

A Model of the Molecular Rectifying Diode Type Aviram-Ratner

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Abstract—Due to the huge power consumption and expensive fabrication methods required, down scaling silicon devices to sub-100 nm dimensions is becoming very unattractive. On the other hand, it is easier to build electronic circuits using molecules since they are small and their properties can be tuned. The molecular rectifying diodes are made of two metallic electrodes connected by a molecule, which contains acceptor and donor subunits, separated by insulating bridge. Both subunits are modeled as quantum dots with discrete energy levels, isolated from each other by potential barrier and weakly coupled to both electrodes through tunnel junctions. Analytic formula for the current is found in the case of the Aviram-Ratner ansatz of rectification and current-voltage characteristic is obtained. It is shown that rectification current depends on the position of the acceptor's LUMO and donor's HOMO levels with respect to the Fermi energy of the electrodes before bias is applied, and their shift due to the bias voltage.

Index Terms—Molecular diode, Current-voltage characteristic, LUMO, HOMO, Fermi energy.

I. INTRODUCTION

MOLECULAR electronics involves using molecules as replacements for conventional devices and interconnects. Conventionally, electronics has scaled as per Moore's law viz. there has been a doubling of devices per chip every 18-24 months. However, there are potential roadblocks in the near future arising from both monetary and physical constraints. A current fabrication line costs \$2.5 billion to construct, and the cost is projected to rise above \$200 billion by year 2015 – a main reason why many semiconductor firms prefer to go “fabless”.

The fast paced developments in the field of semiconductor technology in the recent past have proved without doubt that the efforts to miniaturize the transistors will reach the physical limits earlier than anticipated due to the laws of quantum mechanics and limitations of fabrication methods [1]. Scaling down silicon devices to sub 100 nm and packing millions of them in a chip will not be an attractive idea as these systems consume huge power and will become very expensive to fabricate. Therefore, we need to look beyond silicon to make ultra-high density electronic systems and it is important that

alternate methods such as using molecules to make devices at the nanoscale are explored and exploited [2].

Silicon devices operate based on the movement of a large number of electrons in bulk matter while molecular devices take advantage of the quantum mechanical effects taking place at the nanometer scale. The building blocks of molecular electronics are single or small packets of molecules. While efforts are on to replace the conventional wires and semiconductor devices with molecules, what would be desirable is to build molecular architectures with addressable electronic properties [3]. The main advantage of molecular electronics is the lower cost, compatibility with flexible substrates and simpler packaging when compared to the conventional inorganic electronics.

Since molecules are small, their functionality can be tuned because of their special properties. Either synthesis or self-assembly processes can be used to manipulate the molecules. The most important molecular backbones are: 1) polyphenylene-based chains and 2) carbon nanotubes. Unlike in the case of silicon technology, the bottom-up approach of manipulating molecules is expected to be not only cheap but also will result in higher speeds of information processing with less power. Making electronic rectifiers using molecules was first proposed by Aviram and Ratner [4]. There are two types of molecular diodes: rectifying diodes and resonant tunneling diodes which can both be used in realizing monomolecular digital logic circuits [5]. In addition, we also need molecular wires [6] to connect the molecular devices into a complex circuit with specific applications [2].

II. MOLECULAR RECTIFYING DIODE

A diode or a rectifier, which conducts only in one direction, is the building block of any three terminal semiconductor electronic devices such as a bipolar transistor or a field effect transistor. Diode based logic circuits using AND/OR gates are well known for building logic families by using the rectifying diodes at the input and connecting a resistor between the supply or the ground. A molecular diode too contains two terminals and functions like a semiconductor pn junction and has electronic states which can be clearly distinguished between highly conductive state (ON) and less conductive state (OFF).

The seminal work of Aviram and Ratner in 1974 led to several experimental attempts to build molecular diodes

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Aviram and Ratner have suggested that electron donating constituents make conjugated molecular groups having a large electron density (N-type) and electron withdrawing constituents make conjugated molecular groups poor in electron density (P-type). According to them, a noncentrosymmetric molecule having appropriate donor and acceptor moieties linked with an σ -bridge and connected with suitable electrodes will conduct current only in one direction acting as a rectifier. They showed that in this D- σ -A molecule, the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) can be aligned in such a way that electronic conduction is possible only in one direction making it function like a molecular diode. Asymmetric current-voltage characteristics for an σ -bridged system were first reported in 1990 [7].

The structure of the mono-molecular diode is shown in Fig. 1. This diode is based on a molecular conducting wire consisting of two identical sections (S1, S2) separated by an insulating group R. Section S1 is doped by at least one electron donating group (X e.g. -NH₂, -OH, -CH₃, -CH₂CH₃) and section S2 is doped by at least one electron withdrawing group (Y e.g. -NO₂, -CN, -CHO). The insulating group R (such as -CH₂-, -CH₂CH₂-) can be incorporated into the molecular wire by bonding a saturated aliphatic group (no pi-orbitals). To adjust the voltage drop across R, multiple donor/acceptor sites can be incorporated. The single molecule ends are connected to the contact electrodes e.g. gold.

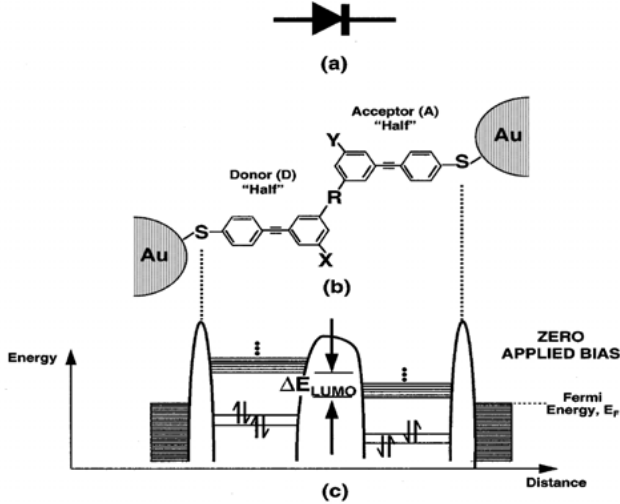


Fig. 1. Equilibrium state of the molecular rectifier.

The band diagram of the mono-molecular diode under zero-bias conditions is shown in Fig. 1. We notice that there are three potential barriers: one corresponding to the insulating group (middle barrier) and two corresponding to the contact between the molecule and the electrode (left and right barriers). These potential barriers provide the required isolation between various parts of the structure. The occupied energy levels in the metal contacts and the Fermi energy level E_F are also shown. On the left of the central barrier all the p-type energy levels (HOMO as well as LUMO) are elevated due to the presence of the electron donating group X and similarly on the right of the central barrier the energy levels

are lowered due to the presence of the electron withdrawing group Y. This causes a built-in potential to develop across the barrier represented by the energy difference ΔE_{LUMO} . For current to flow electrons must overcome the potential barrier from electron acceptor doped section (S2) to electron donor doped section (S1) and this forms the basis for the formation of the mono-molecular rectifying diode. The energy band diagram under forward bias conditions (left hand contact at higher potential than the right hand contact) is shown in Fig. 2.a. Here, electrons are induced to flow by tunneling through the three potential barriers from right to left causing a forward current flow from left to right.

The band diagram under reverse bias conditions (left hand contact at lower potential than the right hand contact) is shown in Fig. 2.b. As a result, electrons from the left contact would try to flow towards the right contact which is at a higher potential. However, conduction is not possible because there is still an energy difference between the Fermi energy E_F of the left contact and the LUMO energy of the electron donor doped section. It is assumed that both the applied forward and reverse bias potentials are identical. For a higher reverse bias, however, it is possible for the Fermi energy E_F of the left contact to come in resonance with the LUMO energy of the electron donor doped section causing a large current to flow in reverse direction and this is akin to the breakdown condition in a diode.

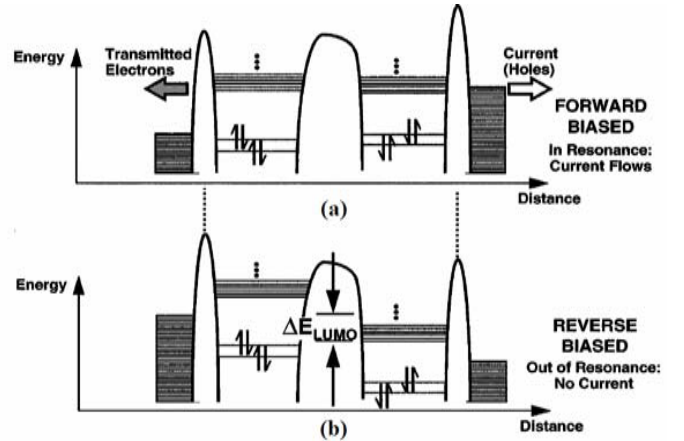


Fig. 2. Rectifier operation under (a) Forward bias (b) Reverse bias.

III. CURRENT FORMULA

Here we assume that the electronic states of particular segments of the molecule (donor and acceptor parts) are perfectly isolated from each other (no hybridization) due to insulating spacer (bridge). Since only HOMO and LUMO levels are the most important in the transport description, we focus our attention on the mentioned energy levels only. General formula for the current flowing through the device can be written as follows:

$$I(V) = I_0 \int_{-\infty}^{\infty} d\varepsilon' \int_{-\infty}^{\infty} d\varepsilon f(\varepsilon, \mu_1) \zeta(\varepsilon - \varepsilon_L^A) [1 - f(\varepsilon', \mu_2)] \zeta(\varepsilon' - \varepsilon_H^D) - I_0 \int_{-\infty}^{\infty} d\varepsilon' \int_{-\infty}^{\infty} d\varepsilon f(\varepsilon, \mu_2) \zeta(\varepsilon - \varepsilon_L^D) [1 - f(\varepsilon', \mu_1)] \zeta(\varepsilon' - \varepsilon_H^A). \quad (1)$$

In the above double-integration procedure: $f(\varepsilon, \mu_{1/2})$ is the equilibrium Fermi distribution function:

$$f(\varepsilon, \mu_{1/2}) = \left(1 + e^{\frac{\varepsilon - \mu_{1/2}}{k_B T}} \right)^{-1}, \quad (2)$$

and $\zeta(\varepsilon - \varepsilon^{A/D})$ is the so-called broadening function of molecular energy level, which is assumed to be of Lorentzian shape:

$$\zeta(\varepsilon - \varepsilon^{A/D}) = \frac{1}{2\pi} \frac{\Gamma_{1/2}}{(\varepsilon - \varepsilon^{A/D})^2 + \frac{1}{4}\Gamma_{1/2}^2}. \quad (3)$$

The strength of the coupling between the molecule and the metallic electrodes (due to the thiol linkages) is described by widths parameters Γ_1 and Γ_2 , which are assumed to be energy and voltage independent [8]. Both electrodes are treated as semi-infinite reservoirs of free electrons at thermal equilibrium, which are characterized through the electrochemical potentials: $\mu_{1/2} = E_F \pm eV/2$.

Furthermore, the magnitude of the current flowing through the device is proportional to a prefactor I_0 , which takes into account the transfer rate between acceptor and donor subunits (multiplied by an elementary electronic charge e):

$$I_0 = \frac{e}{\tau_s} e^{-\beta R_{DA}}. \quad (4)$$

Here: β is a structure-dependent attenuation factor, R_{DA} is the distance between donor and acceptor species (the length of a bridge) and τ_s is donor-acceptor tunneling time. Such time τ_s is approximately equal to experimentally-determined time involved in bridge vibrations and generally can be temperature-dependent. When donor and acceptor subsystems are weakly coupled with the help of σ -bonded bridge, the electron transfer takes place directly from donor to acceptor via tunneling process (also referred to as superexchange mechanism) and exhibits exponential decay as a function of distance [9].

Instead of superexchange theory, it is also possible to describe intervalence donor-acceptor tunneling process with the help of Marcus theory [10]. In this case of a classical description of the transfer rate, the expression for prefactor I_0 is given by [11]:

$$I_0 = e \frac{k_B T}{h} e^{-\frac{\Delta G^*}{k_B T}}, \quad (5)$$

where: k_B is Boltzmann constant, T is absolute temperature and ΔG^* is the activation free energy associated with donor-acceptor electron transfer reaction. However, both approaches indicate that the reduction of the current is caused mainly by some exponential factor.

IV. AN EXAMPLE

The possibility of utilization of DNA molecules as the building elements for molecular electronics has been largely discussed in recent years and many controversial reports of the conducting behavior of DNA exist in the current literature. According to different experimental studies and theoretical

models, the DNA molecule can be an insulator, wide-gap semiconductor, semimetal, or conductor.

Now we proceed to apply presented formalism to the case of proposed model of molecular diode (shown in Fig.3). The scheme of an electric circuit where an adenine-thymine (methyl-adenine methyl-thymine) DNA base pair is chemically bound to the Au (111) model contacts is shown in Figure 3. The terminal hydrogen atoms of the base pair were removed or have been replaced by sulfur atoms as displayed in Figure 3 to compare directly our results with the data for the benzene-1, 4-dithiolate (BDT) molecule. BDT was one of the first structures proposed as the molecular wire for which both experimental and theoretical [12] current-voltage dependencies are known. The substitution of terminal hydrogen atoms is also useful to facilitate bonding of the A-T base pair to the gold surface because it is known that the sulfur atoms create strong covalent bonds with the Au (111) surface in the tetrahedral position, where the distance to the nearest gold atoms is 2.53 Å [13].



Fig. 3. Scheme of the DNA base pair attached to the Au (111) contacts.

In general, the electronic structure of molecular systems can be calculated by various techniques, including: empirical, semiempirical, ab initio or density functional approaches, which are based on different degrees of approximation. Hence, energy levels for both subsystems are (given in eV): $\varepsilon_H^D = -11.2$, $\varepsilon_L^D = -8.6$, $\varepsilon_H^A = -12.4$ and $\varepsilon_L^A = -10.6$. Since the voltage is dropped entirely at the tunnel barriers, the energies of the molecular states depend on the applied bias through the relations: $\varepsilon_A = \varepsilon - eV/2$, $\varepsilon_D = \varepsilon + eV/2$. For saturated hydrocarbon chains $\beta = 0.9 \text{ \AA}^{-1}$ [14], the length of the bridge is $R_{DA} = 1.99 \text{ \AA}$ and molecular vibration period for that bridge is of order of $\tau_s \sim 10^{-12} \text{ s}$ [15]. Fermi energy of the electrodes is usually located somewhere in between the HOMO-LUMO gap [16], and in this work it is arbitrarily chosen to be equal to $E_F = -10.9 \text{ eV}$. To simulate bad contacts with the electrodes (as a typical situation in experiments) we take the parameters responsible for that coupling as: $\Gamma_1 = \Gamma_2 = 0.02 \text{ eV}$.

Fig. 4. shows the current-voltage (I-V) and conductance-voltage (G-V) characteristics for molecular diode proposed in

this section (depicted in Fig. 3.) at temperature $T = 290$ K. Such type of molecular junction rectifies current in the forward direction (positively biased) relatively to that the reverse direction (negatively biased). Asymmetry of the I-V dependence is due to asymmetry in the structure of the molecule itself. Substituting all the parameters indicated in the previous paragraph, an estimation of the current in the usual units is: $I_0 \approx 6$ nA. In order to obtain the same result from Marcus theory we should assume that: $\Delta G^* = 0.16$ eV. Character of the I-V curve and the evaluation of the peak value of the current are similar to some experimental results [12].

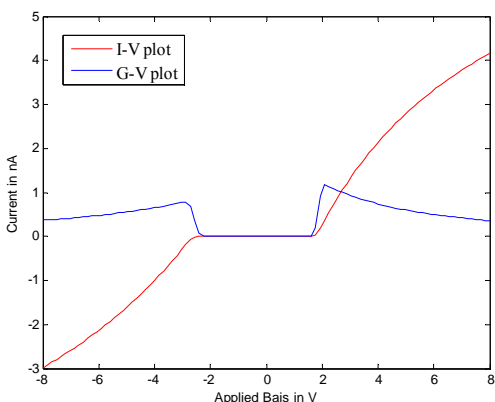


Fig. 4. The I-V and G-V characteristics for analyzed model of molecular rectifying diode type Aviram-Ratner.

V. CONCLUSION

Presented model qualitatively reproduces the rectifier behavior of complex molecular devices. The magnitude of the predicted current is comparable with experimental data in the conditions that we match all the parameters. So rectification is attributed to asymmetry of a molecule with an acceptor-bridge-donor structure (A- σ -D), where mechanism of diode-like behavior results from the Aviram-Ratner ansatz. However, this model seems to be useful as a simple theoretical tool in designing molecular devices of the donor-bridge-acceptor type, which demonstrate rectifying features. One of crucial problems stems from the task of finding Fermi energy of the electrodes (while experimental control of this level is realizable through the choice of metal, which play the role of the electrode).

Moreover, the tunneling of an electron through the acceptor-bridge-donor junction is treated as a sequential process, in which the molecular species are successively charged and discharged. In fact, after the initial tunneling step an electron can have enough time to redistribute charge along the molecule (i.e. to polarize this molecule). Such phenomenon can have an influence on the shifts of molecular energy levels, and transfer-induced dipole momentum can affect transport characteristics. However, here we do not include this effect into our formalism, completely ignoring such phenomena like Coulomb blockade. In the frames of this work we also neglected all the effects of electron correlations as well as inelastic scattering.

It should be also noted that several experiments on symmetric

molecules have shown rectification, while others have found very little or no rectification. Such effect is justified by asymmetric electrode coupling, which can result in an asymmetric potential drop along the length of the molecule. If the potential profile is asymmetric, molecular energy level through which an electron is propagated can line up differently in positive and negative bias, resulting in rectification. Rectifying features of molecular systems can also be explained as a consequence of conformational changes due to: thermal effects, inelastic tunneling or application of electric field.

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