On theory of single-molecule transistor

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Abstract. The results of the study on single-molecule transistor are mainly investigated in this paper. The structure of constructed single-molecule transistor is similar to a conventional MOSFET. The conductive channel of the transistors is a single-molecule of halogenated benzene derivatives. The chemical simulation software CAChe was used to design and implement for the essential parameter of the molecules utilized as the conductive channel. The GUI of Matlab has been built to design its graphical interface, calculate and plot the output I-V characteristic curves for the transistor. The influence of temperature, length and width of the conductive channel, and gate voltage is considered. As a result, the simulated curves are similar to the traditional MOSFET’s. The operating temperature range of the transistors is wider compared with silicon semiconductors. The supply voltage for transistors is only about 1 V. The size of transistors in this research is several nanometers.

Keywords: Single-molecule transistor, benzene ring, nanotransistor.

1. Introduction
There are many studies on molecular transistors which exhibit structure and properties similar to conventional MOSFET but much smaller in size [1-5]. In several research papers the U_{DS} voltage on I-V curve of molecular transistor is reported to be as high as 40 V [6] and even 100 V [7]. This paper presents the results of research on molecular transistors which have the structures like traditional MOSFET’s in shape, but the conductive channel is made from commercial chemicals, such as 1,4-dihalo-benzenes (1,4-C_6H_4X_2, with X: F, Cl, Br, and I).

Regarding the structure of molecules, every disubstituted benzene ring falls into three isomers, namely 1,2-; 1,3-; and 1,4-isomer). Only 1,4-isomer is chosen due to the suitable symmetrical contact to drain (D) and source (S) electrode of MOSFET structure.

The chemical simulation software CAChe is applied to design molecules used for conductive channel and to determine the parameters for I_{DS} current computation and draw I-V curve. To evaluate the applicability of transistors in practical purposes, investigation of the effect of temperature to I-V curve is needed. The dimension of molecules used for conductive channel is computed via limitation of Van der Waals force. The effect of dimension quantization to I-V curve is also considered. Every molecule which has one benzene ring of 1,4 associated with two halogen atoms is completely the same. However, when using molecules as a conductive channel, the electrical characteristic may be different due to the non-identical size. The above modification in parameters of molecule is under investigation via a Matlab GUI interface.

2. Theory
Figure 1 shows the configuration outline of a transistor, which has the electrode symbols like electrodes of an insulated-gate field-effect transistor (MOSFET).
The conductive channel is the molecules of 1,4-dihalo-benzenes (1,4-C_6H_4X_2, with X: F, Cl, Br, and I). The simulation results in CACHe show that all atoms of above molecules are coplanar. Therefore, the selected G electrode has a rectangular area and was opposite to the plane of the molecules to increase the control effect of the voltage $V_G$. The length L and the width W of the molecule calculated on the surface of the Van der Waals force were considered to be the dimension of the electrode G. Every halogen atom has a single bond with carbon atom in the benzene ring and three double bonds with three Gold atoms at the electrodes.

A molecular channel must have an energy spectrum which is separated into three bands at the beginning state. The valence band of an inorganic semiconductor corresponds to the highest occupied molecular orbital (HOMO), whilst the lowest unoccupied molecular orbital (LUMO) represents the conduction band (the difference between the energy levels of the HOMO and LUMO). The band gap energy is wide enough so that no electron receives thermal effect.

Considering the case of the transistor with the structure as in figure 1a, the beginning energy level is distributed so that Fermi level is in the middle of the band gap.

The supply voltage $V_D \neq 0$ leads to the electrochemical potential difference $\mu_1 - \mu_2 = qV_D$ between two electrodes. The gate voltage $U_G \neq 0$ causes the conduction band or the valence band of a molecular channel, and then the current $I_{DS}$ of the external circuit is created.

Contact 1 (S-Channel) would like to see $f_1(\varepsilon)$ electrons, while contact 2 (D-Channel) would like to see $f_2(\varepsilon)$ electrons occupying the state, where $f_1$ and $f_2$ are the source and drain Fermi functions, respectively. The average number of electrons $N$ at steady state will be some number intermediate between $f_1(\varepsilon)$ and $f_2(\varepsilon)$. The steady-state current per spin is determined by formula

$$I = \frac{q}{\hbar} \frac{\gamma_1 \gamma_2}{\gamma_1 + \gamma_2} \left[ f_1(\varepsilon) - f_2(\varepsilon) \right].$$

We can interpret the rate constants $\gamma_1 / \hbar$ and $\gamma_2 / \hbar$ as the rates at which an electron placed initially in the level $\varepsilon$ will be escaped into the S and D contacts, respectively. In principle, these
quantities, $\gamma_1$ and $\gamma_2$, which have a measurement unit of Joule energy, could be measured experimentally [9]. Hence, only energy levels between the electrochemical potentials of $\mu_1$ and $\mu_2$, which have $f_1(\epsilon) \neq f_2(\epsilon)$, are responsible for the creation process of $I_{DS}$.

In the conductive channel, the energy spectrum is expanded to a band with density of state (DOS) $D(E)$. For both spins over the energy level of $\epsilon$ we have

$$D_{\gamma}(E) = 2\gamma \pi \left[ (E - \epsilon)^3 + (\gamma/2)^3 \right],$$

where $\gamma = \gamma_1 + \gamma_2$. From studying a molecular channel with a defined size, we have: $D(E) = m_{WL} / \pi \hbar^2 \nu(E - E_C)$ and $\gamma_1 = \gamma_2 = \hbar \nu_L / L$ [9]. With respect to the electrical aspect, we can see the molecular channel like a point and the capacitive circuit is showed in figure 1b. So its potential energy is given by the sum of the Laplace potential $U_L$ and an additional term proportional to the change in the number of electrons

$$U = U_L + \frac{q^2}{C_L} \Delta N. \tag{3}$$

The number of electrons $N$ and the current $I$ show the energy level with extended effect [9].

$$N = \int_{-\infty}^{\infty} dE D_{\gamma}(E - U) \frac{\gamma_1 f_1(E) + \gamma_2 f_2(E)}{\gamma_1 + \gamma_2}, \tag{4}$$

$$I = \frac{q}{\hbar} \int_{-\infty}^{\infty} dE D_{\gamma}(E - U) \frac{\gamma_1 \gamma_2}{\gamma_1 + \gamma_2} \left[ f_1(E) - f_2(E) \right]. \tag{5}$$

The self-consistent field (SCF) method of two expressions in a loop is applied for the calculation. If we know the number of energy levels in the regions, we can calculate the total current through the molecular conductive channel.

**Figure 3.** Algorithm diagram flow for plotting $I_{DS}$.  

![Algorithm Diagram](image)
Figure 3 represents the diagram algorithm with a self-compatible method for plotting $I_{DS}$ in Matlab [10]. The conditions can be applied for this algorithm is:

- The size of the molecules (according to Van der Waals force) has to be able to be defined, and this value is almost considered as the channel size of transistors; it is also the size of the capacitive side $C_G$ in an equivalent circuit shown in figure 1b.
- The Van der Waals surface of molecules is almost smooth (like the surface of a dish). It can be combined with opposite capacitive side G to form a capacitor $C_G$ controlling the molecules in the channel.
- The number of energy levels in each band and the level density of conductive band which is a factor of generative activities of current $I_{DS}$ must be able to calculate.
- The energy level density of conduction band is small enough to satisfy conditions for this application of self-consistent field (SCF) method.

3. Results and discussion

3.1. The parameters of molecules used to form conductive channel of transistors

The CAChe software was used to simulate and define the parameters of molecules. The CAChe software can be used to design the molecules and optimize the structure, examine the electron bonds, measure the size of the molecule according to Van der Waals force, calculate the energy level and also the density of energy levels in the band. These are necessary parameters to apply to a loop algorithm with a self-compatible method for calculating and plotting output characteristic curve of $I_{DS}$.

![Figure 4](image)

**Figure 4.** Molecules used for forming conductive channel of transistor in this research.

| Orbits | Eigenvalues (eV) |
|--------|------------------|
|        | 1,4_C6H4S2 | 1,4_C6H4O2 | 1,4_C6H4Cl2 | 1,4_C6H4F2 | 1,4_C6H4Br2 | 1,4_C6H4I2 |
| 26     | 1.282      | 2.086      | 2.292      | 2.113      | 2.216      | 2.361      |
| 25     | 0.157      | 1.890      | 1.329      | 2.060      | -0.182     | -0.064     |
| 24     | 0.135      | 1.718      | 1.294      | 2.042      | -0.202     | -0.140     |
| 23     | -0.178     | 0.873      | -0.052     | -0.295     | -0.295     | -0.484     |
| 22     | -1.088     | 0.027      | LUMO -0.243| LUMO -0.332| LUMO -0.318| LUMO -0.653|
| 21     | LUMO -3.291| LUMO -1.707| HOMO -9.235| HOMO -9.870| HOMO -9.869| HOMO -8.947|
| 20     | HOMO -9.489| HOMO -10.922| -10.236    | -10.492    | -10.314    | -9.470     |
| 19     | -9.522     | -11.162    | -10.661    | -12.876    | -11.319    | -9.500     |
| 18     | -9.862     | -11.453    | -10.680    | -13.276    | -11.322    | -9.544     |
| 17     | -11.418    | -11.684    | -10.716    | -14.837    | -11.376    | -10.166    |
| 16     | -12.754    | -14.194    | -12.155    | -15.007    | -12.303    | -11.105    |
| Band gap | 6.198      | 9.215      | 8.992      | 9.538      | 9.551      | 8.294      |

Figure 4 shows the results for designing the molecules, optimizing the structure, and examining the double bonds. Atoms forming the molecules are on the surface. Each atom in the halogen group at two ends of the molecule remains six free electrons. When putting the molecule on the conductive channel,
three double bondings with three Gold atoms at electrodes will be created. Mechanically, three couples of bonds at the same side, together with symmetric characteristics of molecules will be excellent conditions for good location ability in the channel.

The levels of LUMO, HOMO and band gaps were calculated by using chemical simulation software. The calculated results of ten basic energy levels of molecules are shown in table 1 and figure 5.

The first band must have enough numbers of energy levels to obtain the saturation value of current responding to supply voltage less than 1 V. If the band contains many energy levels the saturation current at U_DS will be large. However, according to the theoretical research [6, 7], nanotransistors with required large U_DS are not feasible due the penetrating electric field depletes. In order that the curve at saturation point lasts, the energy levels in the next conduction band must be far away from the present one. If this condition is not satisfied, the characteristic curve will be in stair shape. Table 1 also introduces the data of molecules of Dithio-p-benzoquinone (C_6H_4S_2) and p-Benzoquinone (C_6H_4O_2). The simulated and calculated results for these molecules show that levels of HOMO energy band on valence band satisfies the conditions to become conductive channels of transistors with negative polarization (U_G < 0). Calculation and sketch of characteristic curves of transistors with molecular channel of 1,4_C_6H_4S_2 by NEGF method are published in reference [1].

The Van der Waals surface of molecules in this topic has the same shape, almost as smooth as the surface of a dish. Observing the following perpendicular direction to the surface containing the atoms in the molecule, limitation surface of Van der Waals force is shaped like a six-petal flower. The area of the dish is a rectangle shape with the length of L and width of W. The sizes shown in table 3 are average values. Following the CACHe software, the size of molecules is able to be presented at seven different values and equally distances. We can consider that the size of molecules is also quantized and their effects on I-V curve should also be evaluated. Figure 6 shows the measured results of 1,4-difloro-benzene, and table 2 also presents the average size value of molecules in this research.
The molecules of 1,4-dihalo-benzenes (1,4-C₆H₄X₂, with X: F, Cl, Br, and I) have three couples of electron for double bonding at each side. CAChe software is used to simulate this bonding and to explore the effect of Gold atom on energy levels used to form conductive channels (figure 7). As the results shown in figure 7, after bonding with Gold atoms and being optimized, the structure of molecules which are used to form the conductive channel is not deformed. Therefore, the measured results in table 3 can be used for calculation programming for IDS of transistors.

Figure 6. The size of molecules calculated by the Van der Waals force.

| Molecule     | 1,4-C₆H₄S₂ | 1,4-C₆H₄O₂ | 1,4-C₆H₄F₂ | 1,4-C₆H₄Cl₂ | 1,4-C₆H₄Br₂ | 1,4-C₆H₄I₂ |
|--------------|------------|------------|------------|-------------|-------------|------------|
| High H nm    | 0.3797     | 0.3309     | 0.3839     | 0.3366      | 0.3803      | 0.3530     |
| Long L nm    | 0.9584     | 0.7699     | 0.7957     | 0.9340      | 1.0025      | 1.0321     |
| Wide W nm    | 0.6574     | 0.6770     | 0.6782     | 0.6696      | 0.6714      | 0.6637     |

Figure 7. The molecule of 1,4-C₆H₄F₂ bonding with Gold in two different observation directions.

3.2. Transistor simulation with GUI in Matlab

From the main interface, in popup menu, we can click the mouse to choose one of the four molecules used to make the transistor’s channel, then, click mouse on “Transistor characterize” to move to the next interface (figure 8). The interface includes image of transistor’s construction, basic information of channel material’s molecule and four slides to modify parameters of: length L, width W, gate voltage, temperature and I-V characteristic.
3.3. Transistor’s characteristic curves family

The result of transistor characterizing four kinds of transistors which are made of a 1,4-dihalo-benzene molecule varying $U_G$ from 0 to 0.5 V, shows that its characteristic has the shape of traditional MOSFET’s. The family of characteristic curves is divided into two separate regions: the steep region ($I_{DS}$ current increases rapidly) when $U_{DS} < 0.2$ V and saturation region ($I_{DS}$ current increases quite slowly) when $U_{DS} > 0.2$ V. Supply voltage for these kinds of transistor is merely about 1 V.

The result of testing impact of temperature from -80 to +120°C demonstrates that output characteristics keep unchanged for all four channel material molecules. Impact levels of temperature on the value of current $I_{DS}$ are different with these four molecules. The range of working temperature with them is also larger than semi-conductor devices such as Si and Ge.

The result of impact of quantizing length and width of molecules on output characteristic shows that current $I_{DS}$ increases when the width increases. In contrast, value of length does not give impact on current $I_{DS}$. This is compatible with quantum theory: conductivity at a level of energy is a constant.

In the same condition of temperature, voltages $V_D$ and $V_G$, current $I_{DS}$ of the transistors using molecular channel of 1,4-dihalo-benzenes (1,4-C$_6$H$_4$X$_2$, with X: F, Cl, Br, and I) has different values. This is related to the ability of power supply at the output of specific schematic when using molecular transistor. Among four kinds of testing, the largest power supply ability is the transistor with molecular channel of 1,4-diiodo-benzene, the second largest is the transistor with molecular channel of 1,4-dibromo-benzene, and the smallest is the transistor with molecular channel of 1,4-dichloro-benzene.

4. Conclusion

Dithio-p-benzoquinone [1] and p-Benzquinone can be used as the p-type conductive channel for transistors but with the voltage $V < 0$. Chemically, each of oxygen and sulfur atoms has six valence electrons. Based on chemical structure, either oxygen or sulfur atom has one double bond with carbon atom in the benzene ring. Therefore, it is necessary to have four single bonds or two double bonds between atoms of oxygen and sulfur and electrodes of D and S. On the other hand, the transistor requires the negative bias to increase supply voltage. The higher value of supply voltage leads to the less density of devices in nanoelectronic circuits.
Based on the molecular transistor theory and the chemical simulation software of CAChe and Matlab, the author has outlined a nanotransistor. The molecule transistor’s structure is similar to that of the conventional MOSFET, and the conductive channel is a 1,4-substituted benzene ring. The size of this transistor is about one nanometer. In comparison to a conventional MOSFET, these transistors are more advantageous with the simpler circuit and the lower required value of supply voltage due to the positive bias. The effect of other relating factors for each transistor using the conductive channel from molecules mentioned above has been investigated in order to evaluate its application and verify experimental results in future.

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