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HIGH-TEMPERATURE SINGLE-ELECTRON TRANSISTORS BASED ON MOLECULES AND SMALL NANOPARTICLES

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Abstract: **The material of the defense of the dissertation for the degree of Doctor of Physical and Mathematical Sciences – the first in Russia doctoral dissertation on molecular singe-electronics is presented. The relevance of the development, creation and research of single-electron transistors with high charge energy and operating temperature for the creation of fundamentally new nanoelectronic devices applicable in wide practice and ensuring breakthrough research in various fields is noted, the necessity of using quantum dots (molecules/nanoparticles) of atomic-molecular scale for this is shown, the formulation of the research problems is formulated, the physical and technological methods of fabrication and analysis used are listed, the main results of the work are presented and their significance for the development of highly sensitive sensing, quantum informatics and quantum metrology is discussed.**

Keywords: **single-electron tunneling, molecules, clusters, nanoparticles, nanostructures, nanoelectronics, molecular electronics**

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July 17, 2021 at the Dissertation Council of the Physics Faculty of Lomonosov Moscow State University Evgeny Sergeevich Soldatov defended his dissertation entitled "High-temperature single-electron transistors based on molecules and small nanoparticles" for the degree of Doctor of Physics and Mathematics.

Tunneling nanosystems with an extremely low capacity based on single molecules and small nanoparticles was **the object** of the study, and the processes of creating such nanostructures, as well as the course and characteristics of tunneling electron transport through them under different experimental conditions was **the subject** of the study.

In general, the work is devoted to the study of the formation of controllable single-electron systems based on single molecules and small nanoparticles, the development and creation on their basis of single-electron transistors with high charge energy and, accordingly, the operating temperature, as well as the study of electron transport in such transistors at high (more than 77 K) temperatures.

Such nanoelements are absolutely necessary for realizing the possibilities of using in wide practice the unique properties of the effect of correlated (single-electron) electron tunneling, allowing the construction of fundamentally new electronic devices and a dramatic (by several orders of magnitude!) improvement in the characteristics of existing devices. Only the use of such elements can increase the operating temperature of devices based on this effect from the typical level of 50-100 mK for traditional elements

to values of 100-300 K, which are acceptable in practice.

This has led to a great and constantly growing interest in the development of methods for creating planar tunneling single-electron elements based on individual molecules, clusters, small nanoparticles, reproducible production of such elements by technological methods already mastered by modern microelectronics, and the study of their characteristics. In addition to the above-mentioned issues of the experimental implementation of such extremely small nanostructures at the level of individual molecules and atoms, this work also solves the problems of a detailed elucidation of the mechanisms of electron transport through these quantum nanoobjects.

The research in this work is focused on the development and creation of key elements for any single-electronic device – single-electron transistors with high values of the charge energy, which determines the quality and usefulness of such transistors, as well as on the study of the characteristics of these nanoelements at the most convenient for practice, but at the same time extremely high for single-electronics temperatures above 77 K. At the same time, a monotonic improvement in their qualitative parameters and an increase in the operating temperature up to room temperature with a decrease in the size of one-electron elements down to the molecular and even to the atomic level is a main peculiarity of single-electron systems.

The creation of nanoelements was carried out by combining two innovative approaches to the formation of nanoelectronic elements:

- the use of single molecules (and/or small nanoparticles) of the required size as a nanoelement base and
- using a scanning tunneling microscope (STM) as a device both for the formation of tunnel nanosystems based on extremely small objects with sizes from 5 to 50 angstroms, and for studying the electrical characteristics and structure of these systems.

As part of the implementation of these approaches and the achievement of the set goal, three key problems were consistently solved, which stand in the creation of single-electron elements applicable in wide practice and determine the content of the specific main tasks of this work:

1. Investigation of the processes of formation of stable nanostructures based on single molecules/nanoparticles and, as a result, the formation of a methodological and technological basis for the creation of the studied nanoelements.
2. Development and creation of tunnel systems based on single molecules or nanoparticles using STM, as well as experimental and theoretical studies of electron transport through such systems, which has proven its correlated nature even at room temperature.
3. Development, manufacture and research of planar molecular one-electron transistors, efficient at high, up to 300 K, temperature.

In the course of solving the first problem, methods were developed for the formation of stable nanostructures on a solid substrate from extremely small molecules, as well as methods for studying the structure and characteristics of the formed nanostructures using STM. At the same time, two approaches to the formation of such nanostructures tolerant to studies by STM were proposed, developed, and implemented based on the creation of mixed Langmuir monolayers with

molecular-scale objects (1--5 nm) that are promising for single-electronics electronics, stable when they are studied in STM.

In the first approach, ready-made molecules, including non-amphiphilic ones, are included in the classical Langmuir monolayers of surfactants. Its development and implementation has shown the possibility of purposefully and reproducibly obtaining on a substrate measurement-stable samples of the required quality with molecular nanostructures of various dimensions: both 0D (single molecules) and regular 1D (chains) and 2D ensembles. This approach also ensured the creation of research prototypes of nanoelectronic elements using STM, both on the basis of single molecules and on the basis of multimolecular 1- and 2-dimensional systems of molecules. It was found that in 2-dimensional systems of molecules of this type, under certain conditions, their self-organization occurs with the formation of quasi-crystalline planar nanostructures with distinguished crystallographic axes.

In the second approach, the formation of nanostructures that are promising for single electronics is carried out just on a sample during its fabrication by synthesizing nanoparticles with the required properties and characteristics directly in mixed Langmuir monolayers at the water-air interface by carrying out chemical reactions and/or physical effects in them during preparation of a monolayer. This made it possible to controllably obtain, due to the discovered effect of anisotropic growth of nanoparticles in a longitudinal magnetic or electric field, both individual magnetic particles with given sizes (from 3–5 nm and above) and shape, and their chains. The constructed theoretical model of the process of such growth showed good agreement between the calculated shape, size of nanoparticles and their growth rate with experimental data. This indicates a key role in the growth of interparticle dipole-dipole interactions, which underlie the model, which determines the observed strong dependence of the shape and size of nanoparticles on the orientation of the applied field.

In addition to such magnetic particles, an improved version of this approach made it possible to control both monolayers with separately lying nanoparticles of noble metals (gold and palladium) with a diameter of 1--2 nm, and organized composite polymer films with 1D and 2D ensembles of such in situ synthesized nanoparticles. It also made it possible to obtain polymer films with 1D and 2D ensembles of ready-made cluster molecules embedded in a planar monolayer monomolecular dielectric matrix. The sizes of the obtained nanoparticles satisfy the conditions for the realization of the effects of single-electron tunneling at room temperature, which makes it possible to create in this way reliable and stable single-electron nanosystems.

The technological base created in the course of the first key task made it possible, while performing the second key task of the work, to implement a method for creating single-electron elements based on single cluster molecules using STM and for the first time experimentally show the decisive role of the ligand shell of a molecule/nanoparticle in the transformation of the system "STMtip-cluster-substrate" from one-junction to two-junction and, accordingly, in the implementation of the single-electron mode of tunneling electron transport.

With the help of this technique, a single-electron transistor based on a single cluster molecule has been realized for the first time

at room temperature. The experimentally studied main characteristics of the formed transistors showed, despite the significant difference in the structure and electronic spectrum of the studied cluster molecules, the realization in all such nanosystems of the mode of correlated electron tunneling with record high values of the Coulomb blockade of tunneling (more than 500 mV) and charge energy (~250 meV). In these systems, a close to 100% modulation of the tunneling current by the control voltage and a charge sensitivity typical of single-electron systems no worse than ~10^{-3} e/$Hz^{1/2}$ were obtained. This served as convincing evidence of the correlated nature of the tunneling electron transport in the fabricated molecular systems even at room temperature.

Within the framework of a theoretical study of electron transport through such systems, an approach was proposed and developed to determine and calculate the main parameter for single-electronics – the electric capacitance of extremely small, up to single atoms, quantum objects, and a formula was obtained for calculating the intrinsic effective capacitance of single isolated atomic-scale nanoobjects by the values their ionization potentials and electron affinity. An analysis of its dependence on size, shape and topology showed that with a sufficiently large number of atoms, this dependence is qualitatively similar to the classical case – the capacitance is proportional to the size of the object, and the functional dependence of the intrinsic capacitance of such objects on the number of atoms in them is determined by the dimension of these objects.

Taking these results into account, a theoretical model of tunneling transport through molecular single-electron nanoelements was proposed and developed, taking into account the quantum discrete nature of the energy spectrum of their basis - a single quantum dot (molecule, small nanoparticle). It also took into account the effects of electron relaxation in a molecule/quantum dot for the first time. On the basis of the developed model, a computer simulation of the characteristics of electron transport of manufactured molecular single-electron nanoelements for cases of extremely fast and extremely slow (compared to the rate of electron tunneling) energy relaxation of electrons in a molecule is carried out. The proposed and implemented efficient scheme for calculating the canonical distribution of electrons in a molecule by the recursive method provided its acceleration by several orders of magnitude in comparison with direct enumeration of combinations and made it possible to simulate and study the I–V characteristics of molecular transistors using conventional laboratory computing power.

Comparison of theoretical and experimental I–V characteristics of molecular single-electron transistors showed their best agreement precisely at slow relaxation of electrons in the molecule. This allows us to conclude that the mode of operation of molecular single-electron transistors fabricated and investigated using STM is correlated tunneling of electrons with their slow energy relaxation in the molecule.

On the whole, this leads to the conclusion that small cluster molecules can serve as a reliable basis for the creation of single-electron nanosystems capable of operating at room temperature as elements of operating fundamentally new nanoelectronic devices. In this case, the greatest progress is provided by the use of the created molecular single-electron transistors for the construction

on their basis of supersensitive charge/field sensors, computer memory elements, fundamental standards (for example, a current standard), qubits, cells of a quantum cellular automaton.

In the course of work on solving the third key problem of this work, in order to ensure a wide and effective practical implementation of the above prospects, which is possible only for planar molecular devices in an integrated design, a method was developed for the manufacture of planar electrodes of a molecular transistor by controlled narrowing of the nanowire formed by electron beam lithography using the effect electromigration.

This technique, due to the use of the created original algorithm for carrying out the electromigration process, provided the production of electrodes with a distance between them required for high-temperature single-electronics electronics of 1.5÷5 nm with a yield of more than 90% usable at a high leakage resistance (R > 300 GΩ). These parameters indicate the suitability of such electrodes for creating molecular transistors on their basis.

The developed method of controlled embedding using the dielectrophoresis effect of small (2-4 nm) gold nanoparticles into the fabricated nanogaps between metal electrodes made it possible to ensure the targeting of such embedding and to obtain a high (~20%) yield of suitable samples, which is 3-4 times higher than for the traditional method of drying a solution with nanoparticles.

Measurements of electron transport through such molecular transistors showed a single-electron form of their stability diagrams at T = 77 K, demonstrated high (more than 150 meV) values of the charge energy of the manufactured single-electron transistors. An oscillating (single-electron) form of the characteristics of control of electronic transport through them at temperatures of 77 K÷220 K was recorded, and the correlated nature of electron transport in these nanoelements in a wider temperature range of 77 K÷300 K was shown.

Thus, the studies carried out made it possible to obtain the following main new results:

A method for the formation of mixed Langmuir monomolecular layers with a controlled surface density of non-amphiphilic molecules rigidly fixed on the substrate, providing the possibility of non-destructive reproducible study in STM of the structural and electrical characteristics of nanosystems based on such single molecules, has been proposed, developed, and for the first time implemented.

A method for the controlled formation of stable nanostructures on a solid substrate from single gold nanoparticles with a diameter of 1–3 nm promising for high-temperature single-electronics was proposed and implemented for the first time by carrying out chemical reactions of metal reduction directly in a monolayer; self-organization of such nanoparticles into 1-dimensional chains was found. The correlated nature of electron transport through double-junction tunnel systems based on such single nanoparticles at room temperature is shown.

An original method for the controlled formation on a solid substrate of stable 0-dimensional, 1-dimensional and 2-dimensional nanostructures from small (3÷5 nm) magnetic nanoparticles by means of direct decomposition of iron pentacarbonyl and dicobaltoctacarbonyl just in the monolayer under the action of ultraviolet radiation with subsequent aggregation is proposed and implemented.

The anisotropic growth of forming magnetic nanoparticles in a longitudinal magnetic or electric field has been discovered and theoretically explained, which makes it possible to controllably obtain magnetic particles of the sizes and shapes required for the formation of nanoelements.

The effect of self-organization of molecules of the thallium derivative of carborane in mixed monomolecular Langmuir films with the formation of two-dimensional quasi-crystalline nanostructures with lattice parameters close to the corresponding parameters of a three-dimensional molecular crystal of this substance is found.

For the first time experimentally demonstrated the fundamental importance for single-electronics of the presence of a ligand shell in a nanoparticle or molecule for the implementation of the single-electron tunneling regime and the correlation of the size of the Coulomb blockade of electron tunneling with the size of the molecule/nanoparticle. At the same time, the possibility of purposefully changing the structure and characteristics of an already finished nanosystem directly on a substrate was demonstrated.

For the first time, a prototype of a molecular single-electron transistor operating at room (300 K) temperature was created and studied, in which a nanosystem with a charge energy of up to 250 meV was created, which provided control of the tunneling current of a single-electron transistor based on a single molecule, and such control was experimentally demonstrated at room temperature.

The proposed theoretical model of correlated electron tunneling in molecular systems taking into account the effects of electron relaxation in a molecule/quantum dot made it possible for the first time to prove the slowness of electron relaxation in such systems in comparison with the tunneling rate, in contrast to traditional single-electron metallic systems, and to ensure agreement between experimental and theoretical data. obtained for molecular transistors.

The proposed and developed method for determining the electrical capacity of quantum objects of atomic-molecular scale showed that the value of the intrinsic capacitance of objects of molecular and atomic scale is directly and closely related to their chemical and spectral properties, with the structure of the electron shells of atoms and the topology of molecules. A formula is obtained for calculating its value from the values of the ionization potential and the electron affinity of molecules and atoms. This allows, when designing and analyzing the operation of practical single-electron devices, to calculate the parameters of quantum nanoelements using a well-developed apparatus of classical electronic circuitry without cumbersome consideration and taking into account the specific quantum properties of such objects, which greatly facilitates the widespread practical implementation of single-electron atomic-molecular devices.

An original technique has been developed for the reproducible formation at room temperature of a key element of molecular single-electron transistors in a planar thin-film design - nanogaps between transistor electrodes with a width of less than 4 nm, a leakage resistance of more than 300 G with a high (90–95%) yield of suitable samples. As a result, this ensured, in the manufacture of planar molecular single-electron transistors, the realization of the main advantage of using molecules/nanoparticles in them – the achievement of a high charge energy and,

accordingly, the operating temperature of such transistors.

For the first time, the quantum dynamics of changes in the conductivity of quantum wires from gold atoms formed at the final stage of the electromigration process was discovered and studied at room temperature. These changes occur during the restructuring of quantum wires due to relaxation of mechanical stresses in them, which ultimately leads to rupture of quantum wires with the formation of nanogaps less than 4 nm wide.

A technique was developed and implemented for the targeted embedding of single small (2-4 nm) gold nanoparticles into the formed nanogaps between the tunnel electrodes of the transistor, which provided the formation of high-temperature molecular single-electron transistors with a yield of suitable samples of about 20%.

For the first time, planar single-electron transistors with a charge energy of up to 150 meV, in which correlated tunneling electron transport is realized at temperatures up to 300 K inclusive, have been manufactured and investigated at temperatures of 77–300 K.

Thus, the main result of this work was the creation of molecular single-electron transistors in a planar design with a high (~200 meV) charge energy and parameters that are the best achieved to date for planar single-electron elements. This opens up a wide window of new possibilities for the actual design, manufacture and use of such elements at high operating temperatures, up to room temperature, and, therefore, makes it possible to create on their basis those applicable in a wide practice fundamentally new nanoelectronic devices with unique characteristics and capabilities necessary to solve the most pressing problems in various fields:

- simple/affordable and fast DNA sequencing – in biology and medicine;
- creation of quantum computers, quantum cellular automata, neural networks – in quantum informatics;
- creation of a quantum standard for a unit of electric current and closure, finally, a "metrological triangle" of quantum standards – «Voltage (Josephson effect) – Current (single-electronics) – Resistance (quantum Hall effect)» – in quantum metrology.

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