crystallization; $K_{im}^{x} = C_c^{im}/C_l^{im}$ is the equilibrium coefficient of impurity segregation depending linearly ον χρψσταλ χομποσιτιον ; $K_{1\mu}^{\phi}$ ισ τηε χοεφφιχιεντ οφ ιμπυριτψ σεγρεγατιον appropriate to the composition of $Ge_{1-x}\,Si_x$ initial feeding ingot; $\gamma = L / L_0$ is the given length of final molten zone. Parameter value $\gamma = L / L_0$ in (2) has been determined by the following formula obtained in thesis

$$\gamma = \frac{L}{L_0} = 1 - \exp\left[\int_{C_l^{0,im}}^{C_l^{im}} \frac{dC_l^{im}}{C_l^{im}(1-K_{im}^{x})}\right] \quad (3)$$

The solution of the integral in (3) are performed according to the data of Si concentration distribution in the crystal length from the beginning of the second stage of its crystallization ( Fig.1 ( b ) ) .

In Fig.2 by solid lines the final calculated curves of Ga and Sb concentration profile in ingots are presented. At the first stage the impurity concentration along the crystal remains practically flat. It is related to the melt volume constancy and its composition by main components at the first stage, as well as to rather low values of Ga and Sb segregation coefficients. At the final stage at $L > L_f$ regularities of impurity concentration growth in crystal are in good agreement with the concentrations in traditional Bridgman method. As it is seen that the agreement between calculated and experimental data is rather good both at the first and the second stages of crystal growth.




• Fig.2. Dependences of Ga (1) and Sb (2) impurity concentrations in two crystals with concentrations profile of matrix components given in Fig.1 ( B ) : lines are the calculation with formulae ( 1 ) and ( 2 ) for sections with constant ( 1 ) and varying ( 2 ) concentrations of silicon ( $C_l^{0,Ga} = 5.3 \cdot 10^{17}$cm$^{-3}$ and $C_l^{0,Sb} = 4.6 \cdot 10^{18}$ cm$^{-3}$ ).

Comparing theoretical and experimental data on impurity distribution in Ge-Si crystals grown by method of directed concentration supercooling of melt and traditional Bridgman method brings about the result like this.

In the second unit there have been also presented data on modelling concentration distribution of small impurities in Ge-Si crystals grown by the perspective method of melt double feeding.

In Fig.3 ( A ) there has been presented the conceptual scheme of Ge-Si crystal growth and doping by the method like this. Since the beginning of crystal growth from Ge-Si < Ga, Sb > melt of given composition the pure Si and Ge rods are simultaneously inserted in it. By corresponding choice of melt crystallization and feeding rate relationship the main component concentrations in melt and growing crystal remain constant.

The problem of mathematical description of Ga and Sb impurity concentration distribution in Ge (1-x) Si (x) crystals grown by method of melt double feeding solved in Pfann approximation brings about the following relationship:

$$C_c^{im} = C_l^{im} K_{im}^x = C_l^{0,im} K_{im}^x [1 - \gamma(1 - \alpha - \beta)]^{\frac{(K_{im}^x + \alpha + \beta - 1)}{(1 - \alpha - \beta)}} \quad (4)$$

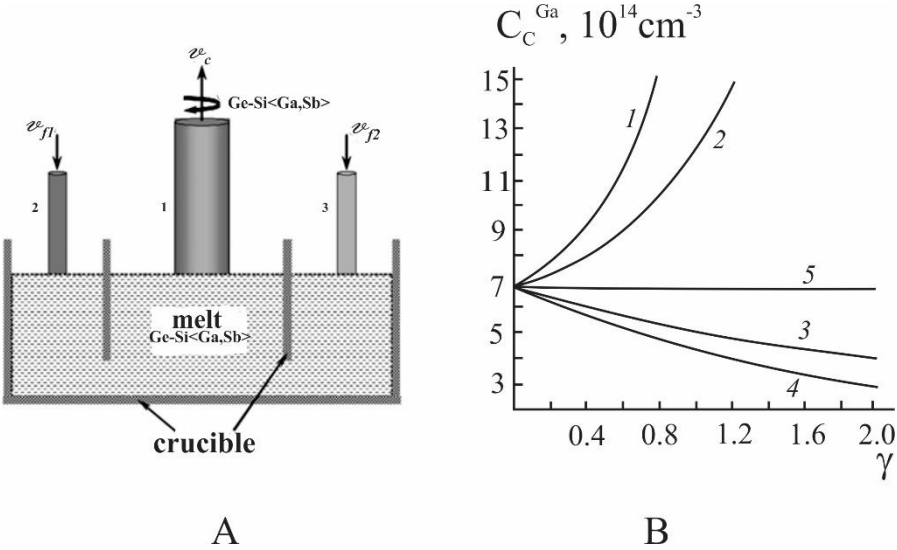



Fig.3 (A) is the scheme of Ge-Si single crystal growth by method of melt double feeding. 1 is the growing single crystal; 2,3 are feeding ingots of Ge and Si. (B) is the concentration profiles of gallium impurity in $Ge_{0.75}$ $Si_{0.25}$ crystal grown at different regimes of melt double feeding. $\alpha+\beta=0.25$, $\alpha = 0.197$ (1); $\alpha+\beta=0.5$, $\alpha=0.215$ ( 2 ) ; $\alpha+\beta=1.25$ , $\alpha=0.268$ ( 3 ) ; $\alpha+\beta=1.50$ , $\alpha=0.285$ ( 4 ) ; $\alpha+\beta=0.933$ , $\alpha=0.245$ ( 5 ) .

$\gamma$ is the fraction of crystallized melt in units of initial melt volume, $\alpha$ and $\beta$ are relationships of melt feeding rates by the second (Si) and the first (Ge) components to the melt crystallization rate, respectively. In Fig.3 (B) for instance there have been presented characteristic curves of Ga impurity concentration distribution along the crystals grown by method of double feeding in 5 various regimes providing $Ge_{0.75}$ $Si_{0.25}$ composition growth. The initial impurity concentration in melt for all regimes is taken to be $C_i^{0im} = 1 \cdot 10^{17}$ cm$^{-3}$. As it is seen in the case of double melt feeding there has been taken the possibility of controlling the gradient of Ga and Sb impurity concentration in crystal with given composition of main components over wide ranges. The possibility of production of completely homogeneous of Ge-Si solid solution both

by main component composition and impurity concentration profile in matrix are worthy of notice (curve 5).

In thesis on the base of result set on mathematical modelling of Ga and Sb impurity concentration distribution in Ge-Si crystals there have been validated wide possibilities of double melt feeding method in technology of solid solution single crystal growth with the given composition of main components and impurity axial distribution including homogeneous one.

**In the third unit** techniques of sample measurement and thermal treatment are described. There have been covered the problems related to Hall factor of free charge carriers in semi conductive structures of Ge- and Si-typed and their solid solutions with the ratio and factor of Ni, Ga and Sb impurity state degeneracy in matrix of these materials as well. On the base of evidence of Hall coefficient of $Ge_{1-x} Si_x$ $(0 \leq x \leq 0.15)$ complex –doped crystals within T 77-300 K the main energy states of deep impurity centers as well as the influence of high –temperature treatment on these state spectra have been determined. The possibility of controlling electron and hole concentration in Ge – Si < Ni, Ga, Sb > complex – doped crystals by their thermal treatment within T 850-1150 K has been shown. There have been determined the conditions of additional electrically active complexes formation in crystals between Ga and Ni impurities at sample high – temperature treatment.

For Hall measurements, Ge and Ge-Si ingots, grown and doped by the methods described in the second chapter, were cut into disks in the direction perpendicular to the axis of their crystallization. The thickness of the discs was ~ 1–2 mm. Then, parallelepiped-shaped specimens with dimensions (1-2) x (2-3) x (10-14) $mm^3$ were made from these disks. After appropriate grinding of the samples with abrasive powders, they were washed with distilled water and then subjected to chemical etching in a mixture HF: HNO3: H2O = 4: 1: 1 for 10-15 min. After washing in distilled water, the samples were again subjected to chemical etching in a 3% mixture of boiling hydrogen peroxide for several minutes. Such processing of the samples leads to a fairly good adhesion of the solder Sn: In = 2: (1–2) to the material

surface and ensures the mechanical strength and ohmicity of the contacts in a wide temperature range (4.2–350 K). Solder from Sn-In was applied to the places where ohmic contacts were created using a microsoldering iron. Fusion of the solder into the sample was carried out in vacuum at a temperature of ~ 300-3500C for 20-30 minutes. To the contacts created in this way, communication taps from copper wires were then soldered.

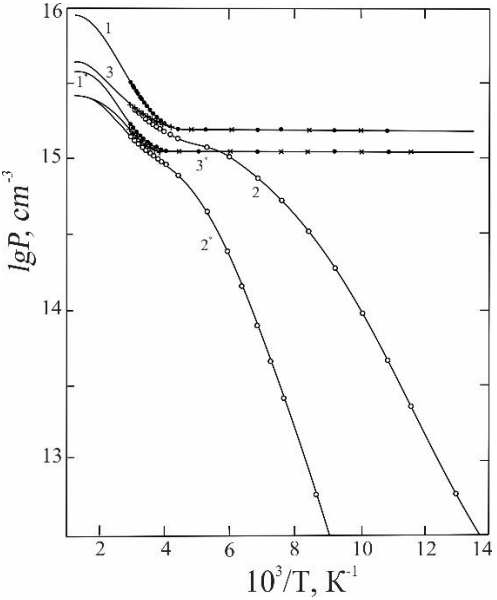
The cryomagnetic system for measuring the temperature dependences of electrical conductivity and Hall coefficient of samples in the range of 60-350 K, which we used, belongs to the category of standard ones. Here we restrict ourselves to the note that the temperature regimes below 77 K were obtained by pumping out liquid nitrogen from the Dewar in which the sample holder is located.

The voltages on the conductivity and Hall probes were measured at a constant electric current at field voltages that ensure the fulfillment of Ohm's law. The Hall coefficient was determined at a constant magnetic field with a strength of 3000 Oersted.

Taking into account the fact that in the present work the classical methods of measuring the Hall coefficient and electrical conductivity were used, we do not present an analysis of the experimental error in determining these parameters. Here we restrict ourselves to the statement that the total absolute error in determining the Hall coefficient is <10%, and the electrical conductivity is <5%.

It is known that studies aimed at studying the effect of heat treatment on the electronic properties of semiconductors require the solution of two main problems. The first task is associated with ensuring a high level of cleanliness of technological operations to minimize the uncontrolled ingress of impurities onto the sample surface. The second task is to create conditions for rapid quenching of samples from high annealing temperatures to low ones. The importance of solving the second problem is determined by the need to reliably fix the states of impurity atoms, lattice defects, and various complexes in the matrix for a given high-temperature annealing of the material under study.

The principal aim of our investigations on impurity states in Ge and Ge-Si complex –doped crystals is the analysis of conditions of additional electroactive center formation in matrix formed as a result of impurity interactions. Here we have restricted ourselves to the brief presentation of results in this direction. It is shown that by diffusion method in $Ge_{1-x}$ $Si_x$ < Ni, Ga, Sb> ($0 \leq x \leq 0.15$) crystals doped by Ni at the temperature of its maximum solubility (1150-1175 K) due to the set of mentioned impurity concentrations the various levels related only to the substitution atoms of impurities like these have been manifested in Hall measurements. However, the results of data analysis of sample wide set undergone the subsequent thermal treatment within T 800-1100K show that in crystals quenched at T 1020-1050K the additional levels arranged below $Ni_s$ first acceptor are originated. In Hall measurements these levels are revealed in samples with gallium concentration of the order of $10^{16}$ $sm^{-3}$ at high level of acceptor state compensation of given impurity. In Fig.4 by way of example the temperature dependences of hole concentration (p) for two samples Ge<Ni, Ga, SB> and $Ge_{0.9}$ $Si_{0.1}$ < Ni, Ga, Sb> have been presented.




- Fig. 4 Temperature dependences of free hole concentrations (p) for two samples Ge < Ga, Sb, Ni> (1-3) and $Ge_{0.9}$ $Si_{0.1}$ <Ga, Sb, Ni > (1*-3*):1,1* is after Ni sample doping at T 1150 K and 1165K , respectively ;2,2* is after thermal treatment at T 1020 K and 1030 K, respectively; 3,3* is after annealing at T 560K for 18 hours. Solid lines are theoretical calculations showing the best fit of the experimental data.

Before Ni doping both samples have hole conductivity due to the gallium impurity with $N_{Ga}$· equal to $1.5 \cdot 10^{15}$ $sm^{-3}$ in Ge and $1.1 \cdot 10^{15} sm^{-3}$ in $Ge_{0.9}Si_{0.1}$. The evidence on dependences of p on T after sample doping by Ni (curves 1 and 1*) are well described by the theory with regard to the activation of Ni $_s$ first level shunted by Ga small acceptor states with appropriate concentration. As it is seen from the figure the thermal treatment of $Ge_{0.9}$ $Si_{0.1}$ samples at T 1020 K and 1030 K leads to the significant change of the course of the curves p with T for both samples (curve 2 and 2*). The activation of two various levels in samples clearly manifest on curves. Exponential decay of p in T within the low temperature being characteristic at the activation of partially compensated level in semiconductor is indicative of both the appearance of additional deep acceptors (DA) in matrix and complete compensation of Ga acceptor states with $N_{Ga}^{*}$ concentration. At high temperatures the growth of p in T is determined by $Ni_s$ first level ionization. The formation of additional DA in all complex-doped crystals undergone the thermal treatment at above mentioned conditions has been taken place. Additional DA generate in all $Ge_{1-x}$ $Si_x$< Ga, SB, Ni > ($0 \leq x \leq 0.15$) samples under investigation. Activation energy of centers like these rises linearly with the silicon concentration in matrix and makes up 75 meV in Ge, 138 meV in $Ge_{0.85}$ $Si_{0.15}$. To set up the character of additional DA there has been carried out the additional annealing of samples at T ~550-570 K. It is established that at this temperature DA decay occurs and sample annealing for 18 hours brings about their disappearance. In Fig.4 the curves 3 and 3* show the temperature dependences of hole concentrations in samples at issue after such annealing. As it is seen for both samples the evidence is in good agreement with the theory in view of $Ni_s$ first level activation with the concentration equal to Ni solubility at the temperature corresponding to the sample thermal treatment. Here as in the case of the curves 1 and 1* the concentration of Ga shunting atoms agree with the corresponding initial effective concentrations of $N_{Ga}^{*}$ in Ge and $Ge_{0.9}$ $Si_{0.1.}$ On the base of obtained result analysis according to the data of a great number of samples it is

shown that pairs of $Ni_s$ $Ga_s$ or $Ni_I$ $Ga_s$ should be considered the most probable samples leading to DA formation.

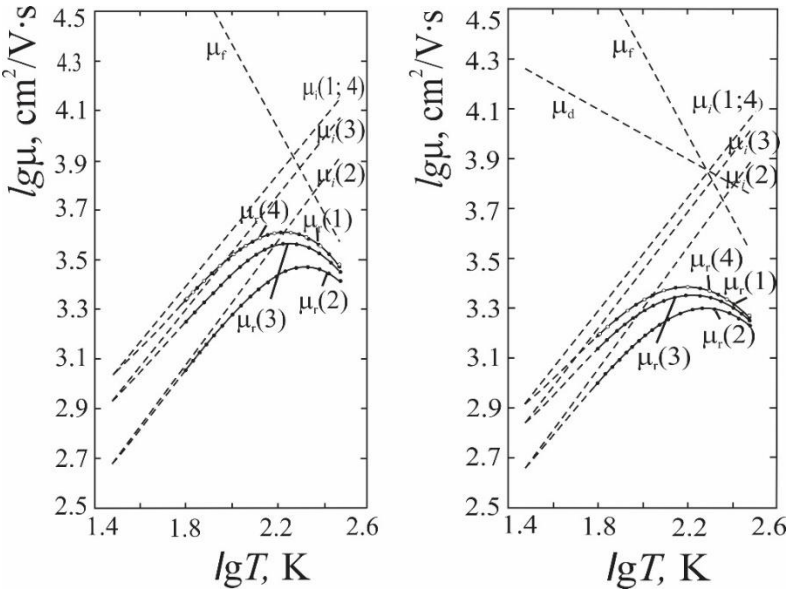
In thesis there have been presented the final diagrams of energy levels in $Ge_{1-x}$ $Si_x$< Ga, SB, Ni > ($0 \leq x \leq 0.15$) band gap before and after the appropriate thermal treatment of crystals and at different relationships of impurity concentrations.

**The fourth unit** presents the data on the investigation of $Ge_{1-x}$ $Si_x$< Ga, SB, Ni > ($0 \leq x \leq 0.15$) crystal electrotransport properties and the influence of thermal treatment on the concentration and mobility of electrons and holes in matrix. There has been carried out quantitative interpretation of the evidence for temperature dependences of electron and hole mobilities in crystals within T 77-300 K in additivity approximation of three main scattering mechanisms of free charge carriers: on the phonons, alloy disorders and impurity ions.

The main parameters defining electric properties of the material are the concentration and mobility of free electrons and holes in matrix. Here we consider the mobility of free carriers as the main physical parameter controlling charge transfer in semiconductors. The magnitude of the given parameter is determined by interaction of free electrons and holes in matrix with acoustic and optic phonons, specific zone structure imperfections. It should be noted that the additional scattering of free electrons and holes by alloy disorders due to the composition fluctuation of nanoobjects in matrix has been occurred in solid solution crystals.

Experimental values of free charge ohmic mobility in all crystals under investigation have been determined by Hall coefficient and electroconductivity within T 77-300 K using appropriate reference by Hall factor of electron (holes) in Ge and Ge-Si.

Fig. 5 there have been presented characteristic temperature dependences of ohmic electron mobility in complex-doped crystals Ge(A) and $Ge_{0.95}$ $Si_{0.05}$ (B) before and after Ni doping and subsequent thermal treatment of samples including the conditions of both formation and decay of additional acceptor complexes (AC) in matrix. The evidence is given by symbols. All samples before and after Ni




- Fig.5. Temperature dependences of electron ohmic mobility (μ*)* in Ge < Ga, Sb, Ni > (A) and $Ge_{0.95}$ $Si_{0.05}$ < Ga, Sb, Ni > (B). Symbols are the evidence. Solid and dotted lines are calculated ones $\mu_f$ is at the scattering from lattice vibrations; $\mu_i$ (1) , $\mu_i$ (2) are at the scattering by impurity ions before and after Ni doping at T 1150 K ; $\mu_i$ (3), $\mu_i$ (4) are the subsequent annealing at T 1050 and 770 K$_i$ $\mu_r$ (1) – $\mu_r$ (4) are the resulting mobilities of electrons before and after Ni doping and subsequent thermal treatments. Calculated curves $\mu_r$ (1) - $\mu_r$ (4) are in agreement with the following impurity concentrations and additional acceptor complexes of free electrons:
(A) – 1-$N_{sb}$ = $5.28 \cdot 10^{16}$ $sm^{-3}$, $N_{Ga}$ = $3.45 \cdot 10^{16}$ $cm^{-3}$; 2-$N_{sb}$=$5.28 \cdot 10^{16}$ $cm^{-3}$, $N_{Ga}$=$3.45 \cdot 10^{16} cm^{-3}$, $N_{Ni}$ =$8.0 \cdot 10^{15}$ $cm^{-3}$; 3-$N_{Sb}$=$5.28 \cdot 10^{16}$ $cm^{-3}$, $N_{Ga}$=$3.21 \cdot 10^{16} cm^{-3}$, $N_{Ni}$ =$2.8 \cdot 10^{15}$ $cm^{-3}$, $N_{AK}$ =$2.4 \cdot 10^{15} cm^{-3}$; 4-$N_{Sb}$ = $5.28 \cdot 10^{16}$ $cm^{-3}$, $N_{Ga}$ = $3.45 \cdot 10^{16}$ $cm^{-3}$ ,$N_{Ni}$=0, $N_{AK}$=0.
(B)– 1 - $N_{Sb}$=$5.65 \cdot 10^{16} cm^{-3}$, $N_{Ga}$= $4.22 \cdot 10^{16} cm^{-3}$; 2-$N_{Sb}$=$5.65 \cdot 10^{16} cm^{-3}$, $N_{Ga}$=$4.22 \cdot 10^{16} cm^{-3}$, $N_{Ni}$=$5.8 \cdot 10^{15} cm^{-3}$; 3-$N_{Sb}$=$5.65 \cdot 10^{16}$ $cm^{-3}$, $N_{Ga}$=$3.98 \cdot 10^{16} cm^{-3}$, $N_{Ni}$ =$2.8 \cdot 10^{15} cm^{-3}$, $N_{AK}$=$2.4 \cdot 10^{15} cm^{-3}$; 4-$N_{SB}$=$5.65 \cdot 10^{16}$ $cm^{-3}$, $N_{Ga}$ =$4.22 \cdot 10^{16} cm^{-3}$,$N_{Ni}$=0, $N_{AK}$=0

doping and subsequent thermal treatments have electron conductivity due to Sb effective concentration $N_{Sb}^{*} = N_{Sb} - (N_{Ga} + 2N_{Ni})$. As it is seen from Fig.5 after Ni doping the electron mobility in both samples substantially decreases. Subsequent thermal treatment of crystals brings about $\mu e$ growth and final treatment at T~ 770 K leads to the real agreement of electron mobility values with $\mu e$ of corresponding samples before their Ni doping.

Interpretation of all evidence set obtained in this direction have been made out based on the following factors:

- within T 77-330 K Ga and Sb small impurities are completely ionized in all crystals under investigation; Ni in crystals is the deep double acceptor center;
- $Ge_{1-x}$ $Si_x$ < Ni; Ga, Sb > crystal thermal treatment at T 1050 – 1080K brings about the formation of additional deep acceptor complexes including Ni atom in them.
- $Ge_{1-x}$ $Si_x$<Ni, Ga, Sb> thermal treatment at T ~ 770 K leads to the complete decay of Ni supersaturated solution in matrix.
- $Ge_{1-x}$ $Si_x$ < Ga, Sb > sample thermal treatment within T 770-1150 K does not influence electric properties of crystals.

Quantative analysis of temperature dependences of $\mu_e$ on T has been carried out based on subsequent main mechanisms of scattering: for Ge is the scattering by phonon and ion impurities, for Ge-.Si is the scattering phonons alloy disorders and impurity ions. Evidence interpretation has been conducted in additivity approximation of various mechanisms of scattering. In this case according to the reference we take into consideration the fact that by electron scattering from lattice vibrations and alloy disorders in germanium-like crystals the mobility is determined within the temperatures under investigation by the following expressions

$$\mu_f = A_{Ge-Si} \cdot T^{-1.66} см^2 / B \cdot c \text{ и } \mu_d = \beta \cdot T^{-0.5} см^2 / B \cdot c .$$

respectively. Here the coefficients $A_{Ge-Si}$ and $\beta$ are the constant for each magnitude composition. Mobility $\mu_i$ limited by electron scattering by impurity ions based on impurity ion electric field

screening by the electrons in conduction band has been calculated by familiar Brooks-Herring formula.

As it is seen from Fig.5 both for Ge and $Ge_{0.95}$ $Si_{0.05}$ solid solutions the agreement between calculated and evidence is rather good after all technological stages of crystals treatment. We should focus our attention on $\mu_r$ significant decrease within the temperature range for all crystals after Ni doping at T 1150 K. Given decrease is related to the additional electron scattering on Ni double ionized atoms. Further thermal treatment brings about $\mu_r$ growth both in Ge and Ge-Si at T1050 K. In this case electron mobility increase in matrix is due to the part of Ni atom fallout and transition of this impurity to electrically passive state. Final thermal treatment of crystals at T 770 K leading to the practical coincidence of $\mu_r$ (1) with $\mu_r$ (4) (See Fig.5.1-5.4) results from almost complete fallout of all Ni atoms and decay of additional acceptor complexes (AC) in investigated material matrix.

The thesis also presents the results of the analysis of experimental data on the temperature dependences of the hole mobility in complexly doped crystals Ge <Ga, Sb, Ni> and germanium-like compositions of solid solutions Ge-Si <Ga, Sb, Ni> taking into account the double acceptor action of the nickel impurity and the appearance of additional acceptor complexes in the matrix.

The interpretation of the experimental data on the mobility of holes in the samples, as in the case of the electron mobility, was carried out taking into account the fact that in the temperature range under consideration, the main scattering mechanisms of free charge carriers are phonons and impurity ions in Ge, and in $Ge_{0.9}$ $Si_{0.1}$ additionally are alloy disorders.

There has been taken place the agreement of experimental data on charge carrier mobility in crystals with the calculated ones both for electron and hole crystals of Ge and germanium like compositions of Ge-Si solid solutions.

## Results

1) In Pfann approximation the theoretical problems of concentration distribution of matrix and small impurities (Ga, Sb) components in Ge-Si system bulk crystals grown from the melt by modified Bridgman method and floating zone method, methods of directed concentration supercooling of melt and double feeding.
2) In approximation of completely stirred melt the problem in Ge-Su solid solution growth dynamics by the new hybrid method providing single crystallinity of the whole ingot by Tiller criterion has been solved.
3) There have been developed techniques of Ge-Sb crystal growth and Ga and Sb impurity complex doping with given compositions of main components and impurity concentrations modified by Bridgman methods using Si seed and Ge-Si feeding ingot as well as method of spontaneous concentration supercooling of melt.
4) Experimental results on axial concentration profile of main components and small impurities in crystals grown from the melt at rates below 5,5 mm/h are adequately in agreement with the calculated ones in approximation of completely stirred melt and models of virtual medium for liquid and solid phases of binary systems.
5) Energy spectrum of main impurity systems in $Ge_{1-x}Si_x$ <Ga,Sb,Ni> ( $0 \leq x \leq 0.15$ ) crystals doped by Ni by diffusion method at the temperature of its maximum solubility ( ~ 1150 K ) involves the set of appropriate spectra of its doping elements in materials like these.
6) Quenching of $Ge_{1-x}Si_x$ <Ga,Sb> ( $0 \leq x \leq 0.15$ ) complex doped with impurity concentration of the order of $10^{15}$ -$10^{16}$ $cm^{-3}$ properties of the material at T~ 770 – 1150 K does not influence electric properties of the material.
   Ge-Si < Ga,Sb,Ni > crystal quenching at T 1050-1080 K induces the creation of additional acceptor centers in matrix with the

energy level arranged below Ni first acceptor state. The most reliable model to identify these centers appears to be the complex of pairs including $Ni_s$ and $Ga_s$ – $Ni_s$ $Ga_s$ impurity substituting atoms from $Ni_i$ interstitial atoms and Ga substituting atoms of $Ga_s$ – $Ni_i$ $Ga_s$.

7) There has been shown the possibility of precious control over a wide range of concentration and mobility of electrons and holes in Ge <Ga,Sb,Ni> and germanium like Ge-Si <Ga,Sb,Ni > crystals by their thermal treatment at different temperatures within 770-1150 K
8) Ohmic mobilities of free charge carriers in $Ge_{1-x}Si_x$ <Ga,Sb,Ni > ( $0 \leq x \leq 0.15$ ) over T 77-300 K are adequately described by the theory within additivity approximation of three main mechanisms of electron and hole scattering in matrix: on lattice vibrations, disorders of solid solution alloy and ionized impurity centers.

**The main results of the dissertation are reflected in the following publications:**


1. Исламзаде, Э.М. Электроактивный комплекс в сложнолегированном кристалле Ge<Ga,Sb,Ni> / Э.М. Исламзаде, З.А. Агамалиев, З.М. Захрабекова [и др.] // Известия НАН Азербайджана, серия физико-математических и технических наук, - Баку: - 2013. 33(5), - с. 64-69.
2. Аждаров, Г.Х., Агамалиев, З.А., Исламзаде, Э.М., Кязимова, В.К. Гибридный метод выращивания однородных монокристаллов твердых растворов из расплава. Система германий-кремний // International Conference “Novel Semiconductor Materials and structures”, - Baku: - 4-8 july, - 2013, - Fizika, - 2013, - XIX(2), - p 80-84.
3. Аждаров, Г.Х., Агамалиев, З.А., Исламзаде, Э.М. Гибридный метод вы¬ра-щи¬¬вания однородных монокристаллов бинарных твёрдых растворов из расплава // V Международная научная конференция

«Кристаллофизика XXI века», - Москва: - 28 октября–2 ноября, - 2013, - с.17.
4. Исламзаде, Э.М., Агамалиев, З.А., Захрабекова, З.М., Аждаров Г.Х. Акцепторный комплекс в термообработанном кристалле Ge<Ni,Ga> / V Международная научная конференция «Кристаллофизика XXI века»,- Москва: -28 октября–2 ноября, - 2013, - с.82.
5. Azhdarov, G.Kh., Agamaliev, Z.A., Islamzade, E.M. Hybrid Technique for Growing Homogeneous Single Crystals of Semiconductor Solid Solutions from melt // Crystallography Reports, - 2014, 59(3), - p. 442–445.
6. Islamzade, E.M. Deep Acceptor Complex in Thermally Processed Ge–Si⟨Ga,Ni⟩ Crystals / E.M. Islamzade, Z.A. Agamaliev, Z. M. Zakhrabekova [et al.] // Crystallography Reports, - 2014. 59(4), - p. 623-626.
7. Агамалиев, З.А., Рамазанов, М.А., Исламзаде, Э.М., Аждаров, Г.Х. Условия роста однородно легированных монокристаллов полупроводниковых твердых растворов методом двойной подпитки расплава // BDU-nun Fizika Problemləri İnstitutunun yaradılmasının 10 illiyinə həsr olunmuş “Opto, nanoelektronika, kondensə olunmuş mühit və yüksək enerjilər fizikası” Beynəlxalq Konfransının materialları, - Bakı: - 17-26 dekabr, - 2015, - s. 264-267.
8. Аждаров, Г.Х., Агамалиев, З.А., Исламзаде, Э.М. Распределение примеси Ga в твёрдых растворах Ge-Si, выращенных методом двойной подпитки расплава рост полностью однородных монокристаллов // Шестая международная конференция «Кристаллофизика и деформационное поведение перспективных материалов», посвященная 90-летию со дня рождения профессора Ю.А. Скакова, - Москва: - 26 – 28 мая, - 2015, - с. 28.
9. Агамалиев, З.А., Исламзаде, Э.М., Захрабекова, З.М., Аждаров, Г.Х. Электроактивный комплекс в сложнолегированных кристаллах Ge-Si<Ga, Ni> // Шестая

международная конференция «Кристаллофизика и деформационное поведение перспективных материалов», посвященная 90-летию со дня рождения профессора Ю.А. Скакова, – Москва: - 26 – 28 мая, - 2015, - с. 27.
10. Agamaliyev, Z.A., Islamzade, E.M., Azhdarov, G.Kh. Modeling the Distribution of Ga and Sb Impurities in Ge-Si Single Crystals Grown by Double Feeding of the Melt // Crystallography Reports, -2016. v.61. - p. 327-330.
11. Аждаров, Г.Х., Агамалиев, З.А., Исламзаде, Э.М. Подвижность дырок в Ge и $Ge_{1-x}Si_x$ ($0<x\leq0,13$), комплексно-легированных примесями <Ga, Sb, Ni> // - Баку: Известия НАН Азербайджана, серия физико-математических и технических наук, - 2018. с. XXXVIII, № 5, - с. 100-104.
12. Islamzade, E.M., Agamaliyev, Z.A., Azhdarov, G.Kh. Electron mobility in $Ge_{1-x}Si_x$ ($0<x<0.13$) crystal complex doped by <Ga,Sb,Ni> impurities // - Baku: Azerbaijan Journal of Physics, Section:En, - 2018. XXIV (2), - p. 37-40.
13. Агамалиев, З.А., Исламзаде, Э.М., Аждаров, Г.Х. Условия роста полностью однородных монокристаллов при моделировании распределения примесей Ga и Sb в монокристаллах Ge-Si, выращенных методом двойной подпитки расплава // Akademik H.B. Abdullayevin 100 illiyinə həsr olunmuş “Modern Trends in Condensed Matter Physics MTCMP – 2018” beynəlxalq konfransının tezisləri, - Bakı: - 24-26 sentyabr, - 2018, - s. 28.
14. Исламзаде, Э.И. Электротранспортные характеристики комплексно легированных кристаллов $Ge_{1-x}$ $Si_x$ < Ga, Sb, Ni>($0\leq x\leq0,13$) с электронной проводимостью // - Баку: Известия НАН Азербайджана, серия физико-математических и технических наук, - 2019. XXXIX(5), - с. 78-84.
15. Исламзаде, Э.И. Основные энергетические состояния примесей в термообработанных сложнолегированных кристаллах $Ge_{1-x}$ $Si_x$ < Ga, Sb, Ni>($0\leq x\leq0,15$) // - Баку: Известия НАН Азербайджана, серия физико-математических и технических наук, - 2020. XL(2), - с. 54-60.

The defince will be help on "29" september 2021 at 14$^{00}$ at the meeting of the Dissertation council ED 1.14 of Surpreme Attestation Commission under the President of Republic of Azerbaijan operating at the Institute of Physics of Azerbaijan National Academy of Sciences.

Address: AZ-1143, H. Javid Ave., 131.

Dissertation is accessible at the Institute of Physics of ANAS Library.

Electronic versions of dissertation and its abstract are available on the official website of Institute of Physics of ANAS.

Abstract was sent to the required addresses on "27" august 2021.

Signed for print: 23.08.2021

Paper format: A5

Volume: 35435

Number of hard copies: 20