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EXCITON AND PHONON PROPERTIES IN QUANTUM DOT NANOSTRUCTURES

131.04 - COMPUTATIONAL PHYSICS AND MODELLING OF PROCESSES

Abstract of doctor thesis in physics

CHIȘINĂU, 2023

The thesis was written in the E. Pokatilov Laboratory of Physics and Engineering of Nanomaterials of the State University of Moldova

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The defence of the Thesis will be held on February 09 2024, at 15:00,
on the session of the Specialized Scientific Council D 131.04-23-87 within the Moldova State University, aud. 222, bl. 4, A. Mateevici str. 60, MD-2009, Chisinau, Republic of Moldova

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The abstract was sent out on 27 December 2023.

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CONTENTS

GENERAL CHARACTERISTIC OF THE WORK

For the last decades, semiconductor nanostructures remain the object of close attention of researchers. Their characteristic feature is confinement, which causes quantization of the energy spectrum of charge carriers and phonons [1–12]. Silicon, being the second most abundant element on earth and having excellent mechanical and electronic properties, has become the main material in microelectronics with the advent of microelectronics, semiconductor industry and is likely to remain so for the foreseeable future. Silicon quantum dots (QD) (nanocrystals) have demonstrated different unique physical properties [2], [3], [13], [14], allowing their applications in optoelectronics (light-emitting diodes (LEDs), single electron transistors, or memory devices), in photonics (different energy sources) as well as in biomedicine for photosensitization of singlet oxygen [15]. Qualitative and quantitative information about the optical, exciton, phonon, and thermal properties of silicon-based nanostructures is necessary for the improvment of the characteristics of silicon-based devices.

Optimization of thermal transport in nanoscale structures is one of the priority tasks in modern nanoelectronics. Efficient heat management at the nanoscale can prevent overheating of electronic chips and may lead to an increase of their operation speed. The low thermal conductivity of nanoscale structures makes them potentially promising for thermoelectric applications, since the quality factor of thermoelectric conversion ZT contains thermal conductivity in the denominator: $ZT = \frac{S^2 \sigma T}{(\kappa_{ph} + \kappa_{el})}$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, κ_{ph} and κ_{el} are the phononic and electronic thermal conductivity, respectively. At the same time, efficient heat removal from micro- and nanosized electronic chips requires nanomaterials with high thermal conductivity. Thus, the theoretical and experimental search for different ways to both reduce and increase thermal conductivity continues [16], [17]. Phonon engineering, i.e. improving of electrical, and thermal properties of nanostructures by changing their phonon properties was found as a powerful tool for the optimization of thermal, electric and thermoelectric properties at the nanoscale [6], [18], [19]. It has been shown that phonon engineering is particularly effective in nanostructured materials composed of layers or segments of different shapes, sizes, and/or materials. A strong drop of lattice thermal conductivity (up to one order of magnitude) has been demonstrated both experimentally and theoretically in silicon nanolayers containing germanium QD [20], in silicon nanowires with rough surfaces [21], in Si/Ge nanowires of constant and variable cross sections [7], [8], [22], [23], as well as in segmented nanowires [23–

28]. At the same time, there is some lack of investigation of the physical properties of quasi-one-dimensional quantum dot superlattices (1D-QDSL), i.e. arrays of quantum dots ordered in one spatial dimension. Such structures combine the possibility of free moving of charge carriers or phonons in one direction with strong spatial confinement in the other two directions. In this Thesis, we theoretically investigate the exciton, phonon, and thermal properties of Si-based one-dimensional quantum dot superlattices and Si/SiO_2 multishell nanotubes (MNT) and discuss optimization of their parameters for optical, energy transfer, and thermal management applications.

Goal and objectives:

- Development of theoretical models for electron, hole, and exciton states in Si-based 1D-QDSLs;
- Investigation of electron, hole, exciton, and photoluminescence properties of Si-based 1D-QDSLs and their optimization for optical and energy transfer applications;
- Development of theoretical models for phonon states and thermal conductivity in Si-based QDSLs and Si/SiO_2 multi-shell nanotubes;
- Investigation of phonon and thermal properties of Si-based 1D-QDSLs and Si/SiO_2 MNTs and their optimization for heat management applications.

Research hypothesis:

- Three-band Bart's Hamiltonian should be used to quantitate description of exciton states in Si quantum dots;
- The broadening of photoluminescence lines in Si QDs can be theoretically explained by the dispersion of QD's shapes and sizes;
- Thermal transport in Si/Ge 1D-QDSLs is significantly suppressed due to trapping of many phonon modes in nanostructure segments and phonon scattering at Si/Ge interfaces;
- L-fold drop of the thermal conductivity in a wide temperature range from $50\,\mathrm{K}$ to $400\,\mathrm{K}$ is predicted for Si/SiO_2 MNTs with L shells in comparison with one-shell Si/SiO_2 NT.

Scientific research methodology

Exciton in the QD:

1. *Effective-mass approach* with *three-band hole Hamiltonian* for the theoretical investigation of the electron, hole, and exciton states. This approach has also taken into account anisotropy of the electron and hole effective masses and self-actions;
2. *Finite differences method* for numerical solution of Schrodinger equations
3. *Davidson-Liu method* [29] for diagonalization of huge matrix (up to 10^7 elements).

4. *An iterative method of Jacobi-Seidel* for numerical calculation of Coulomb potentials in the considered nanostructures.

Phonon spectra and thermal conductivity:

5. *Face-centred-cubic cell model of lattice vibrations* for theoretical investigation of phonon modes in Si-based 1D-QDSLs and Si/SiO_2 MNTs.
6. *Boltzmann transport equation approach within relaxation time approximation* [30–33] for the theoretical study of thermal fluxes in Si-based 1D-QDSLs and Si/SiO_2 MNTs. All main mechanisms of phonon scattering in QDSLs and MNTs were taken into consideration: three-phonon Umklapp scattering, boundary, and impurity scatterings [31–38].

The scientific novelty of the work is related to the comprehensive theoretical study of exciton, phonon, and thermal properties of the recently-discovered class of nanostructures: Si-based one-dimensional quantum-dot superlattices and Si/SiO_2 multi-shell nanotubes. The following new theoretical results have been obtained:

- An increase in the potential barrier height leads to an enhancement of electron and hole spatial confinement and the corresponding increase of their energies and distance between energy levels;
- Both binding energy and total exciton energy decrease with the rise of QD's volume due to the weakening of the spatial confinement of electrons and holes;
- The shape of the Si QDs strongly influences electron, hole, and exciton states. It has been shown that conical QDs possess lower values of ground exciton energy in comparison with the cuboid and pyramidal QDs for volumes $V < 32\ \mathrm{nm}^3$, while for $V > 32\ \mathrm{nm}^3$ cuboid QDs demonstrate lower values of ground exciton energy;
- The outer media parameters influence the electron and hole ground energy only for Si QDs with narrow SiC shell with thickness < 1 nm because maximal penetration of hole and electron wave functions into barrier media in considered Si/SiC/air or Si/SiC/water QDs is about 1 nm.
- The large broadening of photoluminescence (PL) bands in Si QDs as well as the dependence of exciton energy on annealing temperature reported recently in experimental works [13], [39], [40] can be theoretically explained by the dispersion of QD's shapes and sizes.
- Phonon modes in Si/Ge 1D-QDSLs are trapped in their segments due to an acoustical mismatch of materials. The slope of the phonon dispersion in 1D-QDSLs is smaller than

in Si nanowires. Many high energy modes in Si/Ge QDSLs are dispersionless and possess low group velocities close to 0 value.

- The average phonon group velocities in Si/Ge 1D-QDSLs are significantly lower than those in nanowires for all phonon energies in 1D-M-QDSLs (QDSL with modulated cross-section) and for phonon energies $\hbar\omega > 5\,\text{meV}$ in 1D-C-QDSLs (QDSL with constant cross-section). The effect of average phonon group velocity drop is stronger in the case of 1D-M-QDSLs due to the interplay between segmentation and cross-section modulation.
- Thermal transport in Si/Ge 1D-QDSLs is significantly suppressed due to phonon deceleration and reinforcement of phonon scattering at Si/Ge interfaces. Up to 7-times (13.5-times) drop of TC was demonstrated for C-QDSLs (M-QDSLs) as a function of temperature. At room temperature, the thermal conductivity in Si/Ge 1D-C-QDSLs is by a factor of 2.6 – 2.9 lower than that in silicon nanowires with the same cross-section.
- Phonon average group velocities in multi-shell Si nanotubes are close to 0 for phonon energies $\hbar\omega > 10$ meV .
- A large number of phonon modes in Si/SiO_2 MNTs are scattered on Si/SiO_2 interfaces. As a result, an *L*-fold drop of the thermal conductivity in a wide temperature range from $50\,\text{K}$ to $400\,\text{K}$ is predicted for Si/SiO_2 MNTs with *L* shells in comparison with one-shell Si/SiO_2 NT.

Structure of the Thesis

The Thesis consists of an Introduction, 3 Chapters, and General conclusions and Recommendations. The Thesis contains 157 references, 145 pages, 79 figures, 53 equations, and 1 table.

Publications and approval of the obtained results

The results of the current work were published in 8 articles, including 4 in international press. The results presented in this work were discussed at 32 international and national conferences. Two articles and two conference abstracts were published without co-authors.

CONTENTS OF THE THESIS

The **Introduction** presents a general analysis of the thesis, argues the relevance of the researched topic, and describes the state of research on this topic in the world. The Introduction elucidates the scientific novelty of the obtained results, and the theoretical and practical

importance of the research is highlighted. The main scope and objectives of the work are also defined.

Chapter 1 contains a review of scientific papers published in the literature on the problem under study and methods of solution. We analysed works that study, both theoretically and experimentally, excitonic, photoluminescence, and thermal properties of the different nanostructures and the comparison of these properties with analogical bulk materials. The presented works are dedicated to the Si/SiO_2 QDs and their PL properties, and the influence of the sample tailoring conditions on PL energy, line form, and its intensity. There are described practical applications of the QD of different origins, especially as CMOS-compatible and non-toxic sources of energy for both radiative and non-radiative energy transfer. For investigation of exciton and optical properties of nanostructures both effective mass approach [41] and tight-binding models were widely employed. The methods of the theoretical study of the electron, hole, and exciton properties of the QD are described, as well.

The second part elucidates research in the field of phonon engineering and thermal transport. It provides details about different approaches to the theoretical study of the thermal flux in heterogeneous nanostructures, such as multilayered planar structures, and heterowires. It has been demonstrated that multi-layer nanostructures possess wide possibilities for charge-carrier or phonon engineering by tuning their shape and size as well as layer materials.

At the same time, there is some lack of investigation of exciton and phonon processes in quasi-one-dimensional quantum dot superlattices (1D-QDSL).

The main goal of the Thesis is a comprehensive theoretical investigation of exciton, phonon, and thermal properties of quasi-one-dimensional Si-based nanostructures (1D-QDSL and core/shell nanotubes) and their optimization for optical, energy transfer, and thermal management applications. To achieve this goal, the following objectives are formulated:

- Development of theoretical models for electron, hole, and exciton states in Si-based 1D-QDSL;
- Investigation of electron, hole, exciton, and photoluminescence properties of Si-based 1D-QDSL and their optimization for optical and energy transfer applications;
- Development of theoretical models for phonon states and thermal conductivity in Si-based QDSL and Si/SiO_2 multi-shell nanotubes;
- Investigation of phonon and thermal properties of Si-based 1D-QDSL and Si/SiO_2 MNTs and their optimization for heat management applications.

Chapter 2 describes the theoretical study of the electron, hole, exciton, and PL properties of the Si QD embedded in a dielectric matrix. The electron and hole spectra were calculated in the framework of the effective mass approach, taking into account self-action energy, finite potential barrier, and anisotropy of the effective mass in Si. In our calculations, we used two different approaches for the holes: one-band Hamiltonian and three-band Bart's Hamiltonian.

In Fig. 1 we compare hole energies calculated using 1-band Hamiltonian for heavy and light holes with those calculated within 3-band Hamiltonian. The first 3 lowest energy curves are depicted for all types of considered holes: heavy, light, and 3-band. The black lines correspond to the 3-band holes, while blue lines are for the holes calculated in the one-band approach: dash-dotted lines are heavy holes energy levels and continuous lines for the light holes spectrum. The ground level of the 1-band Hamiltonian approach, i.e. ground level of heavy holes possesses smaller energy than the ground level of 3-band holes. Higher energy levels of 3-band holes demonstrate similar behaviour with higher levels of heavy or light holes. However, the energy difference reaches $\sim 20\ \mathrm{meV}$ in dependence on QD's radius. Hole levels calculated via Bart's Hamiltonian have lower energy and less energy distance between levels than the heavy hole levels calculated using one-zone Hamiltonian.

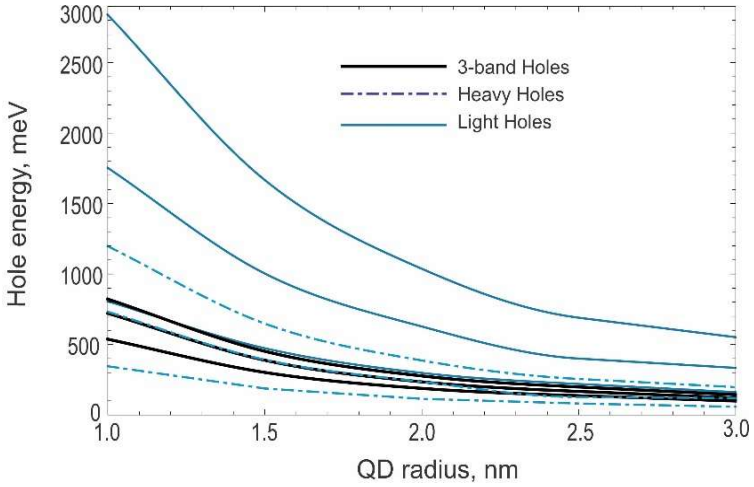

Fig. 1. Comparison of the 3 lowest hole energy levels calculated within 3-band and 1-band Hamiltonian approaches

Exciton energies were calculated taking into account the mixing of charge carriers levels with higher energies. Exciton Hamiltonian can be represented in the following form:

$$H_{exc}(\vec{r}_e,\vec{r}_h)\Phi^n_{exc}(\vec{r}_e,\vec{r}_h) = E^n_{exc}\Phi^n_{exc}(\vec{r}_e,\vec{r}_h), \quad (1)$$

where exciton Hamoltoninan is given as:

$$H_{exc}\left(\vec{r}_e,\vec{r}_h\right) = H^{SA}_{e}\left(\vec{r}_e\right) + H^{SA}_{h}\left(\vec{r}_h\right) + V_{Coulomb}\left(\left|\vec{r}_e - \vec{r}_h\right|\right). \quad (2)$$

In Eqs (1-2) $\Phi^{n}_{exc}(\vec{r}_e,\vec{r}_h)$ denotes exciton wave functions, $H_e(\vec{r}_e)$ and $H_h(\vec{r}_h)$ are electron and hole Hamiltonians respectively, $V_{Coulomb}$ is the Coulomb interaction potential.

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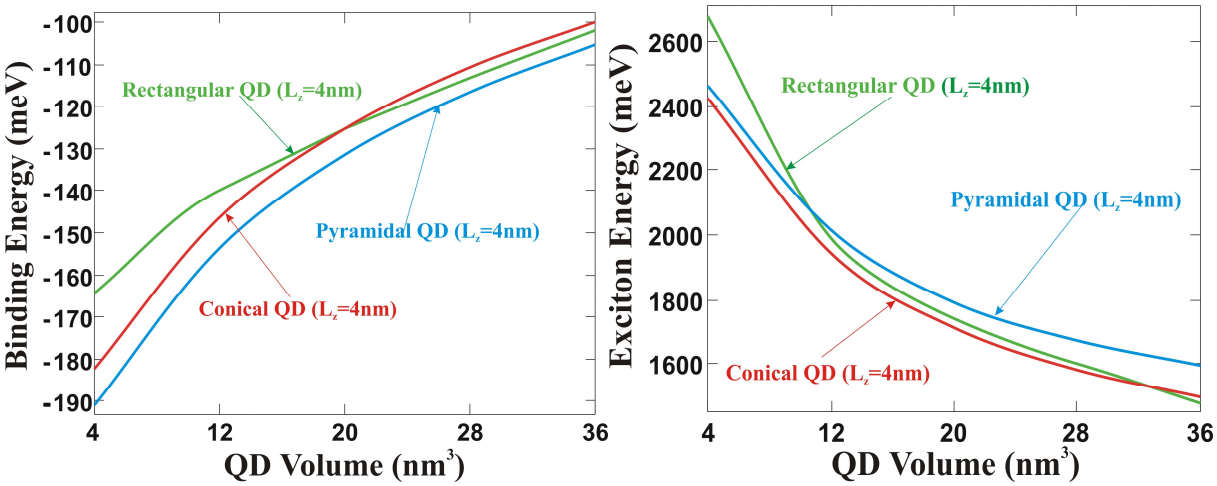


Fig. 2. Influence of the QD shape on exciton energy

The influence of QD's shape on the binding energy of exciton (panel a) and on total exciton energy (panel b) is illustrated in Fig. 2 for Si/SiO_2 QDs. Energy curves are depicted as a function of QD volume. In both panels energies for the pyramidal QDs are represented with blue curves, for the conical QDs with red curves, and for the cuboid QDs with green ones. The binding energy increases together with QD volume. In the pyramidal QDs, its value is smaller than that in conical and cuboid QDs for all considered QD volumes presented in the figure. For the cuboid and conical QDs binding energy curves are crossed: $E^{ground}_{bind,conical\,QD} < E^{ground}_{bind,cuboid\,QD}$ for volumes $V < 20\,\mathrm{nm}^3$ and $E^{ground}_{bind,conical\,QD} > E^{ground}_{bind,cuboid\,QD}$ for $V > 20\,\mathrm{nm}^3$.

Total exciton energy (see Fig. 2. (b)) decreases with QD size due to decrease of electron and hole energy with the weakening of the spatial confinement. All exciton energy curves are crossed: for volumes in the range of $4\,\mathrm{nm}^3 - 36\,\mathrm{nm}^3$ the concial QDs demonstrate the lowest energy values, while for $V > 36\,\mathrm{nm}^3$ energy in cuboid QDs becomes smaller than that in conical or pyramidal QDs. The behaviour of energy curves is explained by behaviour of both the electron and hole energy curves, as well as by dependence of binding energies on volume V (see Fig. 2 (a)).

Mixing electron and hole levels, and using Bart's Hamiltonian gives lower energy of the exciton levels, which gives us better concordance with the experimental results, and makes

our model applicable for predicting exciton energies even for small QD, with diameters $\leq 2\text{nm}$.

We compared our theoretical results calculated for differenet QD shapes and within different approaches with experimental data and theoretical calculations of other groups. In Fig. 3 the comparison of experimental and theoretical results for exciton energy is depicted.

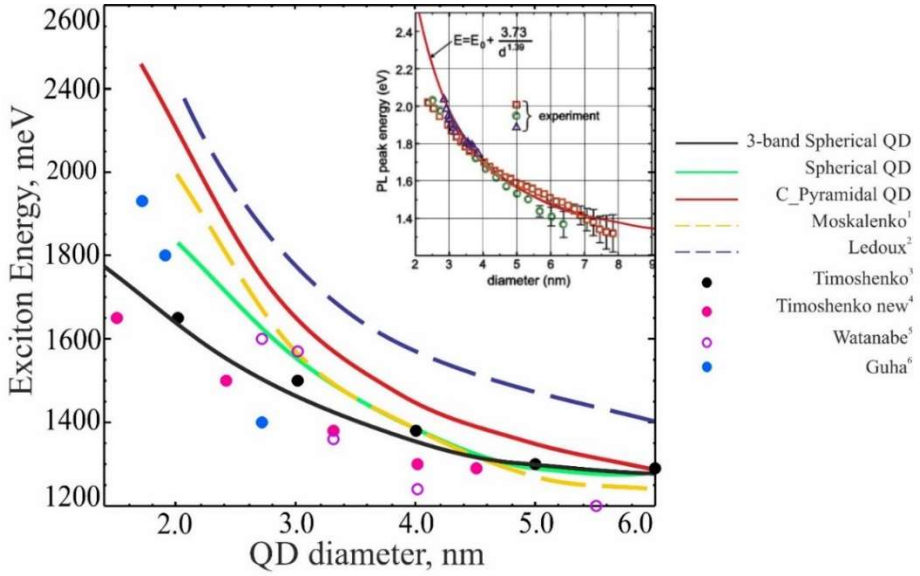


Fig. 3. Comparison of the theoretical calculations and the experimental values of the exciton energies in Si QDs.

Solid lines represent theoretical calculations made in this Thesis. The green line corresponds to the spherical QDs in the approach of 1-band Hamiltonian for holes and without mixing levels for exciton. The black line is for spherical QD too, but the hole's spectra are calculated using a 3-band Hamiltonian for holes and taking into account mixing of energy levels for exciton. The exciton energy of double truncated pyramidal QD is shown with a red line. Dependence was calculated using taking into account the 3-band Hamiltonian and mixing high energy levels of charge carriers. Dashed lines represent theoretical calculations from other works: the yellow line represents theoretical calculations of spherical QD exciton energy from work Ref. [42], and the blue line represents theoretical calculations effectuated by Ledoux et al. in Ref. [43], (same as in inset). Black dots, magenta dots and circles, and cyan dots represent experimental results obtained for exciton energy in works [40], [39], [44], [14], respectively. In the presented experiments Si nanocrystals were embedded into the dielectric matrix SiO_2, while in the work of Watanabe et al. [44], the Er^+ ions were also present in the dielectric matrix. Inset is taken from Ref. [43]. It shows theoretical and experimental data of exciton energy in dependence on QD size.

It is clearly seen that all theoretical curves for spherical QDs have higher energy than experiment data for QD's diameter $D<3\,\mathrm{nm}$, but are in good accordance with measured PL for larger QDs. The best agreement with the experimental data demonstrates theoretical calculations carried out for spherical QD within a 3-band Hamiltonian approach taking into account the mixing of size-quantized electron and hole energy levels. The larger difference between theoretical and experimental results for small QDs can be explained by the following reasons: (i) experimental difficulties in obtaining QDs of the same shape and size as well as insufficient accuracy of QD's size/form determination and size/form dispersion in an experiment, which strongly affects spectra of QDs with $D<3\,\mathrm{nm}$ [13]; and (ii) limited applicability of the continual approach for QDs with $D<3\,\mathrm{nm}$ (the validity of the continual approach is quite discussible in this case).

Photoluminescence curves of the QDs ensemble which have the same dimension and shape should have the form of sharp peaks. But conform experiments presented in Ref. [39] photoluminescence spectra of a spherical QD Si/SiO_2 have the form of Gaussian curves, but not of sharp peaks. In our theoretical investigation, we assume two main possible reasons for photoluminescence band broadening: size dispersion and QDs merge.

Theoretical modelling of photoluminescence lines has been done conform the following equation:

$$I_{PL}\left(\varepsilon\left(K\right)\right)=I_{PL}\left(\varepsilon_{\max}\right)e^{-a\left(\frac{K\left(\varepsilon_{\pm}\right)-K_0\left(\varepsilon_{\max}\right)}{K_0\left(\varepsilon_{\max}\right)}\right)^2}, \qquad (3)$$

where, K_0 – initial radius of QD or maximal distance between the centres of QD, $\varepsilon_{\max}$ – exciton energy of QD with K_0, a – parameter, describing dispersion, and is calculated conform the following expression:

$$\left\langle\left(x^2\right)\right\rangle=\frac{\int_{-1}^{\infty}x^2e^{-ax^2}dx}{\int_{-1}^{\infty}e^{-ax^2}dx}, \qquad (4)$$

where $x=\dfrac{K-K_0}{K_0}$.

In Fig. 4 the comparison of theoretical and experimental curves of photoluminescence intense distribution in dependence on PL energies for different QD sizes is shown. Red continuous lines represent experimental photoluminescence curves, black dashed lines are dependencies obtained via theoretical modelling of QD's size dispersion, while yellow dash-n-dot lines demonstrate the results of theoretical modelling of QD's merging. In Fig. 4 (a) the

photoluminescence for QD with diameter $D=3\,\text{nm}$ is shown with dispersion value $\left\langle\left(x^2\right)\right\rangle=0.0324$. One can see that the theoretical curve for size distribution almost coincides with experimental data (size dispersion is equal to $18\ \%$ from the QD radius). For the QD with a diameter of $4\ \text{nm}$ (see Fig. 4 (b)), the dispersion was taken the same as for QD with $D=3\,\text{nm}$, $\left\langle\left(x^2\right)\right\rangle=0.0324$. But in this case, there is a difference between the size dispersion curve and experimental data at the low-energy region. For QD with diameter $5\ \text{nm}$ dispersion was increased to $\left\langle\left(x^2\right)\right\rangle=0.0484$. Even for greater dispersion value, the theoretical curve coincides with the experimental one only in high-energy region. This occurs because exciton energy increases more slowly with increasing QDs size, the size distribution curve is asymmetric, and it's narrow at the low-energy region, even for size dispersion up to $a=80\%$ from the QD diameter. To explain photoluminescence band broadening we have examined the merge of the QDs. Due to the lower exciton energy of the merged QDs, we have obtained good accordance of our theoretical calculations with the experiment, as is seen in Fig. 4 (c).

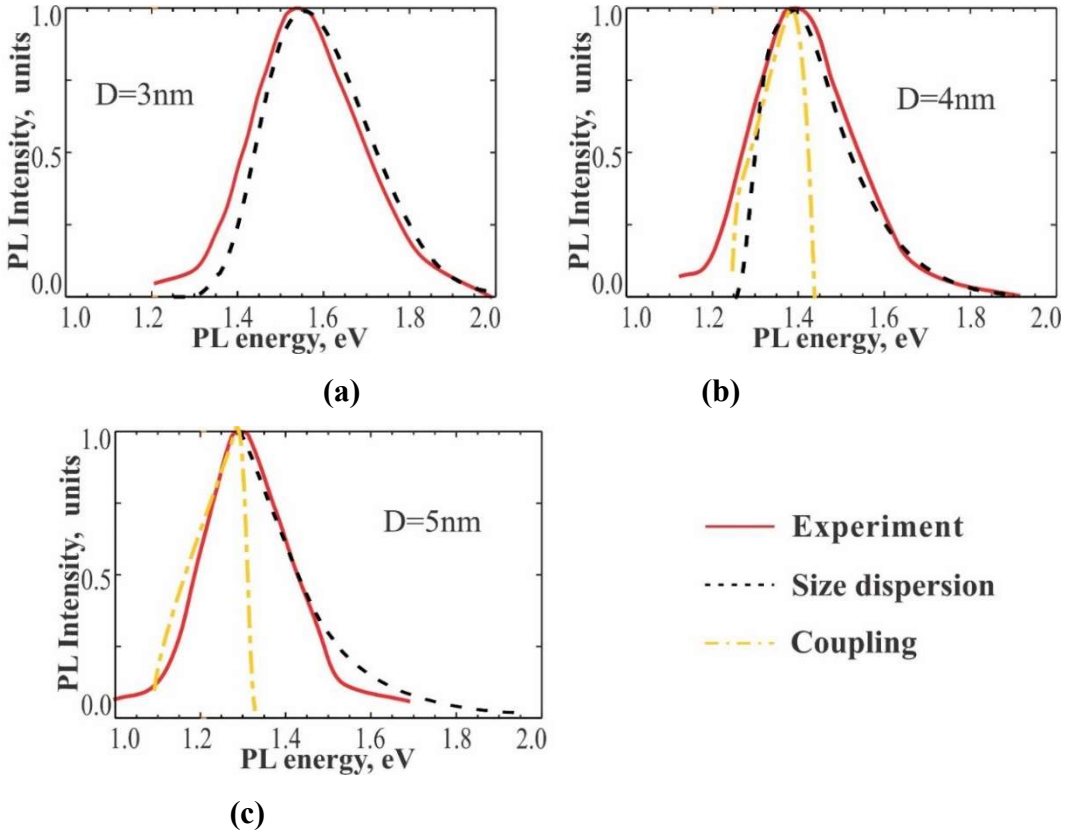


Fig. 4. Theoretical PL intensity distribution in Si/SiO_2 in dependence on PL energy

Therefore, size distribution allows us to explain the broadening of the photoluminescence band in the range of high energies, at the same time merge of the QDs can be a reason for the broadening in low-energy region.

The topic of **Chapter 3** is the thermal properties of the Si-based one-dimensional superlattices.

We studied the possibility of thermal conductivity reducing in 1D-QDSL with a constant and periodically modulated cross-section with and without a shell using principles of *phonon engineering*. We consider here both superlattices with constant (1D-C-QDSL) and modulated (1D-M-QDSL) cross-sections. The influence of both geometrical and materials parameters of QDSLs on phonon spectra, phonon group velocities and thermal conductivity is investigated. We also provide comparative analysis of phonon and thermal properties of multi-shell silicon nanotubes. The presented results are based on the original author's works [24], [45–47].

Phonon spectra were calculated within the lattice dynamic model Face-centred cubic cell. This approach excludes optic oscillations from calculations, however, we do not have any fitting parameters and demonstrated a good qualitative description of the effects. We studied phonon spectra and velocities of the 1D-QDSL.

It was demonstrated that modulated cross-section amplifies the effect of the acoustical mismatch of the materials and reduces thermal transport more effectively. It is demonstrated that contact of the acoustic mismatch materials leads to the redistribution of the phonon density of states toward lower energies. Together with phonon deceleration, it results in a reduction of the thermal transport. Thermal flux was calculated using the Boltzmann transport equation within the approximation of the relaxation time. In order to provide more accurate results, we used a one-dimensional density of states. We took into account three basic mechanisms of scattering: Umklapp, boundary, and impurity [31–38]. It was shown that manipulation of such geometrical parameters as a cross-section, the difference between QDs' cross-section in M-QDSL, translation period can enhance thermal drop in 1D-QDSL.

For calculation of the phonon thermal flux in 1D nanostructures, we used the following expression, which was derived from the Boltzmann transport equation within the relaxation time approximation [30–33] taking into account one-dimensional density of phonon states:

$$\Theta = \frac{1}{2\pi k_B T^2} \sum_{s=1,\ldots,3N} \int_0^{q_{\max}} \left(\hbar\omega_s(q_z)\upsilon_{z,s}(q_z)\right)^2 \tau_{tot,s}(q_z) \frac{\exp\left(\frac{\hbar\omega_s(q_z)}{k_B T}\right)}{\left(\exp\left(\frac{\hbar\omega_s(q_z)}{k_B T}\right)-1\right)^2} dq_z \,. \qquad (5)$$

Here $\tau_{tot,s}$ is the total phonon relaxation time, s is the number of a phonon branch, k_B is the Boltzmann constant, $\hbar$ is the Planck constant and T is the absolute temperature, ω is phonon frequency, υ_z is the Z-th component of the phonon group velocity.

According to the Matthiessen's rule, the total phonon relaxation time is given by:

$$\frac{1}{\tau_{tot,s}(q_z)} = \sum \frac{1}{\tau_{mechanism}(q_z)}, \tag{6}$$

where $\tau_{mechanism}$ is the relaxation time specific for scattering mechanism [31–38].

In Fig. 5 the ratio of the thermal conductivity in Si/Ge 1D-C-QDSL to the homogeneous Si nanowire (NW) with the corresponding cross-section is provided. We varied specularity parameter values $p = 0.9, 0.7, 0.5$ (p can take values between $p = 0$ (pure diffusive scattering) and $p = 1$ (pure specular scattering)) and fixed temperature $T = 300\,\mathrm{K}$ for the dependencies in Fig. 5 (a), and vice versa, fixed the specularity parameter $p = 0.7$ and changed temperatures $T = 100\,\mathrm{K}$, $200\,\mathrm{K}$, $300\,\mathrm{K}$, $400\,\mathrm{K}$ in Fig. 5 (b). Translation period was $N_z = 4\,\mathrm{ML}$ in both cases. The presented ratio dependencies on the QDSL cross-section have maximum. The continues increase of the cross-section means more atoms, and phonons as well, participating in heat propagation either in C-QDSL and in NW. The effect of the modes trapped in the QDSL segments and of additional phonon scattering become not so significant and ratio dependency goes throw its maximum in the range $17\,\mathrm{ML} \times 17\,\mathrm{ML} - 23\,\mathrm{ML} \times 23\,\mathrm{ML}$ at the temperature $T = 300\,\mathrm{K}$ (see, Fig. 5(a)). The maximum drop of thermal flux is up to $2.6 - 2.9$ times. The more significant drop corresponds to smaller specularity parameter value. The shift of the maxima toward larger cross section for smaller specularity parameter is the result of interplay of the increasing number of the phonon modes and boundary scattering. The curves in Fig. 5 (b) demonstrate the most significant drop of the thermal transport is reached at the higher temperatures. The thermal transport drop at $200\,\mathrm{K}$ is with $\sim 25\,\%$ more than at the $100\,\mathrm{K}$. The difference between values at $200\,\mathrm{K}$, $300\,\mathrm{K}$, $400\,\mathrm{K}$ is in the range $1\% - 4\%$. With higher temperatures phonons start to populate higher energy levels with near-zero values of the phonon velocity that leads to the more essential drop of the thermal flux, but subsequent continues population doesn't influence the flux much. The intensification of the Umklapp scattering leads to the shift of the dependencies' maxima toward smaller cross-section with the increase of temperature.

The thermal flux in Si/Ge 1D-C-QDSL is lower than in the Si NWs due to different process that undergoes in 1D-C-QDSL: high energy phonon modes are trapped within Ge segments with lower sound velocity, Umklapp scattering and scattering at segments' interfaces.

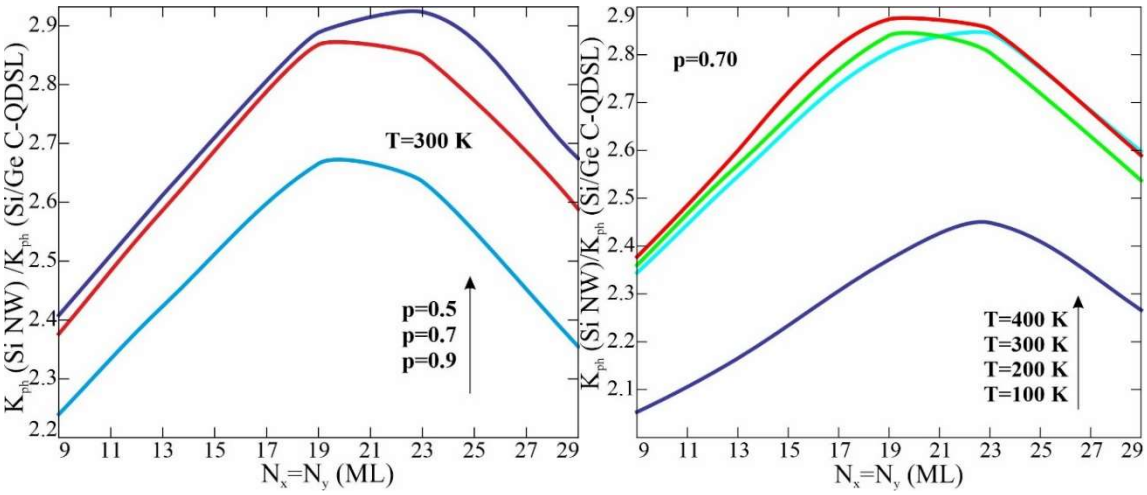
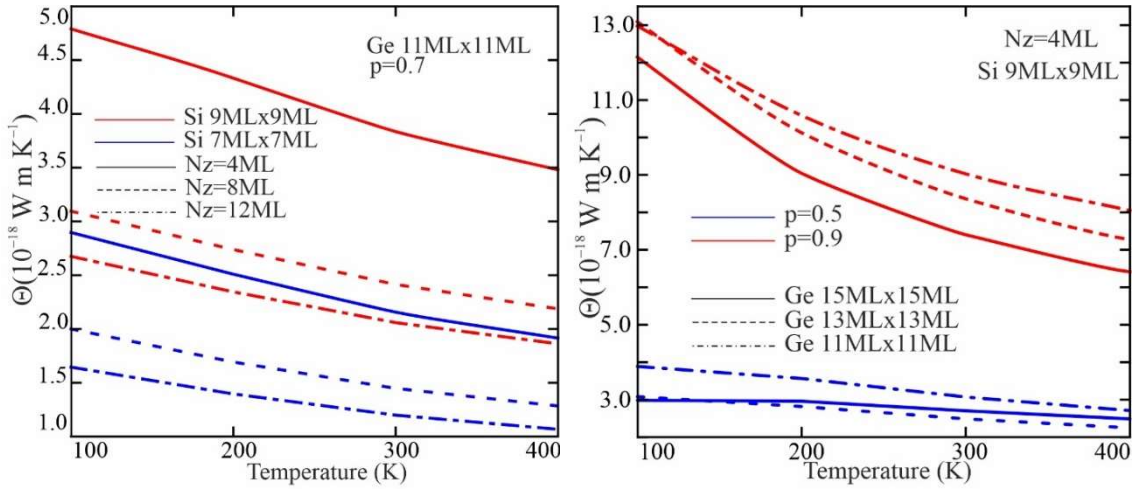


Fig. 5. Cross-section influence on thermal conductivity ratio in Si/Ge 1D-C-QDSL

(a) constant temperature value $T = 300\,\mathrm{K}$; **(b)** constant specularity parameter $p = 0.7$

In Fig. 6 thermal flux dependencies are shown for 1D-M-QDSL with different geometric parameters. In Fig. 6 (a) we fixed dimensions of the Ge QDs at $N_{x,2} = N_{y,2} = 11\,\mathrm{ML}$ and value of specularity parameter. Red curves correspond to the Si QDs with $N_{x,1} = N_{y,1} = 9\,\mathrm{ML}$, while the blue to the $N_{x,1} = N_{y,1} = 7\,\mathrm{ML}$. Solid lines denote 1D-M-QDSL with translation period $N_z = 4\,\mathrm{ML}$, dashed lines are for $N_z = 8\,ML$, and the dot-dashed lines to the $N_z = 12\,\mathrm{ML}$. Dependencies which correspond to 1D-M-QDSL with the larger cross-section have higher values for same translation period length. However, 1D-M-QDSL with larger Si QDs $N_{x,1} = N_{y,1} = 9\,\mathrm{ML}$ and translation period $N_z = 12\,\mathrm{ML}$ have lower values of thermal flux, than ones with smaller Si QD cross-section and $N_z = 4\,\mathrm{ML}$.



(a) **(b)**

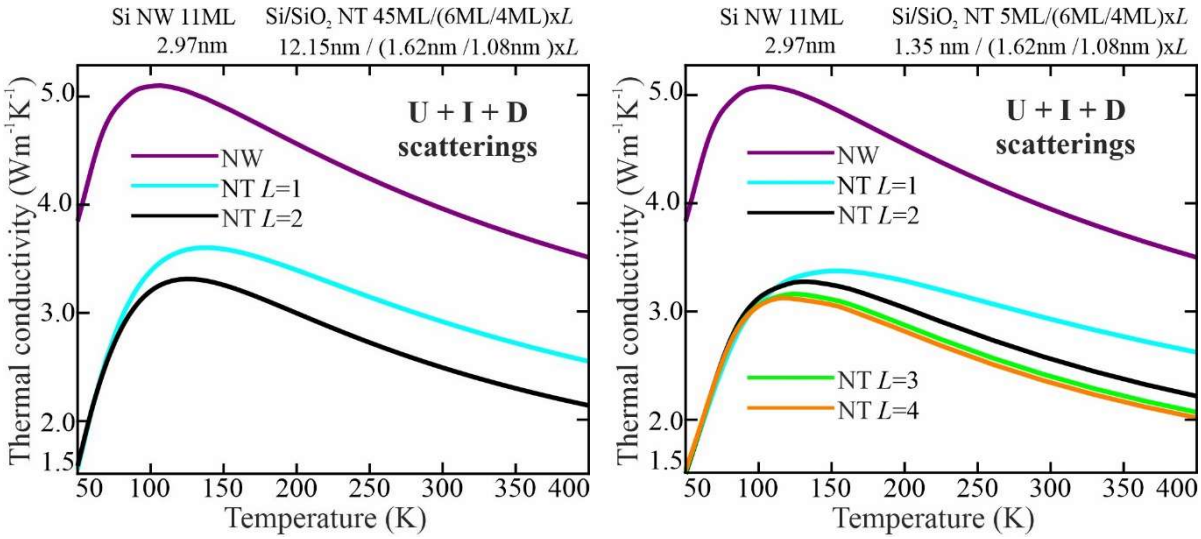
Fig. 6. Thermal flux in Si/Ge 1D-M-QDSL.

In Fig. 6 (b) the dependencies are presented for fixed values of Si QDs $N_{x,1} = N_{y,1} = 9\,\text{ML}$ and translation period $N_z = 4\,\text{ML}$. The dimensions of Ge QDs varied: $N_{x,2} = N_{y,2} = 11\,\text{ML}, 13\,\text{ML}, 15\,\text{ML}$. Red lines are for $p = 0.9$, while the blue ones are for $p = 0.5$. Solid lines denote 1D-M-QDSL with Ge QDs cross-section $N_{x,2} = N_{y,2} = 15\,\text{ML}$, dashed lines are for $N_{x,2} = N_{y,2} = 13\,\text{ML}$, and the dot-dashed lines to the $N_{x,2} = N_{y,2} = 11\,\text{ML}$. Thermal flux is more intensive for 1D-M-QDSL with $p = 0.9$ for all presented values of Ge QDs cross-section. In the case of translation period $p = 0.9$ higher thermal flux values correspond to the larger Ge QDs because of the greater number of the phonon modes, while boundary scattering has low intensity. For the $p = 0.5$ dependencies with $N_{x,2} = N_{y,2} = 13\,\text{ML}$ and $N_{x,2} = N_{y,2} = 11\ \text{ML}$ intersects at the temperatures $\sim 120\,\text{K}$ because boundary scattering and Umklapp contribute become more significant in comparison of the phonon number increase.

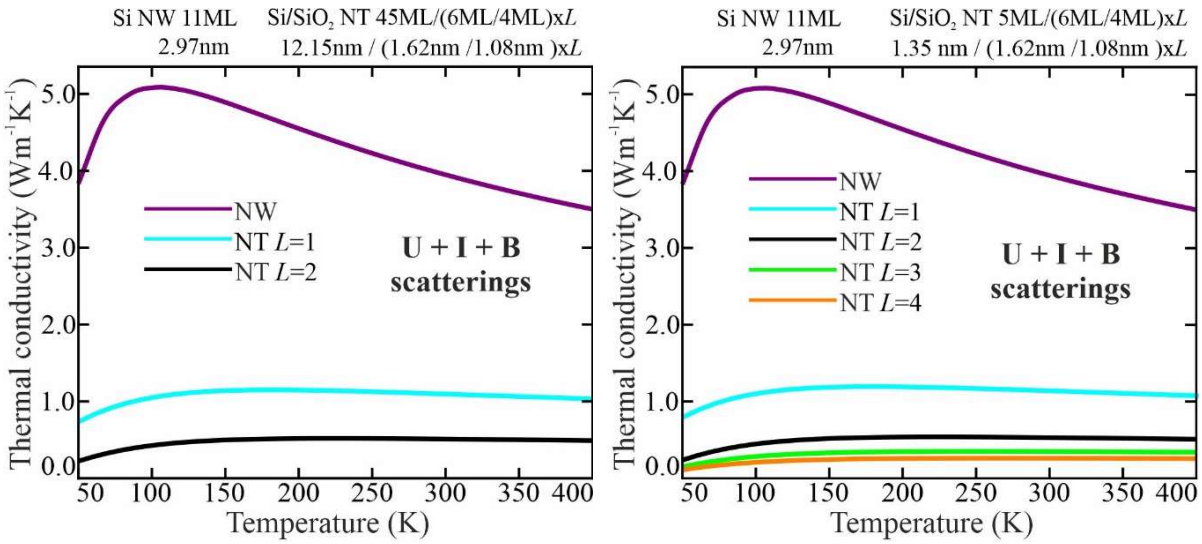
A comparison of thermal conductivity in a Si NW and Si/SiO_2 NTs as a function of temperature is provided in Fig. 7. Average phonon group velocities as a function of phonon energies in Si/SiO_2 MNTs with the cavity cross-section $45\text{ML}\times45\text{ML}$ and $5\text{ML}\times5\text{ML}$, and different numbers of Si/SiO_2 bilayer shells, formed by silicon layer with thickness 6 ML and silica layer with thickness $4\,\text{ML}$. Results for Si NW with cross section $11\text{ML}\times11\text{ML}$ are also shown for comparison. Calculation of the thermal conductivity illustrated in Fig. 7 (a-b) takes into account diffusion transport in SiO_2, while Fig. 7 (c-d) includes the boundary scattering with

the specular parameter $p=0.6$. The values of the thermal conductivity in NTs (even for the NTs with a greater number of phonon modes, see Fig 7 (c)) are lower than the thermal conductivity in the NW in the whole temperature range. This decrease of the thermal conductivity in the NTs occurs due to the acoustic mismatch of Si and SiO_2, density of states redistribution, which leads to a decrease of the phonon group velocities, and an enhancement of the phonon scattering at interfaces.

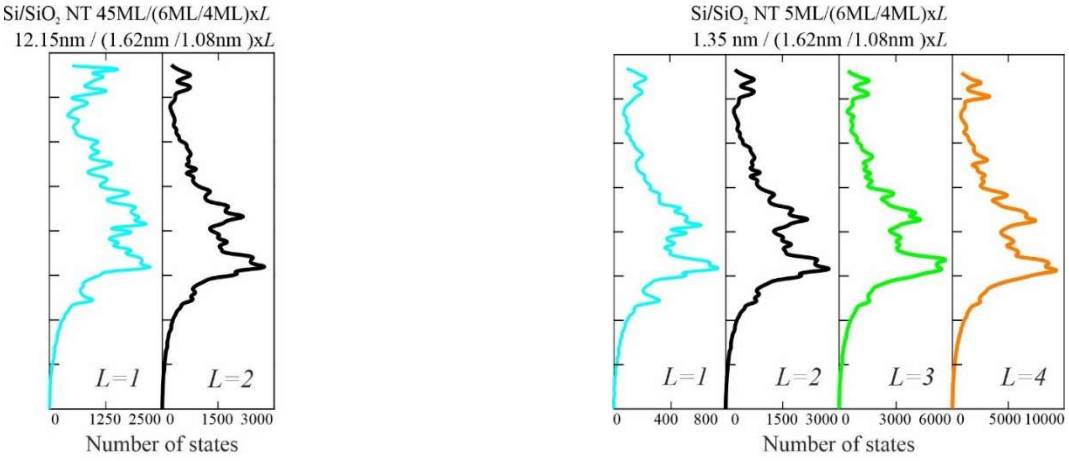
One can see that considering the boundary scattering mechanism instead of amorphous scattering mechanism leads to more significant reduction of thermal conductivity due to a big number of interfaces in multishell NTs, which leads to domination of the boundary scattering mechanism. The thermal conductivity of the NTs with $45\,\mathrm{ML}\times 45\,\mathrm{ML}$ is higher than with the $5\,\mathrm{ML}\times 5\,\mathrm{ML}$ because of a larger number of phonon modes in these structures. Additional interfaces between the shells effectively scatter phonons, hence the TC decreases with augmentation of the number of shells (see panels (b) and (d)) reaching values as low as $0.2\ {}^{\mathrm{W}}\!/_{\mathrm{m}\cdot\mathrm{K}}$ at RT for Si/SiO_2 NT with smaller cavity and $L=4$. A similar dependence of TC on L was demonstrated experimentally for Si/SiO_2 rolled-up nanotubes of 1.9 μm to 3.2 μm radii and a 24-nm-thick shell [48], see Fig. 7 (g).



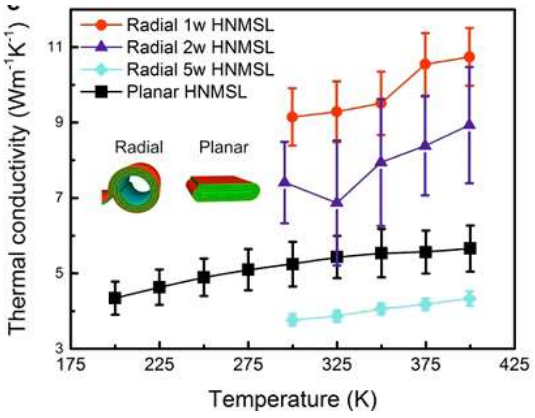
(a)-(b) Umklapp and diffusive scattering



(c)-(d) Umklapp and boundary scattering



(e)-(f) Density of states



(g) Thermal conductivity in rolled-up structures. Figure (g) is adopted from Ref. [48]

Fig. 7. Thermal conductivity in NTs

GENERAL CONCULSIONS AND RECOMMENDATIONS

The detailed theoretical study of exciton, phonon, and thermal properties of the Si/Ge, Si/SiC, and Si/SiO_2 one-dimensional quantum-dot superlattices as well as phonon and thermal properties of the Si/SiO_2 multi-shell nanotubes is carried out in the Thesis. Below is the summary of the obtained results.

1. The effective mass approach was employed for the theoretical investigation of electron, hole, and exciton states in Si/SiO_2 and Si/SiO_2 1D-QDSLs:

- It has been shown that for the qualitative description of exciton states it is crucial to take into account the anisotropy of electron and hole effective masses, mixing of heavy, light, and split-off holes as well as mixing of different electron and hole states. Exciton energies calculated within this theoretical approach with a three-band hole Hamiltonian were in good agreement with experimental exciton energies reported for Si QDs.
- It has been demonstrated that electron, hole, and exciton states in considered 1D-QDSLs can be effectively engineered by changing the QD's shape and size which is particularly important for optoelectronic and biomedical applications of 1D-QDSLs.
- Conical QDs possess the lower values of ground exciton energy in comparison with cuboid and pyramidal QDs for the volumes $V < 32\ \mathrm{nm}^3$, while for $V > 32\ \mathrm{nm}^3$ cuboid QDs demonstrate the lower values of ground exciton energy.
- The outer media parameters influence the electron and hole ground energy only for Si QDs with narrow SiC shells with thickness $< 1\ \mathrm{nm}$ because maximal penetration of hole and electron wave functions into barrier media in considered Si/SiC/air or Si/SiC/water QDs is about $1\ \mathrm{nm}$.
- It has been also revealed that the broadening of photoluminescence lines in Si/SiO_2 QDSLs can be explained by the dispersion of QD's size and shape.

2. The face-centred cubic cell model of lattice vibrations was applied for the theoretical study of phonon modes in Si/Ge and Si/SiO_2 1D-QDSLs and in Si/SiO_2 multi-shell nanotubes:

- It has been theoretically shown that phonon modes in Si/Ge 1D-QDSLs are trapped in their segments due to an acoustical mismatch of materials. The slope of the phonon dispersion in 1D-QDSLs is smaller than that in Si nanowires.
- It has been revealed that many high energy phonon modes in Si/Ge QDSLs are dispersionless and possess low group velocities close to 0 value, resulting in the removal of these modes from heat flux.

3. Boltzmann transport equation within relaxation time approximation was employed for the theoretical study of thermal processes in Si-based 1D-QDSLs and Si/SiO_2 MNTs. All major phonon scattering mechanisms were taken into account: three-phonon Umklapp scattering, impurity, and boundary scatterings.

- It has been revealed that thermal transport in Si/Ge 1D-QDSLs is significantly suppressed in comparison with Si nanowires or bulk. Up to 7-times (13.5-times) drop of lattice thermal conductivity was demonstrated for Si/Ge 1D-QDSLs with constant (modulated) cross-section in dependence of the temperature.
- At room temperature, the thermal conductivity in Si/Ge 1D-C-QDSLs is by a factor of 2.6 – 2.9 lower than that in silicon nanowires with the same cross-section.
- In partially coated Si/SiO_2 1D-M-QDSLs heat propagates through internal silicon channel only, while in the fully coated M-QDSLs, it propagates through both internal Si and external SiO_2 channels. As a result, the reduction of the thermal flux in partially coated Si/SiO_2 M-QDSLs is stronger than that in fully coated M-QDSLs: up to ~ 6.5 times at room temperature for fully-coated M-QDLs and ~ 3.5 times for partially-coated M-QDSLs.
- The thermal conductivity in the Si/SiO_2 multi-shell nanotubes is lower than that in the Si nanowires with the same lateral dimensions due to acoustic mismatch of the materials and lower group velocities.
- A large number of phonon modes in Si/SiO_2 MNTs are scattered at Si/SiO_2 interfaces. As a result, an L-fold drop of the thermal conductivity in a wide temperature range from $50\,\mathrm{K}$ to $400\,\mathrm{K}$ is predicted for Si/SiO_2 MNTs with L shells in comparison with one-shell Si/SiO_2 NT.

Based on the conclusions presented above, the following *recommendations* can be made:

1. For an accurate theoretical description of exciton states in Si/SiO_2, Si/SiC/air and Si/SiC/water 1D-QDSLs is crucial to take into consideration the mixing of different electron and hole states as well as mixing of different hole types: heavy, light and split-off (three-band Hamiltonian).
2. The Si/Ge and Si/SiO_2 1D-QDSLs as well as Si/SiO_2 MNTs can be recommended as prospective candidates for thermoelectric and thermal insulation applications owing their ultra-low thermal conductivity.

3. Engineering of exciton and phonon states in 1D-QDSLs described in the Thesis can be useful for practical enhancement of their optical, thermal, and thermoelectric parameters.
4. Dispersion of quantum dot's size and shape may be a key factor in for interpretation of experimental results in the field of exciton-related processes in silicon QDs with dimensions of several nanometers.

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LIST OF PUBLISHED ARTICLES ON THE SUBJECT OF THE THESIS

The results presented in Thesis are published in 4 articles in ISI journals and 4 articles in national press. Two articles are without co-authors.

Articles in scientific journals

1. NIKA, D.L., COCEMASOV, A.I., **ISACOVA, C.I.**, BALANDIN, A.A., FOMIN, V.M., SCHMIDT, O.G. Suppression of phonon heat conduction in cross-section-modulated nanowires. In: *Physical Review B.* 2012, vol. 85, p. 205439. DOI: 10.1103/PhysRevB.85.205439
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4. FOMIN, V.M.; NIKA, D.L.; COCEMASOV, A.I.; **ISACOVA, C.I**.; SCHMIDT, O.G. Strong reduction of the lattice thermal conductivity in superlattices and quantum dot superlattices. In: *AIP Conference Proceedings*. 2012, vol. 1449, p. 33-36. DOI: 10.1063/1.4731490
5. **ИСАКОВА, К**. Падение фононной теплопроводности в сегментированных Si/Ge нанонитях. In: *Studia Universitatis. Seria ştiinţe exacte şi economice.* 2015, nr. 2 (82), pp. 65-71. ISSN 1857-2073.
6. **ИСАКОВА, К.** Электронные, дырочные и экситонные состояния в кремниевых квантовых точках, помещенных в диэлектрическую среду оксида кремния. In: *Studia Universitatis Moldaviae. Seria ştiinţe exacte şi economice.* 2011, nr. 7 (47), pp. 66-72. ISSN 1857-2073
7. **ИСАКОВА, К.**, НИКА, Д., ПОКАТИЛОВ, Е. Экситонные состояния в квантовых точках Si/SiO_2. In: *Studia Universitatis Moldaviae. Seria Ştiinţe Reale şi ale Naturii.* 2008, nr. 2(12), pp. 232-236. ISSN 1814-3237
8. **ИСАКОВА, К.,** НИКА, Д., АСКЕРОВ, А., ЗИНЧЕНКО, Н., ПОКАТИЛОВ, Е. Исследование кулоновского взаимодействия в квантовой точке Si/SiO_2. In: *Studia Universitatis Moldaviae. Seria Ştiinţe Reale şi ale Naturii.* 2007, nr. 7, pp. 280-284 ISSN 1814-3237

The results presented in this work were discussed at more than 30 international and national conferences. Here there are some of them:

Abstracts of scientific communications

1. **ИСАКОВА, К.**, КОЧЕМАСОВ, А., НИКА, Д. Фононная инженерия в одномерных наноструктурах. In: *Rezumatele ale comunicărilor, Ştiinţele exacte, Ştiinţele ale naturii Conferinţa ştiinţifică naţională cu* participare *internaţională „Integrare prin cercetare şi inovare",* 10-11 Noiembrie, 2022. Chișinău, Moldova, pp. 293-296. ISBN 978-9975-152-48-8.
2. **ИСАКОВА, К.**, КОЧЕМАСОВ, А., НИКА, Д. Фононная инженерия в нанонитях и нанотрубках на основе кремния. In: *Rezumatele ale comunicărilor, Ştiinţele exacte, Ştiinţele ale naturii Conferinţa ştiinţifică naţională cu participare internaţională „Integrare prin Cercetare şi Inovare", dedicată aniversării a 75-a a Universităţii de Stat din Moldova,* 10-11 noiembrie, 2021. Chișinău, Moldova, pp. 194-196. ISBN 978-9975-152-48-8.

3. **ISACOVA, C.**, COCEMASOV, A., NIKA, D., FOMIN, V. Thermal transport in Si/SiO_2 nanoshell nanotubes. In: *CMD2020GEFES, European Physical Society*, 31 August – 4 September, 2020: (online). https://www.cmd2020gefes.eu/_files/_event/_28512/_editorFiles/file/Scientific%20Program_CMD2020GEFES.pdf.
4. **ISACOVA, C.I.**, COCEMASOV, A.I., NIKA, D.L., SCHMIDT, O.G., FOMIN, V.M. Phonon modes and thermal conductivity in Si/SiO_2 multishell nanotubes. In: *DPG Spring Meeting*, 31 March – 05 April, 2019, Regensburg, Germany, DS 10.3.
5. **ISACOVA, C.I.**, COCEMASOV, A.I., NIKA, D.L. Suppression of the thermal flux in Si/Ge and Si/SiO_2 crosssection modulated nanowires. In: *Book of abstracts of the 4th Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC4).* 28−31 August 2017. Chisinau, Moldova, p. 84. ISBN 978-9975-9787-1-2.
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ADNOTARE

Isacova Calina,

teza „Proprietățile electronice și fononice ale nanostructurilor formate din puncte cuantice” / pentru conferirea titlului de doctor în științe fizice, specialitatea 131.04 *Fizica computațională și modelarea proceselor*, elaborată în laboratorul de cercetări științifice „Fizica și ingineria nanomaterialelor „E. Pokatilov” al Universității de Stat din Moldova, or. Chișinău, R. Moldova, în anul 2023.

Structura lucrării: Lucrarea este formată din Introducere, trei capitole, Concluzii generale și Recomandări, Bibliografie din 157 titluri, 145 pagini, 79 figuri, 53 formule și 1 tabel. Rezultatele obținute în teză au fost publicate în 8 articole științifice și au fost prezentate la 32 conferințe științifice internaționale și naționale.

Cuvinte-cheie: suprarețea unidimensională, Hamiltonian multizonal, exciton, fonon, conductibilitate termică.

Scopul și obiectivele: cercetarea influenței parametrilor materiali și geometrici ai suprarețelelor unidimensionale din puncte cuantice (1D-SRPC) Si/SiO_2 și Si/SiC asupra proprietăților electronice, de gol și excitonice; dezvoltarea modelului „face-centred cubic cell” al oscilațiilor rețelei cristaline pentru studierea proprietăților fononice și termoconductibile ale 1D- SRPC Si/Ge și Si/SiO_2, cât și a nanotuburilor multistrat (NTM) Si/SiO_2.

Noutatea științifică și originalitatea: Se arată, că descrierea cantitativă a stărilor excitonice în SRPC cercetate necesită utilizarea hamiltonianului multizonal al golurilor, care permite de a ține cont de amestecarea golurilor grele, ușoare și de tip „split-off”; s-a stabilit faptul, că conductibilitatea termică a 1D-SRPC și NTM cercetate este semnificativ mai joasă decât a nanofirelor corespunzătoare datorită efectului de captare a modelor fononice și împrăștierea fononilor pe suprafețele interioare ale structurilor.

Problema științifică soluționată: au fost teoretic studiate detaliat proprietățile excitonice, fononice și termoconductibile ale 1D-SRPC Si/SiO_2 și Si/SiC, cât și transportul de căldură în NTM Si/SiO_2.

Valoarea teoretică: au fost dezvoltate modelele teoretice ale stărilor excitonice și fononice în 1D-SRPC și NTM.

Valoarea aplicativă a lucrării: implementarea practică a rezultatelor obținute va contribui la apariția unei clase noi de nanomateriale, având perspective promițătoare în aplicațiile optoelectronice, termoelectrice și de izolare termică.

SUMMARY

Isacova Calina, "Exciton and phonon properties in quantum dot nanostructures", Ph. D. thesis in physics, speciality 131.04 *Computational physics and modelling of processes*, was elaborated in "E. Pokatilov laboratory of Physics and Engineering of Nanomaterials", Moldova State University, Chișinău, R. Moldova, 2023.

Work structure. The Thesis consists of an Introduction, 3 Chapters, General conclusions and recommendations, 157 references, 145 pages, 79 figures, 53 equations, and 1 table. The results presented in the work are published in 8 scientific articles and presented at 32 international and national conferences.

Keywords: one-dimensional quantum dot superlattice, multi-band Hamiltonian, exciton, phonon, thermal conductivity

Goals and objectives: the study of material and geometrical parameters' influence on electronic, holes', and excitonic properties in one-dimensional quantum dot superlattice (1D-QDSL) Si/SiO_2 and Si/SiC; development of face-centred cubic cell lattice dynamic model for studying phonon and thermal properties in Si/Ge and Si/SiO_2 1D-QDSL, as well as in Si/SiO_2 multishell nanotube (MNT)

Scientific novelty and originality: it was demonstrated, that three-band Hamiltonian for holes, which takes into account the mixing of the heavy, light, and split-off holes' states, is requires for more accurate quantitative description of exciton states in 1D-QDSL; it was theoretically shown that thermal conductivity of the Si-based 1D-QDSL and Si/SiO_2 MNT is significantly lower than that in corresponding silicon nanowires due to the trapping of phonon modes in nanostructure's segments and phonon scattering at interfaces of the QDSL.

Solved scientific problem: it has been carried out a detailed theoretical study of the exciton, phonon and thermal properties in the Si/Ge, Si/SiC and Si/SiO_2 QDSLs as well as of phonon and thermal properties in the Si/SiO_2 MNTs

Theoretical importance is related to development of the theoretical model of the exciton and phonon states in 1D-QDSLs

Practical significance: practical implementation of the obtained results may lead to the appearance of new nanomaterials promising for optoelectronic, thermoelectric and thermal insulating applications.

АННОТАЦИЯ

Исакова Калина, диссертация «Экситонные и фононные свойства квантоточечных наноструктур» на соискание ученой степени доктора физических наук по специальности 131.04 *Вычислительная физика и моделирование процессов*, выполенная в лаборатории «Физика и инженерия наноматериалов имени Е. Покатилова» Государственного университета Молдовы, г. Кишинев, Р. Молдова, в 2023 году.

Структура работы: Работа состоит из Введения, трех глав, Общих выводов и рекомендаций, Библиографии из 157 названий, 145 страниц, 79 рисунков, 53 формул и 1 таблицы. Полученные результаты опубликованы в 8 научных работах и представлены на 32 международных и национальных конференциях.

Ключевые слова: одномерная сверхрешетка, многозонный гамильтониан, экситон, фононы, теплопроводность

Цели и задачи: исследование влияния материальных и геометрических параметров одномерных квантоточечных сверхрешеток (1D-КТСР) Si/SiO_2 и Si/SiC на электронные, дырочные и экситонные свойства; развитие «face-centred cubic cell» модели колебаний кристаллической решетки для изучения фононных и теплопроводящих свойств одномерных квантоточечных сверхрешеток Si/Ge и Si/SiO_2, а также многослойных нанотрубок (МНТ) Si/SiO_2.

Научная новизна и оригинальность: показано, что для количественного описания экситонных состояний в рассматриваемых 1D-КТСР необходимо использовать многозонный дырочный гамильтониан, который позволяет учесть перемешивание тяжелых, легких и «split-off» дырок; установлено, что теплопроводность 1D-КТСР и МНТ значительно ниже теплопроводности соответствующих нанонитей благодаря эффекту захвата фононных мод в сегментах этих наноструктур и рассеянию фононов на внутренних интерфейсах

Решенная научная задача: проведено подробное теоретическое изучение экситонных, фононных и теплопроводящих свойств 1D-КТСР Si/Ge и Si/SiO_2, а также теплового транспорта в МНТ Si/SiO_2.

Теоретическая значимость: развиты модели экситонных и фононных состояний в 1D-КТСР и МНТ.

Практическая ценность работы: практическое внедрение полученных результатов будет способствовать появлению нового класса наноматериалов перспективных для оптоэлектронных, термоэлектрических и теплоизоляционных применений.

ISACOVA CALINA

EXCITON AND PHONON PROPERTIES IN QUANTUM DOT NANOSTRUCTURES

131.04 - COMPUTATIONAL PHYSICS AND MODELLING OF PROCESSES

Abstract of doctor thesis in physics

Aprobat spre tipar: 20.12.2023	Formatul hârtiei 60x84 1/16
Hârtie ofset. Tipar ofset.	Tiraj 10 ex.
Coli de tipar.: 2,1	Comanda nr. 150/23

Centrul Editorial-Poligrafic al U.S.M.,
str. A. Mateevici 60, MD-2009, Chișinău

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Cu titlu de manuscris
CZU: 539.21

ISACOVA CALINA

PROPRIETĂȚILE EXCITONICE ȘI FONONICE ALE NANOSTRUCTURILOR FORMATE DIN PUNCTE CUANTICE

131.04 FIZICĂ COMPUTAŢIONALĂ ŞI MODELAREA PROCESELOR

Rezumatul tezei de doctor în științe fizice

CHIȘINĂU, 2023