Chapter

EFFECTIVE MEDIUM SIMMONS (EMS) MODEL FOR ACCOUNTING OF MULTIBARRIER TUNNELING IN SINGLE MOLECULAR NANODEVICE

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ABSTRACT

This Chapter reports on development of the Dome model to explain the macroscopic topographic effects in conductivity through mixed single molecular devices. These topographic effects arise from macroscopic nature of electrodes connected molecules to external word and different nature of bonding with these electrodes. We discuss applicability of Dome topography using the Simmons model for a complex case of multibarrier system, in which the barriers can be connected in series and in parallel. These barriers can have a different nature, bonding and transparency. The multibarrier approach is more complex than case of simple tunneling through the gap and it enables development of tunneling model for mixed single molecular devices. We analyze model of multibarrier tunneling using an example of mixed single molecular devices, in which conductive channels compose on aromatic molecular wires, 2-[4-(2-mercaptoethyl)-phenyl]ethanethiol (Me-PET). Me-PET molecules are embedded during molecular self-assembly into more insulating matrix. The insulated matrix is composed on saturated aliphatic molecules, penthane 1-thiol (PT). The heterogeneity of Me-PET/PT system is controlled by mixing ratio r, which produce a single molecular devices if the $r < 10^{-6}$. In this system, the Me-PET molecules are spatially "isolated" from each other by less conductive 2D structure of PT molecules (designated as molecular "insulators"). While the conductivity in such system is dominated by current passing through Me-PET molecules, the transport passes through PT molecules should be accounted as well.

Moreover, few experimental observations vote for necessity to account the topographic effect to explain the single molecular transport in Me-PET/PT system. We demonstrate in this chapter that Dome conductivity model, which is a specific case of model of multibarrier tunneling, can serve well for accounting of these topographic effects. We discuss peculates of Simmons dependence in mixed single molecular devices to model transport in Me-PET/PT system and propose an effective medium Simmons (EMS) model for accounting of multibarrier tunneling in molecular nanodevices with a macroscopic topology.

1. INTRODUCTION

A growing number of reports on experimental molecular nanoelectronics are dedicated to studies on clarification of real structure of molecular tunneling barriers and independent measurements of tunneling effects [1]. This recent trend in molecular nanoelectronic is not a simple coincidence. The major contemporary problem of molecular nano-electronics is indeed lack of knowledge on real structure of molecular nano-devices and capability to fabricate nano-dimensional devices with a predicable structure and properties. This fact result in lack of basic understanding on structure-property relationships in organic solids results in a knowledge gap that impedes rational efforts to design organic nanodevices. Indeed, measurements of electronic properties of nanoscale and molecular junctions do not provide direct structural information about molecular junction [2].

This chapter reports on study of studies of single molecular transport in self-assembled solid state mixtures. Section 2 of this chapter describes relevant studies of this nanomaterial system. Section 3 of this chapter describes one of the examples of self-assembled solid state mixtures –Me-PET/PT system. Section 4 summarizes set of remaining questions on single molecular transport in self-assembled solid state mixtures. These questions are linked to relationship of macroscopic features in Me-PET/PT devices into nanoscopic transport mechanism of this system. These questions are addressed in chapters 5-7. Section 5 reports on simulation of single molecular transport in self-assembled solid state mixtures using Dome model. The Dome model is generalized in section 6 to model of multibarrier tunneling in molecular systems. In this section summarize our consideration on parallel and series connection of molecular wires and spacers in PT/Me-PET mixed self-assembled solid state mixtures. These barriers can have a different nature, bonding and transparency.

Eventually Section 7 is dedicated to discussion of these results and introduces the effective medium Simmons (EMS) model for accounting of multibarrier tunneling in molecular nanodevice with macroscopic topology.

2. STUDIES OF SINGLE MOLECULAR TRANSPORT IN ORGANIC LOW DIMENSIONAL STRUCTURES USING SELF-ASSEMBLED SOLID STATE MIXTURES

We proposed a novel approach to study single molecular transport in molecular electronic devices [3,4,5,6]. The main idea of this approach consists in the possibility to assemble isolated conducting aromatic molecules in otherwise insulating matrix. The insulating matrix is formed by saturated aliphatic molecules in self-assembled films. In aliphatic molecules, unlike aromatic ones, all charges are confined. In aromatic molecules, electrons are delocalized within aromatic core and are much more mobile compared to aliphatic molecules. Therefore, we can define aromatic molecules as "molecular wires." We designate a molecular system with these features as "1D" system. Such systems can be easily integrated in different molecular devices by use of chemical affinity of self-assembled molecules to electrodes. We already measured electrical conductance of aromatic single molecular wires using this approach [3,4,5,6].

We expanded the 1D approach by growing molecular aggregates composed from the same molecular wires within self-assembled films. These structures were self-assembled as a mixture of molecular insulators (e.g.: same aliphatic molecules with a negligible conductivity), with a fraction r of embedded conductive aromatic molecules (usually designated as "molecular wires".) We designated molecular system with these features as "2D" system. We studied electronic, spintronic, and optical properties of these films. Furthermore, we probed phase transition from 1D system (single molecular wires) to 2D system (molecular aggregates) by increasing the r-ratio. In this arrangement, charges in the 2D system should have additional charge delocalization inside molecular stack; therefore, we observed formation of new pseudo-bands inside HOMO-LUMO molecular orbitals. The systematic study of this topic will enable to build a phase diagram of structural transition in molecular nanostructures. The experimental studies of gap states in self-assembled molecular aggregates provided required information on structure-property relationship in low-dimensional molecular system. Despite the progress in study of self-assembled solid state mixtures, there are several fundamental questions on relationship between their structure and properties that have to be clarified. This chapter is dedicated to analysis of macroscopic features of single molecular devices and their contribution to properties of self-assembled solid state mixtures and relationship between nanoscopic and macroscopic scale in these structures. We will conduct this analyze in 'Me-PET device' and "PT device' as example of self-assembled solid state mixtures. The structure of these devices is shown in section 3.

3. STRUCTURE AND PROPERTIES OF 'ME-PET DEVICE' AND 'PT DEVICE' SELF-ASSEMBLED IN SOLID STATE MIXTURE

We use a nanofabrication approach, which deals with an organic monolayer with many molecules acting in parallel [7,8]. It has been demonstrated [3,7] that the organic monolayer in the nanodevice does not need to be homogeneous–it may be composed of a mixture of two different types of molecules: conductive 'wires', and insulating 'spacers'. If electron tunneling is the main conductive mechanism, the reason for the low conductivity of 'spacers' is due to the much higher position of the energy barrier or the absence of chemical bonds with respect to electrodes. A device having properties of a single molecule device could be

achieved when the fraction of molecular 'wires' is small and the device contains many independent conducting molecules acting in parallel.
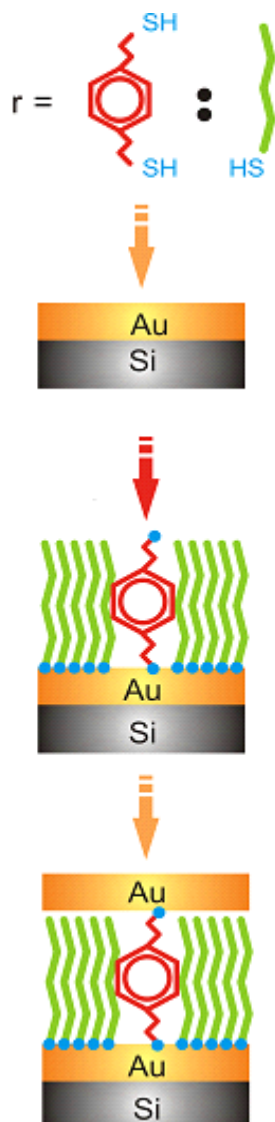

Figure 1. SAM approach to molecular diodes. The fabrication process of SAM solid-state mixture diodes at a ratio $r = 10^{-6}$ of molecular wires (Me-PET in red) to molecular insulators (PT in green) is shown schematically ('$r = 10^{-6}$ device').

This concept was used to grow the self-assembled monolayer (SAM) on metallic electrodes from a diluted mixtures of molecular wires [2-[4-(2-mercaptoethyl)phenyl] ethanethiol (Me-PET)] and molecular insulating spacers [1-pentanethiol (PT)]. Prepared precursor solutions have a concentration ratio $r = N_{Me-PET}/N_{PT}$, where N_{Me-PET} and N_{PT} are their respective molar concentrations. The two-terminal molecular devices have been fabricated using the protocol shown schematically in Figure 1.

In every device material of electrodes was the same. The bottom Au and Al electrodes (about 30-nm thick) was deposited on a SiO_2/Si wafer using a DVSJ/20C Denton Vacuum e-gun. The precursor mixture of Me-PET/PT was diluted with distilled toluene to a 3-mM concentration and air-free transferred into a homebuilt high-vacuum Shlenk line. The self-assembling process was continued for 12 h in an argon atmosphere at room temperature. After the SAM growth had been completed, the samples were thoroughly washed in dry toluene and annealed in vacuum for 1 h at 90 °C to remove any physisorbed precursors. The upper Au and Al electrode was then evaporated through a shadow mask in a vertical cross electrode configuration using the DV-SJ/20C e-gun at 95 °C on the sample holder. In fabricated devices the upper and bottom electrode material was the same. During the self-assembly process, we keep the ratio r, $r = 10^{-6}$. This concentration is typical for a single molecular device [3,4,5,6]. We denote this device as 'r=10^{-6} device'. In this report the conductive molecular channels are composed by Me-PET molecules. Similar studies were done using methylbenzene di-thiol (Me-BDT) molecules [3,4]. The structure of Me-PET/PT and Me-BDT/PT 'r=10^{-6} devices' are very similar. Every Si chip was constituted by three different devices, each one with an active area of about 0.5 mm^2. We have also fabricated several devices with $r = 0$ for the purpose of comparison; these devices were composed of insulated PT molecules with no molecular wires.

We have used a Keithley 236 electrometer for two terminal electrical measurements and Varian/Cary 5G spectrophotometer for recording surface reflectivity spectra. Varian/Cary 5G spectrophotometer was equipped with a custom design sample-holder for reflectivity measurement [4].

Short (~1 nm) organic molecules have substantial probability of direct tunneling due to nonzero wave function across molecular barrier. To approximate a current-voltage response of the fabricated molecular devices, we used the Simmons model [9,10] for electron tunneling through a thin dielectric layer. This model has also been successively applied to describe an electron tunneling through a single molecule [11,12,13]. The model is based on the assumption that if the Fermi level of the metal electrode is closely aligned to a molecular energy level, then the effect of the other, more distant, molecular energy levels on the charge transport is negligible. Depending on position of the Fermi level, the tunneling barrier may be associated either with the highest occupied or lowest unoccupied molecular orbital (HOMO or LUMO, respectively). Simmons has derived a general expression which describes the current density versus voltage over the full range from metal-dielectric-metal to field-emission tunneling [10].

The Simmons model for organic or inorganic tunneling systems is restricted to low biases. If Φ_B^{Sim} defines the lowest Simmons barrier in the system in electron-volts and

applied bias is $V < \Phi_B{}^{Sim}/e$ (where e is the electron charge), then the dependence of the current density J on V can be approximated as:

$$J(V) = G_0 \left\{ \left(\frac{2\Phi_B^{Sim}}{e} - V \right) \exp\left[-\frac{2(m_e e)^{1/2}}{h} \alpha \left(\frac{2\Phi_B^{Sim}}{e} - V \right)^{1/2} d \right] \right.$$
$$\left. - \left(\frac{2\Phi_B^{Sim}}{e} + V \right) \exp\left[-\frac{2(m_e e)^{1/2}}{h} \alpha \left(\frac{2\Phi_B^{Sim}}{e} + V \right)^{1/2} d \right] \right\} \tag{1}$$

Here, h is a Plank's constant, m_e is the electron mass, and d is the barrier width. In molecular junctions, the barrier height can be approximated by the energy offset between the electrode Fermi level and the nearest molecular orbital. For a single monolayer, barrier width d should be close to the molecular length, which has been estimated to be ~ 1 nm from the data obtained by ellipsometric measurements [5]. Parameter α provides a way to apply the model to a nonrectangular barrier and/or to account for the effective mass of the tunneling electrons. The pre-exponential factor G_0 is related to the conductivity at very low biases $V << \Phi_B/e$, when the dependence $J(V)$ becomes linear [14,15]. The G_0 is also known as an 'equilibrium conductivity' [16] and its meaning and contribution can also be extended to the field emission at high-bias range (FN mechanism) based on a different linearized presentation [16,17].

Equation (1) describes a trapezoidal barrier when the applied bias is less than the barrier height. In the zero-bias limit, the barrier is rectangular, and Eq. (1) reduces to

$$J(V) = G_0 V \exp\left(-\frac{2d\sqrt{2m_e^* \Phi_B^{Sim}}}{h} \right) \tag{2}$$

Note that in Eq. (2) α-factor has been incorporated into the electron effective mass so that $m_e^* = \alpha^2 m_e$ [14,15]. These two presentations are equivalent because it is impossible to distinguish the contributions of α and m_e^* in Equation 1.

Table 1 summarizes tunneling parameters for 'r=0' device with Au electrodes, which is composed of PT molecules, and 'r = 10^{-6}'device, which is composed of single Me-PET molecules disperses in matrix of PT molecules. Values of Φ_B, α and G_0 parameters are similar to the corresponding values obtained in other studies of tunneling through single molecules [14, 9,18,19]. A detailed description of self-assembling approach and details of device fabrication are summarized in ref. [20]. The goal was to fabricate predictable and structurally similar devices composed of solid-state mixture wires and spacer molecules with Au-Au electrodes in two-terminal device. The experimental response, $J(V)$, of the molecular devices with Au electrodes, and the best fits with Simmons formula, Eq. (2) for low biases at different temperatures are shown in Figure 2.

Table 1. Tunneling parameters, de-convoluted from the Simmons model at low bias

| Device ID	'r=0' device			'r=10^{-6}' device		
Device structure	1-pentathiol (PT) self-assembled structure, Au electrodes			2-[4-(2-mercaptoethyl)phenyl]ethanethiol (Me-PET) self-assembled at mixing ratio r = 10^{-6} with PT molecules, Au electrodes		
T	Φ_B	α	Go	Φ_B	α	Go
K	(eV)	-	S	(eV)	-	S
15	1.600	0.970	--	1.189	0.872	--
50	1.561	0.956	5.128E-6	1.184	0.882	2.333
100	1.628	0.842	1.230E-5	1.181	0.848	2.415
150	1.492	0.779	5.523E-5	1.178	0.788	3.441
200	1.450	0.800	1.455E-4	1.195	0.734	5.132
250	1.385	0.738	0.018	1.223	0.721	11.304
294	1.345	0.669	0.057	1.261	0.723	14.347
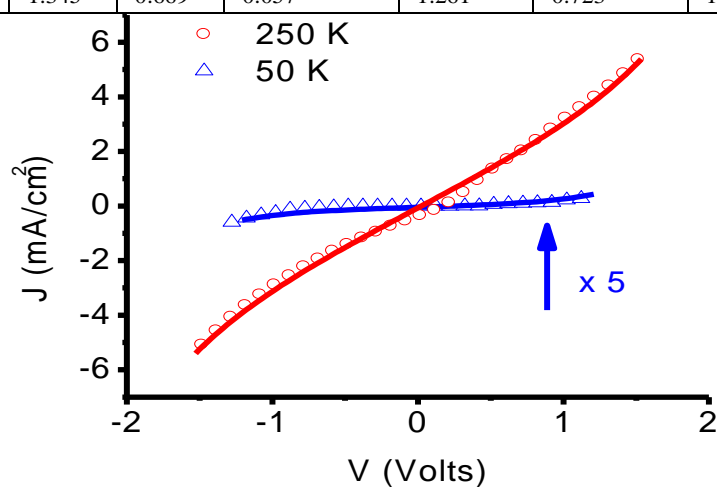
Figure 2. Analysis of electrical transport properties in SAM diodes (Au electrodes) with r = 10^{-6} with the Simmons model fit (solid lines) over experimental data (symbols) at low temperature (50 K) and high temperature (250K) [41]. Fitting results for the Simmons tunneling barrier (Φ_B) for devices with Au electrodes in the temperature range 11-294 K. IV's characteristics for the SAM diodes with r = 0 (only PT molecules, Au electrodes), parameters α and G_0 are summarized in table 1.
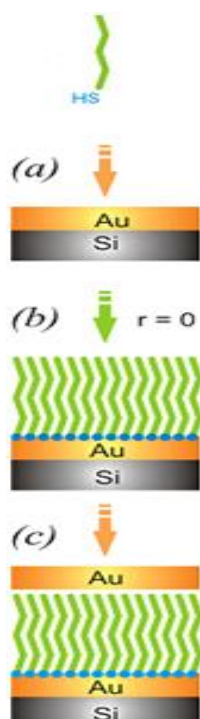
Figure 3. SAM approach to PT (r=0) devices. PT considered to serve as molecular insulators in 'r = 10^{-6} device' (Figure 1).
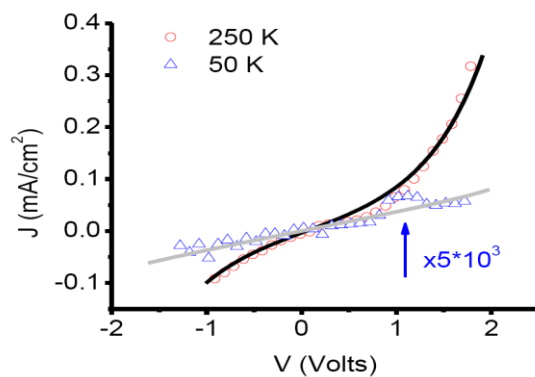

Figure 4. Analysis of electrical transport properties in PT SAM diodes (Au electrodes) with r = 0 with the Simmons model fit (solid lines) over experimental data (symbols) at low temperature (50 K) and high temperature (250K).

We found that the value of Φ_B has a very weak dependence on temperature, which validates this approach even at room temperatures. The best fits at low biases, averaged in all the temperature ranges, gave Φ_B^{Au} values of 1.2 ± 0.1 eV for the '$r = 10^{-6}$ device' with Au electrodes and Φ_B^{Al} values of 2.0 ± 0.1 eV for the same Me-PET with $r = 10^{-6}$, but with Al

electrodes. Same analysis of the devices composed of PT molecules at only ($r = 0$) exhibit the $\Phi_B{}^L$ and α values (Table 1) are in good agreement with similar measurements [21].

4. QUESTIONS ON SINGLE MOLECULAR TRANSPORT IN SELF-ASSEMBLED SOLID STATE MIXTURES

Section 3 of this chapter demonstrates the feasibility of method to grow the single molecular wires in solid state mixtures (*section 2*). This statement does not impose however we know everything about structure-property relationship in these nanodevices. For example, we would like to share few questions arisen from interesting discussion on accounting of macroscopic and nanoscopic features of these devices with our colleague [22].

We believe that origin of most listed comments and questions [22] is confusion between transport properties of single molecules and self-assembled monolayers. We ignore irrelevant (e.g.: "industrial revolution"[22]) and trivial topics (e.g.: regarding use of Simmons [9, 10] and Kirchhoff [3,5] models for single molecular junction), in these questions as well. However there are few interesting questions that are related to relationship between single molecular features in single molecules and macroscopic features of insulated matrix in self-assembled in solid state mixture, which we never consider in mixed solid state self-assembling mixtures. Therefore, we would like to focus our discussion around following question:

1) Why is the resistivity of 'r=0 device' (Figure 4 section 3) in our experiments is small?
2) How does the I-V characteristics of 'r=0 device' similar to simple tunneling through a vacuum barrier?
3) How the geometry of the reported devices is associated with tunneling currents?
4) What are difference and similarities in Simmons modeling of 'r = 0 device' and 'r =10^{-6} device' (e.g.: composed on PT/Me-PET structure). Why and how the Simmons model is capable to describe adequately tunneling in 'r=0 device' at all?
5) How the resistivity of 'r = 0 device' is compared to resistivity of SiO_2 oxide?

It is not only instructive to obtain the answers to these questions. The adequate response to these questions might provide a path to explore the challenging connection between macro and nano-scale phenomena in self-assembled solid state mixtures. It is instructive to consider tunneling mechanism in 'r = 0 device' first and then to generalize the result of this analysis on 'r = 10^{-6} device' and other molecular devices.

5. SIMULATION OF SINGLE MOLECULAR TRANSPORT IN SELF-ASSEMBLED SOLID STATE MIXTURES USING DOME MODEL

Let us simulate the Simmons dependence for every feature of 'r=10^{-6}' device. The Figure 5 below shows a Simmons simulation [9,10] of I-V characteristic for a vacuum gap (barrier height, Φ_B =5 eV [23]) as well as for a molecular gap (1.5 eV) according to eq.1. We assume here that the electrode area is the same as in our reported PT devices, α =1, m*=1; and the tunneling is homogenous throughout the entire electrode area. The barrier height, Φ_B and width, d are given in the Figure 5.
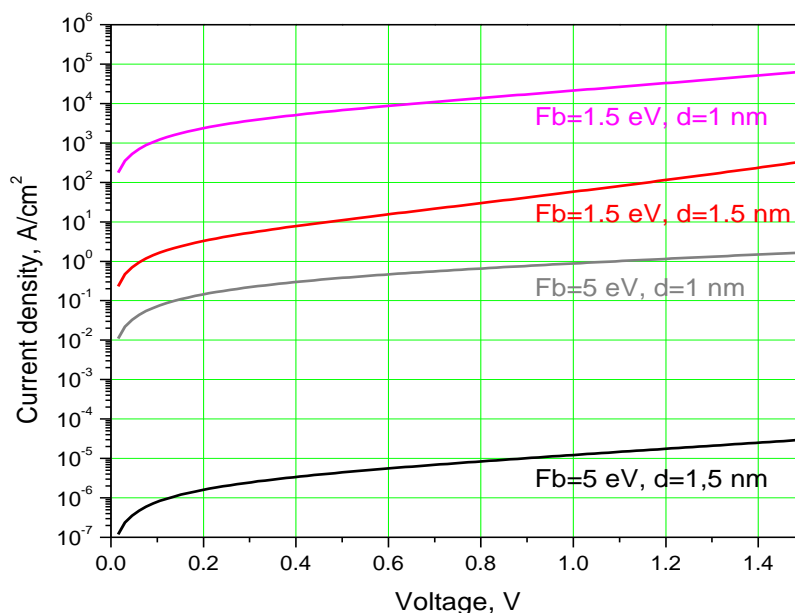

Figure 5. Calculated I-V characteristic of molecular devices using the Simmon's model. The values of barrier height, Fb, in eV and width, d in nm are given in the figure.

The I-V of 'r=0 device' lies in between the grey and black lines in Figure 5, which correspond to tunneling through a vacuum barrier of thickness between 1 and 1.5 nm. As we noted in ref [4], most of the PT molecules in 'r=0 devices' do not have electrical contact with the upper (capped) electrode. Therefore for most of the PT molecules the effective barrier is composed of a relatively small (1.5 eV) barrier of the PT molecule (~1 nm width), and a larger (~5 eV) vacuum barrier, that are connected in series. The maximal width of the vacuum gap between the PT molecule and upper electrode is unknown. For discussion purpose we assume that the maximal value of the vacuum width is 0.5 nm.

This structure of 'r=0 devices' has two obvious consequences. First, for the majority of PT molecules in the device the effective value of the tunneling barrier in the transport channel would in fact be the vacuum barrier, since Φ_B(PT)<< Φ_B(vacuum). Second, the effective

tunneling barrier width would be much larger, *on average*, than the PT molecule length (~1 nm). Taken together, these considerations will produce the 'two barrier' tunneling system in which, *on average,* the barrier value would be 5 eV (neglecting the small value of PT barrier) and width between 1 nm (case of PT molecule with electrical contacts with the upper electrode) and 1.5 nm (PT and vacuum gap width). Our experimental data for PT-device lie in between the grey (Φ_B= 5 eV and d = 1nm) and black (Φ_B = 5 eV and d= 1.5 nm) lines (figure 5). This means that the real vacuum width is, *on average,* between 0.2 and 0.3 nm. The real value for the vacuum gap width depends on the actual values of α and m* in the "two barrier" tunneling system, which was assumed here again to be equal to one.
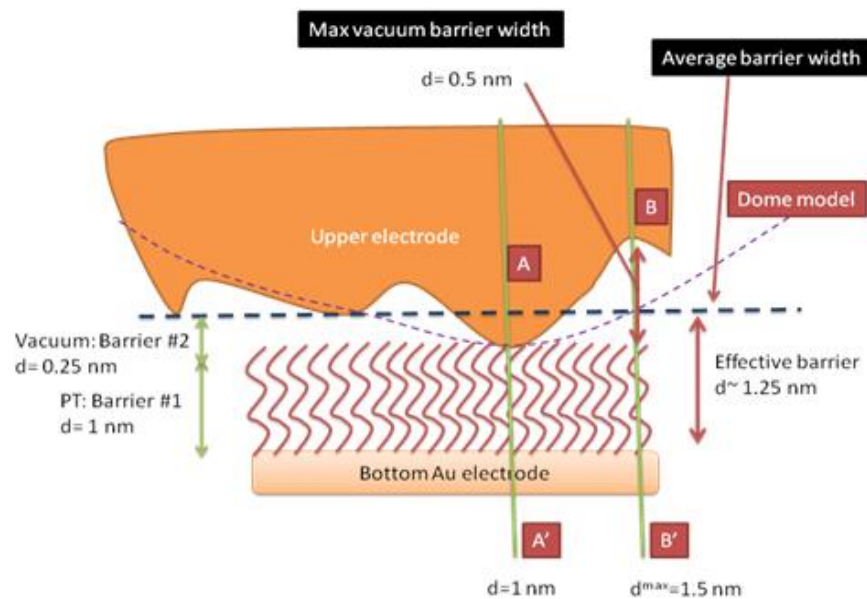

Figure 6. Dome model [25] applied to 'r=0 device' to explain tunneling in SAM devices.

At this point let us come back to discussion of device geometry. Following arguments for the PT-devices, the transport PT molecule channels which are bonded to the upper electrode have a length of ~1 nm (the PT molecular length). Then formally speaking dividing the measured current by the device area to obtain the current density is meaningless in this case since the device is highly inhomogeneous, containing both high and low conducting molecular channels. Dome model, introduces by Aswal et al. [24]to explain tunneling in SAM devices provide more explanation for tunneling in SAM matrix (Figure 6). Aswal's ref. 24 enables one to trace back 10 years of study of tunneling mechanism in SAM structures.

6. ON PARALLEL AND SERIES CONNECTION OF MOLECULAR WIRES AND SPACERS IN PT/ME-PET MIXED SELF-ASSEMBLED SOLID STATE MIXTURES

Dome model is just one illustrative example of many possible organic nanostructures and device configurations. We generalize in this section this model to model of multibarrier tunneling. This is an effective medium approach, which enable to explore the structure-property paradigm in molecular nano-structures without knowledge of exact structure of molecular nanodevice. These barriers can have a different nature, bonding and transparency. The multibarrier approach has more complexity than the case of simple tunneling through the gap [9,10] and it enables, therefore, development of tunneling effective medium models for more complex systems than single molecular devices. For a discussion purpose we designate Simmons model for this case as "effective medium Simmons model".

6.1. Contacts and Tunneling Molecules (Series Connection)

Let us assume that the conductance of the molecule is described by Simmons (tunneling) and is equal to G_T, and the conductivity of the contact G_C –by Ohm's law. In a series connection of resistance is additive. Since conductivity - the reciprocal of resistance, to obtain the total conductivity G:

$$\frac{1}{G} = \frac{1}{G_T} + \frac{1}{G_C} \tag{3}$$

or

$$G = \frac{G_T G_C}{G_T G_C} \tag{4}$$

In case of a small contact resistance, $G_T \ll G_C$ and G_T in the denominator is negligible. We will obtain $G = G_T$ and total conductivity is determined by Simmons law.

However, if the conductivity contact is poor, than surprisingly the $G = G_C$. In case of PT spacers, for example, the tunneling there through role in the overall conductivity is low because the contacts conduct worse than molecule. The intermediate case is much more complicated, as G_T and G_C has a different dependence from both the current and the temperature. In this case $G(V)$ still can look like similar to Simmons dependence (eq.3), however there will be essential difference. This is origin of α dependence on temperature and voltage range from barrier value, Φ_B.

This simple analysis leads to two conclusions, which are even less unexpected. Suppose an ohmic contact and a very conductive molecule. Under decreasing temperature decreases G_C (G_T and does not depend on temperature), therefore at low temperatures current

increasingly determined conductive contacts and not molecules. Thus, in spite of what you would think, Simmons dependence is more pronounced at high temperature than low!

Second. If the contact is really ohmic, than G_C does not depend on bias. On contrary a G_T ncreases with increasing voltage, and its role decreases at larger biases! The tails of Simmons dependence become more and more flat at ramping biases against the case of pure tunneling. This means that the small bias range produces more accurate result in terms of Simmons dependence than large bias range.

Furthermore we can expand (eq. 4) in Taylor series. Let consider below two cases.

6.1.1 First case is case of good conductive contacts (as in case of double-bonded conductive molecules, as Me-PET molecules), wherein $\frac{G_T}{G_C}<<1$ (molecular conductivity is less than contact resistivity). In this case we can rewrite eq.2 as:

$$G = G_T \frac{1}{1+G_T/G_C} \tag{5}$$

Then, up to the first order of smallness in $\frac{G_T}{G_C}$ we will obtain:

$$G = G_T - \frac{G_T^2}{G_C} + \cdots \tag{6}$$

the resistance molecules compared with the contact large under low voltages , i.e. conductivity is low, and the second term can be neglected, G can be described by Simmons. If the voltage is increased, G_T increases according to Simmons dependence and G_C does not change according Ohm's law. Then total conductance G will grow more slowly as it approaches the values of G_T to G_C. Of course, one has to consider terms of higher order at higher voltages. However the signs of terms alternate in Taylor series. As long as $\frac{G_T}{G_C}<1$, we have $\frac{G_T}{G_C}<\left(\frac{G_T}{G_C}\right)^2<\left(\frac{G_T}{G_C}\right)^3<\dots$ So, the increase of voltage G will result in stronger deviation from Simmons dependence in the direction of smaller growth until $G_C \approx G_T$.

6.1.2 Second case: Poor contact conductance (as in case of single-bonded PT 'spacer' molecules). Here, the opposite trend is true. Since $\frac{G_C}{G_T}<<1$ here as a small very parameter, we will get instead of (4):

$$G = G_C - \frac{G_C^2}{G_T} + \cdots \tag{7}$$

Simmons relationship is completely disappears in this case (or present only in contact). Even if we consider the second term, G_T is in the denominator, (i.e, its contribution is inversely proportional to Simmons). In the other hand, we know that conductivity of device is in many orders of magnitude smaller than the conductivity of any another device. It is therefore evident that the higher orders (5) play no role, and in this case we can simply obtain

simply $G = G_C$. The question arise in this point is how the 'r=0 device" show any Simmons dependence? Following section clarify this dependence.

6.2. Breakdowns and Serial Connection (G_P).

In this case, simply the conductivities are additive. The formation of "hot spots" and direct contact of the electrodes is possible in the case of conducting molecules through heterogeneity and discontinuities in the film. In this case the conductivity mechanism is hopping, thermionic emission etc. These mechanisms more or less obey Ohm's law. Therefore, G_P does not depend on voltage. This effect can be accounted for by simply adding a linear correction $V \cdot G_P$ in Simmons dependence $J(V)$, which was used in conductivity data fit in 'r=10^{-6} device'.

In case of 'r=0 device' this additive will not change the $G = G_C$ law. In this case the G_P factor simply increases G, but cannot explain the dependence of the conductivity from voltage (the $J(V)$ dependence of still must be linear). However there is a possibility for another type of "hot spot defect" in 'r=0 device'. Despite the fact that a chemical bond is missing on one of the electrodes, that do not exclude the possibility of accidental formation of this bonds. In this case the conductivity at these points will be determined by tunneling. The number this new "hot spots" is very small in respect to the total the number of molecules on the surface. However this is exactly the case why the current amplitude is so small in 'r=0 device' (PT). These "hot spot defects" change to basic conductivity mechanism, and this conductivity of contacts now can consider the same linear additive Simmons dependence.

Note that the remaining single bonded PT molecules continue to serve as insulators. The conductivity of PT 'spacer' molecule can be comparably large, but the number of such conduction channels is low and this makes the device current extremely low. Furthermore, we believe that even aromatic Me-PET molecules with one-side bonding to electrodes can serve in context of this discussion as 'spacers'. In this case such Me-PET molecules will be less efficient of course in formation of isolated ME-PET channels with two chemical bonds with electrodes.

Similar consideration enables to evaluate the amount of conductive channels in ''r=10^{-6} device' and 'r=0 device. If we assume that conductivity of wires and spacers are similar than the G_0 value in Simmons dependence enable to evaluate the amount of 'conductive' channels in 'r=0' in respect to 'Me-PET device'. We know the concentration of active conductive channels in 'r=10^{-6} device' from the surface titration experiments. This comparison yields that the number of conductive channels in 'PT-device' is smaller in 11 orders of magnitude in respect to ''r=10^{-6} device'. Therefore we prove absolutely negligible effect of PT molecules on conductivity measurements in 'Me-PET device'.

7. DISCUSSION

7.1. On Macroscopic Effect in Single Molecular Devices

One misconception in molecular nanoelectronics, in our opinion, is to compare the heterogeneous self-assembled monolayer with homogenous dielectric layer, like SiO_2 layer (e.g.: *section 4*) [22]. This setting correspond to the structure, in which, all molecules are connected by ohmic bonds with both electrodes. This is definitely not the case for 'PT-device', in which we are underling the existence of vacuum barrier almost in every conductive channel. *Effective medium Simmons* analysis of conductivity in self-assembled mixtures system, which is conducted in *section 6* of this chapter, revel much more complex system than SiO_2 layer model, which was suggested for discussion in *section 4*. It is due to necessity to consider parallel and series connection of molecular wires and spacers in PT/Me-PET mixed self-assembled solid state mixtures. It worth noting the inorganic analog of such molecular nanosystem just does not exist. The "hot-spot" mechanism [26] in semiconductors might be the closer approximation of transport in self-assembled single molecular structures than model of homogenous SiO_2 layer.

There are many open questions to particular approach that we developed that have to be addressed experimentally. For example, we really do not know the number of PT molecules in our devices that have ohmic contact with both electrodes; we could not calculate exactly current density in this specific PT transport channel. The current density values shown in Figure 4 are only effective medium evaluation of tunneling current per area in tunneling device. However, that Simmons model (eq. 1) produces very accurate values of tunneling parameters for 'r = 0 device'. We will discuss this observation in the frame of effective medium Simmons (EMS) model in *subsection 7.2* in more details. The Dome model and its expansion to multibarrier model (*section 5 and section 6)* exemplify a direct contribution of tunneling in vacuum into transport in mixed single molecular structures devices. This interpretation of experimental data and simulation experiments provide complete respond to the question on comparison of tunneling through PT molecules with vacuum barrier [22].

The consistent progress [e.g.: 14,15] and demonstrated success of Simmons modeling of nanomolecular transport [24,25] is in contrast to scientific reports, which misrepresent molecular nanostructures. For example, it is widely recognized nowadays [27] that first report on conductivity in "single molecular devices" [28] was really conducted for large cluster or small crystal of aromatic molecules. Kirczenow and Di Ventra groups [29,30] already reported that aromatic single molecules cannot produce reported response in ref. 28. The authors of ref. 28 never admitted misrepresentation of 'single molecular junction'. To complete this topic, we have to say that the discrepancy between experimental object and experimental results in [28] still remains a major obstacle for insight and theoretic modeling for scientists, which are not aware about this misrepresentation [31].

7.2. Concept of Effective Medium Simmons (EMS) Model for Mixed Self-Assembled Single Molecular Devices

We propose to use an effective medium Simmons (EMS) model for interpretation of I-V(T) dependence in complex single molecular structures. The I-V(T) dependences can serve as a basis for determining the intrinsic characteristics of the molecular structures: the

composition (e.g.: PT and Me-PET molecules and their ratio), bonding with electrodes and vacuum gaps, temperature dependence, etc. We introduce a vector, m, of the unknown model parameters: $m = [\Phi_B{}^1, \alpha^1, Go^1, \Phi_B{}^2, \alpha^2, Go^2...\Phi_B{}^N, \alpha^N, Go^N]$, and a vector, d, of the observed data at different temperatures: $IV(T_1), IV(T_2)...IV(T_N)]$. Thus, we have the following effective medium Simmons (EMS) model inverse problem [32]:

$$d = A_{EMS}(m) \tag{8}$$

where A_{EMS} is a forward modeling operator described by the corresponding equations of Simmons model, Equation (1). This equation have to be account the features of molecular nanostructures, by modifying Simmons model for cases of parallel and series connectivity of tunneling barires, which are listed in section 6 of this chapter. The A_{EMS} has to be developed individually for each molecular nanostructure. Simulation of *Simmons* transport in 'r = 0 device' demonstrates how the simplest forward modeling operator A_{EMS} in equation 8 is functioning for particular structure of molecular nanodevice.

The effective medium should describe the self-assembled solid state mixtures at average. The choice of adequate effective medium for any molecular nano-device has to include main features of this device. For example for 'r=0 device' the effective medium should include bonded PT molecules, vacuum gap, and limited number of physisorbed molecules, which form a "hot spot" for a tunneling current. Tunneling through all these structural features should be described by Simmons model, and accounted either in parallel, or in series. The fact that simple Simmons model (equation 1) can accurately recover the characteristic of bonded PT molecules with very small G_0, actually means that operator A_{EMS} for this problem is composed on tunneling through PT molecules, which are arranged in small number of hot-spots. In the context of inverse modeling, the G_0 is a weight to tunneling through these hot-spot. The tunneling through majority of PT molecules with one-side bond and vacuum gap has much larger G_0, but the tunneling current will be significantly lower due to vacuum gap connected in series to single bonded PT molecules. Therefore the contribution of other than hot-spot system is negligibly small.

The inversion modeling should recover these structural features. We recommend to conduct the sensitivity analysis for each barrier value, width and transparency before inversion analysis and to analyze the convergence of model. At the same time, if inverse analysis fails to model the molecular structure, this means that some major structural feature is missing in this model. For example, system with charge delocalization in Me-PET molecules cannot be modeled, if A_{EMS} does not include charge delocalization in Me-PET molecular stacks. This indeed will occur at $r > 10^{-3}$ in Me-PET/PT system.

7.3. On Use of EMS Models in Self-Assembled Solid State Mixtures

EMS model can be used in cases of:

1)   Unequal bonds of self-assembled molecules with electrodes

2) Complex and non-symmetric device topography due to different evaporation condition for electrodes. In particular case of 'r = 0 device' the pentathiol (PT) molecules can form the chemical bonds with bottom electrode
3) Complex tunneling pathways in devices based on self-assembled solid state mixture
4) Multi-tunneling barrier structure includes all possible combinations of molecular and vacuum tunneling barriers. Moreover the tunneling barriers in these devices can be in series and in parallel
5) Preferable and discriminated tunneling passways in self-assembled solid state mixtures.

The reason why EMS model can model describe transport in 'r = 0 device' is the fact that the preferable tunneling current in these devices maps shortest and most robust structural features in self-assembled solid state mixtures. The same principles are standing behind transport in more complex devices, as, for example, 'r=10^{-6} device' (case of isolated Me-PET molecules in PT matrix), which is shown schematically the insolated Me-PET molecules in insulated matrix of PT molecules. In this case the Me-PET molecules that have two chemical bonds with upper and bottom electrodes form a preferable parallel tunneling passways in 'r=10^{-6} device'(Me-PET). In this case all single-bonded PT tunneling channels would be discriminated in comparison with double-bonded Me-PET molecules.

There is a possibility of tunneling passways formed by single-bond Me-PET molecules in case of incomplete self-assembly with gold electrodes. This case can be treated as two barriers, formed by single-bonded Me-PET molecular barrier and vacuum barrier. This case can be easily reduced to Dome model (Figure 6), in which these one-bonded molecules are discriminated in respect to double-bonded molecules. The case of the isolated single-bond Me-PET molecules dispersed in matrix of PT molecules remains unexplored.

EMS model is capable to explain even more complex molecular structures, which features single molecular transport as membrane transport, photosynthesis and other charge transport mechanisms in biology. Similar analysis for other molecular self-assembled systems can be found in ref. 24 and 25.

CONCLUSION

In conclusion, we report that Dome and multibarrier model can serve for the explanation of topographic effects in single molecular devices. We conducted an effective medium numerical simulation of Dome model for "r = 0 device' and 'r = 10^{-6} device'. This analysis reveal the consistency with real tunneling features in these devices and demonstrates how complex 3D structure can be reduce to pure case of direct intermolecular tunneling. The novelty of this report is in demonstrated applicability of Dome model for self-assembled solid state mixtures and proven feasibility of our experimental approach. We also believe that the Dome model approach might be generalized on vast amount of single molecular devices fabricated in domain of molecular nanoelectronics. The Simmons analysis of parallel and series connection of molecular wires and spacers in PT/Me-PET mixed self-assembled solid

state mixtures revels the complex nature of tunneling phenomena in organic nanosystem. This analysis is a good example of complexity of structure-property relationship in molecular nanoelectronics and problems that has to be studies and accounted in analysis of transport in these nanosystems. We formulate first the Dome model for the 'r=0 device' and then to generalize this case to effective medium Simmons (EMS) model. The multibarrier approach to molecular system can serve as a general effective medium approach (EMS model), which enables evaluation of structure and composition.

APPENDIX: AUTHORS E-MAIL CORRESPONDENCE WITH DR. REED

The authors find useful to share the authors' correspondence with Dr. Reed regarding ref [4]. We are keeping the exact style of our colleague and our exact responses to our colleague. Despite of some roughness in expressions, it was stimulating discussion, which might serve as a good example of contemporary status in insight of molecular nanoelectronics.

From: Mark Reed mark.reed@yale.edu
To: val@physics.utah.edu
Sent: Sat, November 20, 2010 2:13:17 PM
Subject: JAP 98, 034314 (2005)
Prof. Vardeny;
I've just read your 2005 JAP paper, and have a question.
In Fig. 4, you show transport in the PT film having a current density (@1V) of ~ 10^-4 A/cm^2
This is amazingly low; for example, an oxide film of similar thickness is in the 100s of A/cm^2.
Am I misreading this?

1st letter to Reed:
from Vlad Burtman <vlad.burtman@gmail.com>tomark.reed@yale.edu,

Dear Dr. Reed,
Thanks for your question. The current through pentathiol (PT) matrix was really as low as you read. The origin of this observation is connected to construction of our devices. We were utilizing a material science approach for device fabrication, which is known as solid state mixtures of conductive aromatic molecules in less conductive PT molecules, or PT matrix. It is important to note that (in differ to your single molecule or small molecular cluster approach), we were developing the macroscopic single molecular devices, in which we have ~10^6 conductive wires spatially isolated from each other by PT molecules. In this system we were trying to "emphasize" the features of conductive molecules, so isolated matrix (comprise

of PT molecules) should have the lowest possible conductivity. Therefore we use a thiol molecule with one thiol group for the bottom contact, while the second end of molecule could not have thiol group and, due to that, an Ohmic bond with upper electrode. This is a difference between our study and your research, in which you mostly use (with one exception) the bi-thiol molecules.

In the other words, in addition to molecular PT barrier we have a spatial barrier connected in serial to molecular barrier to enhance the effect of "dielectric" matrix. The second reason is that even in this situation (molecular barrier plus space gap) not all PT molecules have an equally good contact with upper electrode, so current was transferred via "hot-spot mechanism" (see Prof. M. Raikh publications for example), with following intramolecular paths (and associated energy dissipation), rather than through classic direct tunneling via dielectric thin film that you mention in your mail.

We probably have to notify that the current through PT matrix is "effective" current, valid in certain effective media approximation. However discussion of PT matrix itself was not the focus of our study. Unfortunately the inherent problem of molecular electronic is lack of appropriate definition to describe these models. For example, your own "single molecular devices" are not very "single" and I am familiar with scientists which were totally confused by this fact. These considerations are the reason of obvious discrepancy between your expectations and our experimental data.

The other reasons, which have to be mentioned in this context, are connected to a second order effects as phonon contribution. Even these effects have the second order in transport through one single molecule, they could play a major role in molecular transport in our system (and effectively decrease the tunneling current). For example Sezler's and Allara's (JACS, Nanoletters and JPC from 2002-2010) publications developed the concept of "rotation molecular barrier" model. In this model the time dependent molecular rotation deviates from optimal position for tunneling and that effectively decreases the tunneling rate. These considerations lead to recent Galperin-Ratner-Nitzan model of inelastic tunneling in molecules. Again, we are dealing with much larger system than "single molecule" or small molecular clusters. Therefore these effects are amplified (due to shared phonons) by millions of conductive channels in our devices, which is quite different from what you have in mind when you have mention inorganic dielectric film. Eventually even charging (or polarization) and charge delocalization phenomena, which could be completely neglected in single aliphatic molecule, (used as conductive bridge in" single molecule" device), have to be considered in our macroscopic version of single devices.

There are more considerations, which have to be taken into account, but we have arrived here at a convenient point to end our explanation. The first chapters in recent Di Ventra's book on molecular tunneling provide more details on your question.

Sincerely
Vlad- Burtman

From: Mark Reed <mark.reed@yale.edu>
To: Vlad Burtman <vlad.burtman@gmail.com>
Date: Tue, Nov 23, 2010 at 2:59 AM

Subject: Re: your question

11/23/10

dear dr burtman;
thanks for responding
i think you may have misunderstood my question, just about the PT matrix.
the PT film (from the JAP paper) shown a current density (@1V) of ~ 10^-4 A/cm^2;
however, a silicon dioxide barrier of a similar thickness is in the 100s of A/cm^2
this implies your barrier is >> that of SiO2
have you calculated the barrier height?
(by the way, what current density would you get for a vacuum gap of the same spacing?)
if this was true, wouldn't this revolutionize the semiconductor industry?

2nd letter to Reed
From: Vlad Burtman <vlad.burtman@gmail.com>
To: Mark Reed <mark.reed@yale.edu>
Cc: Valy Vardeny <valy_vardeny@yahoo.com>,
val@physics.utah.edu
date: Tue, Nov 23, 2010 at 9:00 AM
subject: Re: your question
hide details 11/23/10

Dear Dr. Reed,
   Thanks for responding. Before discussing a strategic plan to revolutionize the semiconductor industry, lets re-exam two questions from college physic.
   First, as you increase the width of tunneling barrier the tunneling current is decreasing exponentially. It is Simmons law. Second, if you have a set of resistors connected in parallel, which are connected to the same source point, and you will start take out resistors from the circuit, than the current will decrease; and if these resistors are distributed in plane, than the current density in this plane will decrease. It is Kirchhoff law. Please let me know first if you agree with these 2 statements.

   sincerely yours
   Vlad Burtman

From: Mark Reed <mark.reed@yale.edu>
To: Vlad Burtman <vlad.burtman@gmail.com>
Date: Tue, Nov 23, 2010 at 11:11 AM
Subject: Re: your question
11/23/10
   note that this implies that either the molecular layer is far thicker, or the effective area is far smaller, than reported

3rd letter to Reed

Dear Dr. Reed,

Following your recent inquiry, we tried to respond your questions that you asked in appended pdf file.

Sincerely
Vlad- Burtman

From: Mark Reed <mark.reed@yale.edu>
To: Vlad Burtman <vlad.burtman@gmail.com>
Cc: Valy Vardeny <valy_vardeny@yahoo.com>
Date: Thu, Jan 20, 2011 at 9:23 PM
Subject: Re: your question

hide details Jan 20

the reply still does not make any sense

first, i questioned why the resistivity of the devices was so large, NOT small if the device is indeed inhomogeneous, then let us calculate what area is conducting.

i will take as a minimum current density of 100 A per sq cm - this is approximately the tunneling current of SiO2 at 0.1V

(you might want to check your Simmons calculation against the literature)

let's consider just the PT, r=0 case

then from Fig. 4b of your 2005 JAP paper,

one has at 0.1V a current of ~ 2nA

reported device area is ~ 0.5 mm^2, = 5E-3 cm^2

so J ~ 2nA/5E-3 = 20E-10/5E-3 = 4E-7 A/cm^2

for SiO2, ~ 10^2 A/cm^2

this would mean that your real area is ~ 4E-9 times smaller, or less

how many molecules are transporting then?

assume the PT molecule is ~ 3A x 3A ~ 1E-15 cm^2

so area of reported device is 5E-3cm^2;

this means the device has 5E12 molecules

reduced by the factor of the "active" area you claim,

this means you haved 2E4 molecules active

so how many molecules for say a r=10-5 device?

this implies less than one.

CONCLUSION NOTE ON EMAIL CORRESPONDENCE

At this point we interrupted our communication with Dr. Reed, as we did not find reasonable Reed's request to compare our devices with ones having SiO$_2$ layer. This is in

differ to Reed's request to clarify the performance of our devices in respect to tunneling in vacuum, which was very appropriate. It is apparent from Reed's response that he did not find any reason to disagree with our response.

The response to the other Reed's questions in his last email was given already in our previous letter. We felt that Dr. Reed was trying to drag us into the discussion of picture, in which, all molecules are connected by ohmic bonds with both electrodes, while were underling the existence of vacuum barrier almost in every conductive channel. Our response to question about comparison of our device with vacuum, which is shown in Figures 5 and Figures 6 in this chapter, ultimately addresses these.

ACKNOWLEDGMENT

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