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Single Electron Transistor Based on Endohedral Metallofullerenes Me@C_{60} (Me = Li, Na, K)

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In this work, within the framework of the density functional theory, the transport properties of a single-electron transistor (SET) based on metallofullerenes Me@C_{60} (Me = Li, Na, K) were investigated by simulation. The optimization of Li@C_{60}, Na@C_{60}, K@C_{60} molecules was carried out using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and the generalized gradient approximation (GGA), which allows the most accurate description of such structures. Electrostatic difference potential, molecular energy spectrum, and total energy of a SET based on Me@C_{60} were calculated. It was found that a SET based on K@C_{60} is more stable than other considered SETs based on C_{60}, Li@C_{60}, Na@C_{60}. The dependences of the total energy of molecules Me@C_{60} (Me = Li, Na, K) on their total charge are determined, as well as the dependences of the total energy on the gate voltage Me@C_{60}-SET. Due to the instability of the state of small molecules with additional electrons of more than two, during the simulation, the values of – 2, – 1, 0, 1, 2 were chosen as the total electric charges for each molecule. It is shown that the energy of a negatively charged metallofullerene under consideration is lower than that of a neutral one, and vice versa, the energy of a positively charged metallofullerene is greater than that of a neutral one. It was found that at negative transistor gate voltages, positive charge states (+ 1, + 2) are more stable compared to negative charge states (– 1, – 2) due to a shift in the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) with a change in gate voltage. The stability diagrams of SETs based on C_{60}, Me@C_{60} were analyzed, and it was also shown that the area of the Coulomb diamond SET on the stability diagram depends on the radius of the encapsulated atom. The results obtained can be useful in the calculation of new types of SETs based on metallofullerenes.

Keywords: Single electron transistor, Fullerene, Endohedral fullerene, Charge stability diagram, Coulomb diamond, Total energy.

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1. INTRODUCTION

After the discovery of one of the allotropic forms of carbon – fullerene, intensive studies of its physicochemical properties began to solve a wide range of applied problems [1-3]. Fullerene has a structure consisting of carbon atoms, which are located at the vertices of regular hexagons and pentagons, covering the surface of a sphere or spheroid. The unusual electrophysical properties of fullerenes makes them a very promising material for electronics. For example, crystalline fullerenes are the semiconductors with a band gap of 1.2-1.9 eV [4, 5], and C_{60} crystals doped with alkali metal atoms have metallic conductivity and go into a superconducting state at temperatures of 19-33 K, depending on the type of alkali metal [6-8]. Among fullerenes, the most common and chemically stable is the C_{60} molecule, representing in the form of regular truncated icosahedron. The C_{60} molecule has extremely high symmetry and due to these positions of all carbon atoms in it are completely equivalent. Fullerenes due to structural resistance to charge changes are one of the promising nanomaterials that are used to create a single electron transistor (SET) [9, 10]. For example, in [11], the influence of electronic vibrational modes on the process of correlated electron tunneling in SET based on two covalently linked C_{70} fullerene molecules was studied, and in [12], combined method was used to study the electron transport of SET, taking into account the combination of electrostatic control of Coulomb Island from fullerene C_{60} with a mechanically controlled nanojunction. At present, the Non-Equilibrium Green's Functions (NEGF) method is widely used to describe the transport characteristics of a molecular transistor (see e.g. [13-15]). In [16], within the framework of the extended Hückel method in combination with NEGF, the transport properties of a fullerene molecular transistor were calculated and the influence of electrode materials on the transport properties of such a transistor was shown. Recently, molecular clusters from fullerenes have been of particular interest for creating SETs [17]. It is known that one of the unique properties of fullerene structures is to enclose one or more atoms inside their carbon skeleton. Such structures are commonly called endohedral fullerenes [18]. The electronic properties of endohedral fullerenes substantially depend on the properties of the encapsulated atom, which allows to control them by selecting the necessary by properties encapsulated atom.

In this work the results of a model study of a single-electron transistor based on endohedral metallofullerenes Me@C_{60} (Me = Li, Na, K) were presented.

2. COMPUTATIONAL DETAILS

The geometry of the studied SET models is presented in Fig. 1. Metallofullerenes Me@C_{60} (Me = Li, Na, K) protrude as the central island of SET. The areas Source, Drain, Gate SET are formed of gold. The width of the electrodes is 14 Å. Other geometric dimensions of SET are shown in detail in Fig. 1.

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The optimization procedure for the geometric structures of the metallofullerenes under consideration was carried out in the framework of the density functional theory (DFT), and the generalized gradient approximation GGA-PBE [19] was used as the exchange-correlation functional, which allows the most accurate description of such structures. To calculate the electrostatic difference potential, molecular energy spectrum, and total energy of fullerenes, DFT in the local density approximation (LDA) was applied. During the simulation, the values – 2, – 1, 0, 1, 2 are selected as the total electric charges for each molecule. The choice of precisely these values of charges is due to the instability of states of small molecules with additional electrons of more than two.

As is known, the lower the charge energy, the easier and faster the system to overcome the Coulomb blockade. To calculate the charging energy and affinity of metallofullerenes, we calculate the total energy of the charged system. To do this, we determine the total energy of the system E^q with charge q:

$$E^I = E(N) - E(N-1) = E^0 - E^{+1}, \quad (1)$$

where E^0 is the energy of the neutral system with N electrons and E^{+1} is the energy of the positive ion with $N-1$ electrons. The affinity energy is given by

$$E^A = E(N) - E(N+1) = E^0 - E^{-1}. \quad (2)$$

Quantum chemical calculations to optimize the geometry of nanodevices and their physical parameters were performed using the Atomistix ToolKit with Virtual NanoLab software package using the DFT method [20].

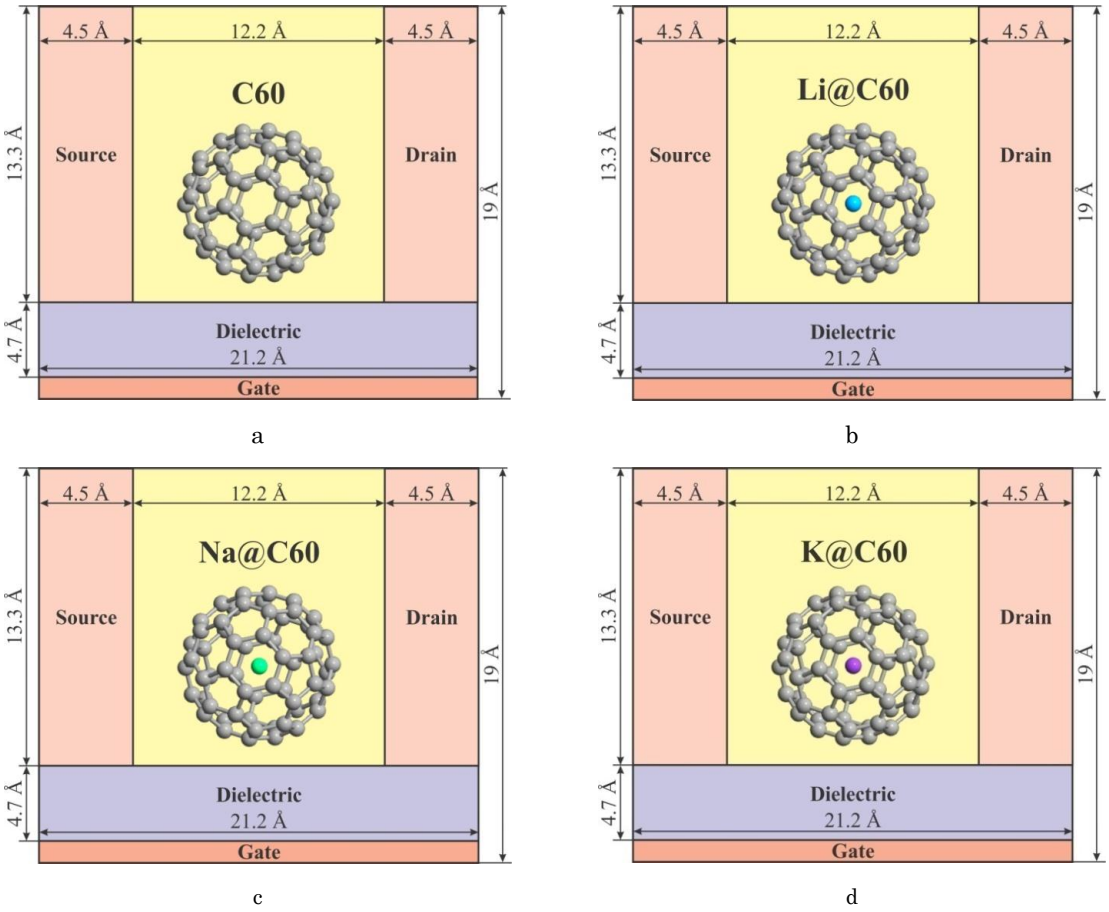

Fig. 1 – Geometry of SETs based on endohedral metallofullerenes: a) C_{60}; b) Li@C_{60}; c) Na@C_{60}; d) K@C_{60}

3. RESULTS AND DISCUSSION

Fig. 2 shows the calculated values of the total energy of fullerene molecules depending on the charge state. Large energy values (from – 9615 eV to – 9435 eV) are explained by the fact that the total energy of the molecule is represented as the sum of the energies of electrons and nuclei; therefore, it is much higher than the energy of individual single-electron levels of the molecule.

As can be seen from Fig. 2, in fullerene and metallofullerenes placed in a nanogap, the negative ion of the molecule is more stable. The energy of a negatively charged fullerene is lower than that of a neutral one, and vice versa, the energy of a positively charged fullerene is greater than that of a relatively neutral one. With a neutral charge, fullerene has a total energy of – 9449.18 eV, and metallofullerenes Li@C_{60}, Na@C_{60}, K@C_{60} have – 9460.79 eV, – 9459.1 eV, – 9611.01 eV, respectively. Among the considered models of SETs based on metallofullerenes, a more stable system is SET based on K@C_{60}.

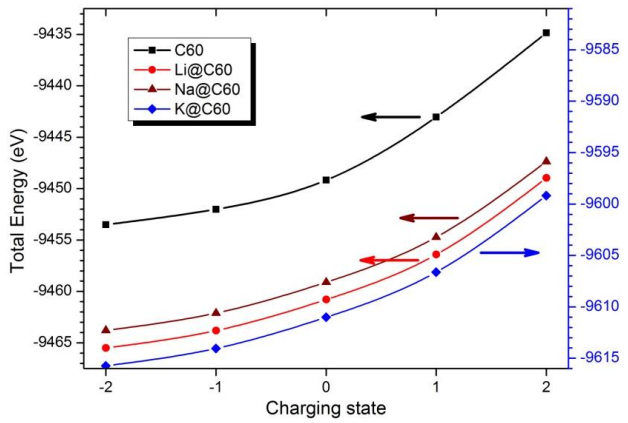

Fig. 2 – Dependences of the total energy of C_{60} and Me@C_{60} (Me = Li, Na, K) molecules on their total charge

Fig. 3 shows the dependences of the total energy on the gate voltage for different states of charge. It is known that if the total energy of a certain state of charge is the lowest at a specific gate voltage, this means that the molecule is most stable in this state of charge corresponding to this voltage (see e.g. [21]). In general, when a positive gate bias voltage increases, negative-charge states (i.e. – 1, – 2) show a significant decrease in the total energy, making them more stable with positive gate voltages.

However, at negative gate voltages, positive charge states (i.e., + 1, + 2) are more stable than other charge states due to a shift in the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels with the gate voltage. When a positive gate voltage is applied, the LUMO level shifts below the Fermi level of the electrode and subsequently attracts the electron, which is responsible for the negative charge of the molecular island, while when the gate voltage is negative, the HOMO level shifts above the Fermi level of the electrode as a result of the electron escaping from the island and charging it positively. SETs based on the reviewed endofullerenes are more stable than C_{60}-SET.

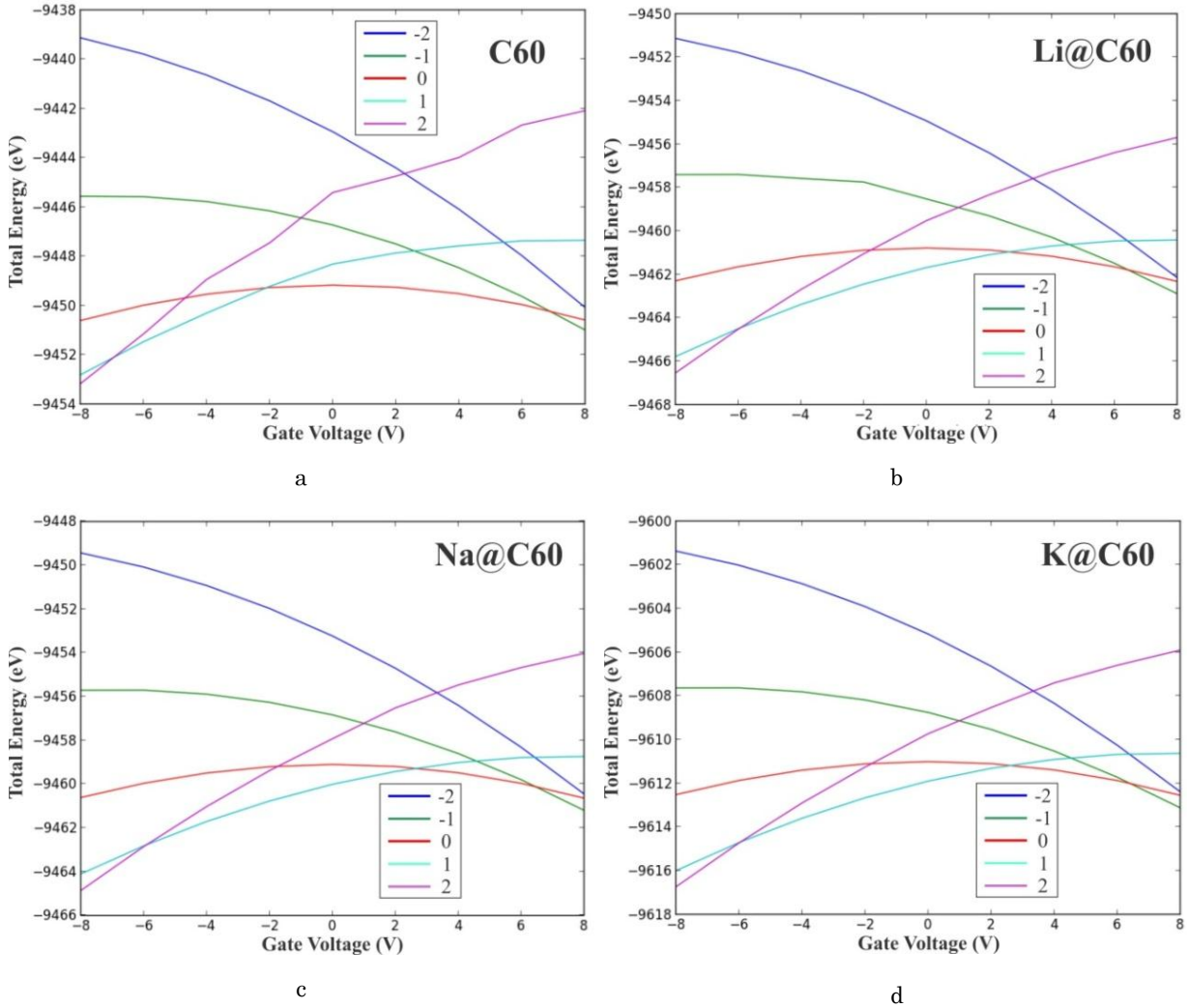

Fig. 3 – Dependence of the total energy on gate voltage for SET based on: a) C_{60}, b) Li@C_{60}, c) Na@C_{60}, d) K@C_{60}. Differently charged states of the molecule are shown by different colored curves: blue (– 2), green (– 1), red (0), turquoise (+ 1), and violet (+ 2)

It is known that charge transport in SET occurs when it overcomes the Coulomb blockade, therefore, sufficient charge energy can be supplied to overcome the Coulomb blockade by adjusting the gate potential and the source-drain. For the given gate and source-drain bias values, the number of molecular energy lev-

els inside the bias window is given by color codes in Fig. 4a-d. As can be seen from the charge stability diagram, SET based on fullerene and metallofullerenes shown in Fig. 1a-d, at zero voltage, the gate bias, and source-drain bias is not possible since the SET operating point is inside the Coulomb diamond (the dark blue region indicated by the number 0), where there is no energy level to support electron transport.

Pure fullerene conducts electric current more efficiently when the shutter is negatively shifted compared to the case when it is positively shifted, i.e. to transfer the C_{60}-SET from the OFF state to the ON state, either $V_{G\min} = -2.119$ V or $V_{G\max} = 6.887$ V must be set (see Table 1). To open SET (switching from the OFF state to the ON state) based on metallofullerenes Li@C_{60}, Na@C_{60}, K@C_{60}, a small positive bias voltage $V_G \sim 2.6$-2.7 V is sufficient in comparison with the C_{60}-SET.

The ranges of the Coulomb blockade associated with each pendant diamond, as well as their areas extracted from Fig. 4, are presented in Table 1, as was done in [22]. A comparative study of Table 1 shows that the area of the center diamond of the Coulomb blockade of K@C_{60} molecule is lower than other molecules.

From Fig. 4 and Table 1 it is clear that the area of Coulomb diamond Me@C_{60}-SET in the stability diagram depends on the radius of the encapsulated atom: the larger the radius of the atom, the smaller the area of Coulomb diamond. These results can be useful in the construction of SET since a decrease in the area of the Coulomb diamond in the stability diagram can lead to smaller fluctuations, therefore, the current fluctuations as a limiter of the SET trigger are reduced and, therefore, SET can operate at higher speeds.

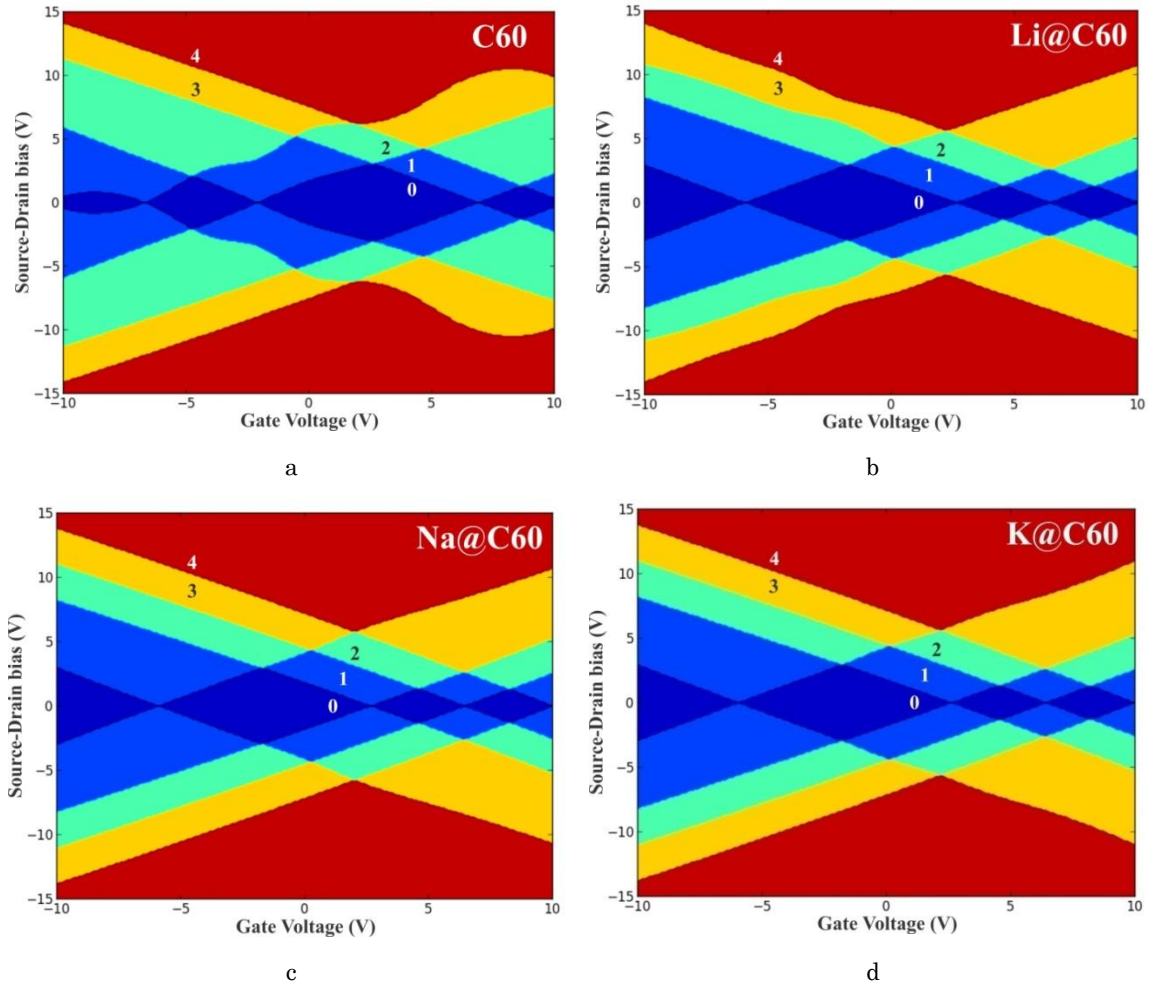

Fig. 4 – Charge stability diagrams for C_{60}- (a), Li@C_{60}- (b), Na@C_{60}- (c), and K@C_{60}-based SETs (d). The number of charge states in the bias window for given bias potentials is given by the specific color. The color map is: blue (0), light blue (1), green (2), yellow (3), and red (4)

Table 1 – The main parameters extracted from the central Coulomb diamond from the stability diagrams presented in Fig. 4

	$V_{SD\min}$	$V_{SD\max}$	ΔV_{SD}	$V_{G\min}$	$V_{G\max}$	ΔV_G	Diamond area
C_{60}	– 3.058	3.078	6.136	– 2.119	6.887	9.006	27.63
Li@C_{60}	– 2.952	2.971	5.923	– 5.912	2.66	8.572	25.986
Na@C_{60}	– 2.929	2.968	5.897	– 5.914	2.715	8.629	25.443
K@C_{60}	– 2.966	2.968	5.934	– 5.965	2.597	8.562	25.403

4. CONCLUSIONS

Thus, in this work, within the framework of the DFT, the geometric structures of Me@C_{60} metallofullerenes (Me = Li, Na, K) were optimized and electrostatic difference potential, molecular energy spectrum, and total energy of SET were calculated based on them. It was found that the most stable system among the reviewed Me@C_{60} is K@C_{60}-SET. The dependences of the total energy of Me@C_{60} molecules (Me = Li, Na, K) on their total charge, total energy on the gate voltage Me@C_{60}-SET, and the stability diagrams C_{60}-, Me@C_{60}-SETs are determined. It is shown that the area of the Coulomb diamond SET in the stability diagram depends on the radius of the encapsulated atom. These results may be useful in the construction of SET.

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Одноелектронний транзистор на основі металофуленів Me@C_{60} (Me = Li, Na, K)

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У роботі в рамках теорії функціональної щільності за допомогою моделювання досліджено транспортні властивості одноелектронного транзистора (SET) на основі металофуленів Me@C_{60} (Me = Li, Na, K). Оптимізація молекул Li@C_{60}, Na@C_{60}, K@C_{60} проводилася використовуючи обмінно-кореляційний функціонал Perdew-Burke-Ernzerhof (PBE) та узагальнене наближення градієнта (GGA), що дозволило найбільш точно описати подібні структури. Розраховано електростатичний різницевий потенціал, спектр молекулярної енергії та повну енергію SET на основі Me@C_{60}. Було встановлено, що SET на основі K@C_{60} є більш стійким, ніж інші розглянуті SET на основі C_{60}, Li@C_{60}, Na@C_{60}. Визначаються залежності повної енергії молекул Me@C_{60} (Me = Li, Na, K) від їх повного заряду, а також залежності повної енергії від напруги затвора Me@C_{60}-SET. Через нестабільність стану малих молекул з додатковими електронами більше двох, під час моделювання величини – 2, – 1, 0, 1, 2 були обрані як повні електричні заряди для кожної молекули. Показано, що енергія негативно зарядженого розглянутого металофулерена нижча, ніж енергія нейтрального, і навпаки, енергія позитивно зарядженого металофулерена більша, ніж енергія нейтрального. Було виявлено, що при негативних напругах затвора транзистора стани позитивного заряду (+ 1, + 2) є більш стійкими порівняно із станами негативного заряду (– 1, – 2) через зміщення HOMO (вища заповнена молекулярна орбіталь) та LUMO (нижча незайнята молекулярна орбіталь) зі зміною напруги затвора. Діаграми стійкості SET на основі C_{60}, Me@C_{60} були проаналізовані. Також було показано, що площа SET на основі кулонівського діаманта на діаграмі стійкості залежить від радіуса інкапсульованого атома. Отримані результати можуть бути корисними для розрахунку нових типів SET на основі металофуленів.

Ключові слова: Одноелектронний транзистор, Фулерен, Діаграма стійкості заряду, Кулонівський діамант, Повна енергія.