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ON TUNNELING THROUGH LANGMUIR-BLODGETT-FILM BASED HETEROSTRUCTURES

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The 1-d model of resonant tunneling through a weakly coupled guest molecule in quantum wires, which has been proposed earlier, is extended on the 3-d case, to examine the role of intermolecular electron-transfer parameters in determining the I–V characteristic of metal-LB-film-metal heterostructures. It is shown that with a reasonable choice of parameters theoretical curve perfectly fits the structure discovered recently in the through-LB-film-current dependence on the applied voltage. This suggests an explanation (alternative to the original version) of the step-like current structure observed in terms of linear resonant tunneling. The key experimental test of our conclusions is also indicated.

Keywords: A. quantum wells, D. tunneling.

THE PERSPECTIVE to obtain novel electrical and optical properties in electronic devices based on organic materials has stimulated a number of attempts to employ molecular aggregates as basic functional units in tunneling junctions [1], quantum wells [2], rectifiers [3, 4], etc. As in the case of semiconductor heterostructures, functioning of the molecular electronic devices is basically determined by tunneling involved processes participated by charge carriers. These processes must be strongly influenced by specific arrangement of molecular energy levels (or narrow conduction bands), by essentially discrete character of molecular functional unites, and by some other factors which are absent or less important in conventional electronic devices. Generally speaking, just distinctions in the energy spectrum and in parameters of the interaction responsible for the electron dynamics give rise to specific behavior of molecular electronic devices in comparison with their semiconductor counterparts.

In a very recent publication [4], the creation of a highly reproducible rectifying device based on the Langmuir-Blodgett (LB) film heterostructure has been reported. Two sets of experiments have been performed with asymmetric and symmetric LB films sandwiched between gold electrodes. In these experiments, the rectifying behavior is revealed only by asymmetric heterostructures. In addition, for both

types of investigated LB films two effects have been observed: a well pronounced step-like structure in the I–V dependence and an abrupt increase in the current above a certain (threshold) voltage value. In this communication, we centre our attention on the manifestation of these effects in a symmetric metal-LB-film-metal heterostructure, to show that they can receive a reasonable explanation within the picture of linear resonance tunneling through a sequence of monolayers. In the original work [4], the step-like structure has been tentatively attributed to the Coulomb charging effect in tunneling through molecular electron levels in the LB film. However, as is shown below the form of the I–V characteristic observed in [4] may reflect, in fact, quite general properties of linear resonant tunneling through a highly ordered molecular system.

Before presenting the strict quantitative description, it is instructive to consider a qualitative picture of the tunneling process through a film consisting of one type of monolayers. This picture is addressed to vertical heterostructures, where the film is placed between the bottom and top electrodes of identical metals. The properties of this structure are supposed to vary only in one (z) direction and to be uniform in transverse (\perp) directions. It is also supposed that the film-to-metal electronic coupling is weak, i.e., that the resonance integral, which determine the electron transfer from

metal to the μ th molecular level of the border layers, \bar{L}_μ , is much smaller, than the interatomic interaction L responsible for the electron mobility in the metal.

In the case of a 1-d quantum wire interrupted by a single weakly coupled guest molecule, characteristics of the resonant tunneling through the guest-molecule electronic state have been studied in detail [5,6]. In particular, it has been shown that if $\bar{L}_\mu/L \equiv \alpha_\mu \ll 1$ (the above mentioned condition of weak coupling), a sharp peak with the half width $\sim \alpha_\mu^2$ appears in the transmission spectrum of the wire at the energy very close to the molecular electron energy E_μ , i.e., the molecular state reveals itself like discrete quantum well state in resonant tunneling.

To adopt the picture of the resonant tunneling just mentioned to the present problem, the 1-d model must be extended on the three-dimensional case and besides, one should take into account that in general, more than one molecular level can participate the electron transfer through LB-based heterostructures. These seem to be minimal complications that makes the model relevant to the real system which has been under study in experiments [4]. The qualitative influence of the intermolecular interaction, which determine the electron transfer between molecules parallel (L_μ^z) and perpendicular (L_μ^\perp) directions with respect to the external field, are clear. In the \perp -direction the device size is macroscopic, so that the intermolecular interaction gives rise to the appearance of the μ th conduction band corresponding to the molecular electron level E_μ . In z -direction, it results in the μ th resonance splitting accordingly to the number of monolayers in the LB film. The interplay between the electron transfer parameters α_μ , $L_\mu^\sigma/L \equiv \beta_\mu^\sigma$ ($\sigma = z, \perp$) and also the relative position of molecular electron levels E_μ determine the transmission properties of the system and thus, the I-V characteristic calculation of which represents the main task of this work.

At first sight the application of the 1s tight-binding model (used [5,6]) for metal electrodes may seem inappropriate. However, we use this model only for the energy interval, where the effective mass approximation is valid. This makes it consistent with the electron dispersion law in metals, $E - E_F \sim k^2$ (the Fermi energy is used here as the point of reference). Another crude approximation made is that the metal-LB-film-metal heterostructure is characterized by a single lattice constant a . A proper improvement of the model, which is not at all problematic, will inevitably lead to the increase of unknown parameters. This seems not reasonable at the present stage of the comparison with experiment. The latter pretends for only qualitative explanation of effects observed in [4], because the quan-

titative comparison will require additional experimental data.

To find the current across the symmetric LB-film-based heterostructure consisting of N identical monolayers, we use the energetic scheme equivalent to that suggested in [4]. Namely, it is assumed that the molecular levels nearest to the Fermi energy are the HOMO and next to it HOMO-1 levels denoted here as E_μ , $\mu = 1, 2$. The electrochemical potential of electrons in metal electrodes is above the HOMO energy, so that at low voltages applied to the heterostructure the current is blocked. The increase of the applied potential eV , which is supposed to shift symmetrically (by $\pm \frac{1}{2}eV$) the electrochemical potential in the source and drain electrodes, subsequently opens molecular levels E_μ , $\mu = 1, 2, \dots$, for the hole transfer. Note that the current-carrying states can also be associated with LUMO and LUMO+1, if they happen to be the nearest to the Fermi level. Obviously, the shape of the I-V curve is dependent only on the relative position of molecular levels and parameters of the intermolecular interaction but not on the HOMO or LUMO state is nearer to the Fermi energy (this is the matter of the direction of the current only). For this reason, we refer to the current-carrying states as to the electron states.

The through LB film current appeared in response to voltage variations can be described by the Landauer formula [7] (for simplicity we consider here only the zero temperature limit)

$$I(E_F, V) = \frac{e}{h} \int_{U(E_F - eV/2)}^{E_F + eV/2} \sum_{j_1 j_2} T_{j_1 j_2}(E, V) dE, \quad (1)$$

where $U(x) = x$ (0) for $x \geq 0$ (< 0), E_F is the Fermi energy in the absence of the source-drain potential difference, and the transmission probability $T_{j_1 j_2}(E, V)$ for the above specified mode takes the form (below we use dimensionless quantities without changing above accepted notations; $|L|$ is used as the energy unit, and a^{-1} – as the wave vector unit)

$$T_{j_1 j_2}(E, V) = 4 \frac{G_{1N}^2(j_1 j_2) \sin k_{j_1 j_2} \sin k'_{j_1 j_2}}{\left[G_{1N}^2(j_1 j_2) - \left[G_{11}(j_1 j_2) - \exp(-ik_{j_1 j_2}) \right] \right] \times \left[G_{11}(j_1 j_2) - \exp(-ik'_{j_1 j_2}) \right]^2}, \quad (2)$$

where

$$G_{1n}(j_1 j_2) = \sum_\mu \frac{\alpha_\mu^2 \sin((N+1-n)q_{j_1 j_2}^\mu)}{\beta_\mu^z \sin((N+1)q_{j_1 j_2}^\mu)}, \quad n = 1, N. \quad (3)$$

It is implied in (1)–(3) that the cross-section of the heterostructure is modelled by a $N_1 \times N_2$ square lat-

tice. The summation over j_1 , and j_2 includes all propagating modes of the transverse (perpendicular to the external field) electron motion. The values of the longitudinal wave vector of propagating and evanescent electron waves in the source and drain leads ($k_{j_1 j_2}$ and $k'_{j_1 j_2}$, respectively) and in the LB film ($q_{j_1 j_2}^\mu$) are determined from the energy conservation law. In particular, for the region of the LB film we have

$$E = E_\mu - 2 \left[\beta_\mu^z \cos \left(q_{j_1 j_2}^\mu \right) + \beta_\mu^\perp \left(\cos \left(\frac{\pi j_1}{N_1 + 1} \right) + \cos \left(\frac{\pi j_2}{N_2 + 1} \right) \right) \right]. \quad (4)$$

By analogy, one can write the corresponding relations between E , eV and $k_{j_1 j_2}$, $k'_{j_1 j_2}$.

It is worth noting that as is shown in [6], the system asymmetry caused by the applied potential ($k_{j_1 j_2} \neq k'_{j_1 j_2}$ at $V \neq 0$) produces a negligible influence on the transmission probability, unless the potential difference between the source and drain leads is smaller, than the Fermi energy. Below, the latter condition is supposed to be fulfilled. Then, the transmission probability can be rewritten in a more convenient form, precisely

$$T_{j_1 j_2}(E) = \frac{\sin^2 k_{j_1 j_2}}{\sin^2 k_{j_1 j_2} + \left(\frac{G_{1N}^2(j_1 j_2) - G_{11}^2(j_1 j_2) - 1}{2G_{1N}(j_1 j_2)} + \frac{G_{11}(j_1 j_2)}{G_{1N}(j_1 j_2)} \cos k_{j_1 j_2} \right)^2}. \quad (5)$$

To facilitate understanding of the above equation, which is used here in calculations of I-V characteristics, it is worth to compare it with the similar result in [6], where the derivation of the transmission probability is given in more detail. To obtain the latter one should set in (5) $N = j_1 = j_2 = 1$ (in this case, $G_{11}(j_1 j_2) = G_{1N}(j_1 j_2) = \sum_\mu \alpha_\mu^2 (E - E_\mu)^{-1}$, $\mu = 1$, and omit the dependence of the longitudinal wave vector on quantum numbers of the transverse motion, $k_{j_1 j_2} \rightarrow k$).

Equations (2)-(5) with $\beta_\mu^\perp = 1$ formally correspond to the one-dimensional heterojunction model in the sense that $T_{j_1 j_2}$ depends on the longitudinal wave vector only (Eq. (1) depends on the density of states and hence, on the dimensionality of the system). However, such a model is not applicable for the description of the LB-film based heterojunctions because presumably, $\beta_\mu^\perp \ll 1$. The latter assumption is consistent with the low electron mobility in molecular systems in comparison with metals and therefore, it is supposed here to be fulfilled. As mentioned above, we also use the effective mass approximation, when considering the electron energy in metal electrodes but not in the

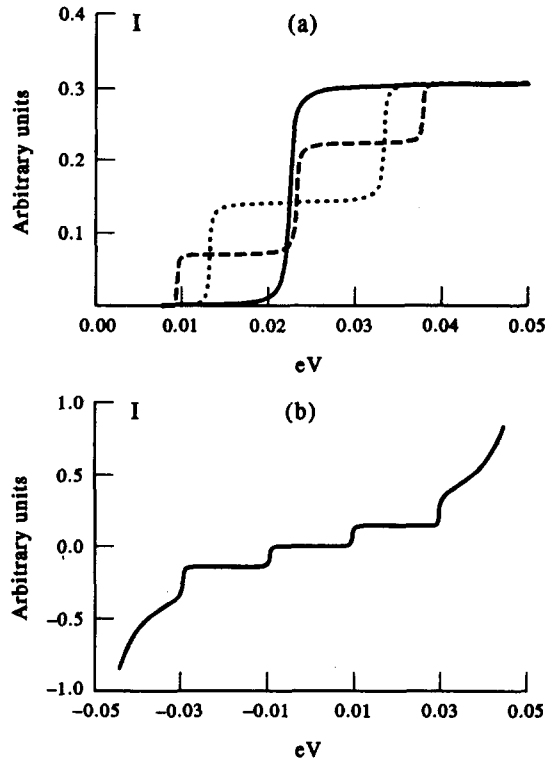


Fig. 1. I-V characteristics for the models of one-level (a) and two-level (b) heterojunctions. (a) Solid, long-dashed, and short-dashed lines correspond to one, two, and three monolayers in the LB film; $\alpha_1 = 0.02$, $\beta_1^z = \beta_1^\perp = 0.005$. (b) $N=2$, $|E_2 - E_1| = 0.155$, $\alpha_2 = 5\alpha_1$, $\beta_2^z = \beta_2^\perp = 6\beta_1^z$, and the values of α_1 , $\beta_1^z = \beta_1^\perp$ are the same as in the case (a).

LB film. This is not a really strict restriction since it is expected that for all energies of interest in the given type of heterojunctions $|E_F| \gg |E_\mu - E_F| \gg \alpha_\mu, \beta_\mu^\sigma$.

Figures 1a,b show I-V characteristics calculated in accordance with (1), (5) for two representative cases of one (a) and two (b) molecular levels which efficiently participate in the through LB film electron transport. These levels, E_1 and E_2 , can be associated either with the lowest unoccupied molecular states, LUMO and LUMO+1, or with the highest occupied states, HOMO and HOMO-1.

(a) **One molecular state.** It follows from (5) that if $\alpha_\mu, \beta_\mu^z \ll 1$, the total transmission coefficient $T(E) = \sum_{j_1 j_2} T_{j_1 j_2}(E)$ exhibits a spike-like energy dependence. For $N = 1$ there is only one peak at the energy $E = E_r^{(1)} = E_1 - 4(\beta_1^\perp - \alpha_1^2)$. The half width of the peak is proportional to α_1^2 , and its value at the maximum $\sim E_r^{(1)}$. Correspondingly, the increase in the applied potential, which makes the electron energy in the source lead higher than the resonance energy, $E + eV/2 > E_r^{(1)}$,

is responded by the step-like increase in the current from nearly zero value to the value proportional to the electron energy (solid curve in Fig. 1a). The resonance level splitting in a double-layer LB film gives rise to the appearance of two peaks in the dependence $T(E)$. As a result, the switching on of the current occurs at lower voltages and the current increase to the maximal value proceeds in two steps (long-dashed curve). It is obvious that accordingly to the present model the number of steps in the I-V characteristic coincides with the monolayer number in the LB film. However, since with the increase of N the distance between the adjacent, the n th and $(n+1)$ th ($n = 1, 2, \dots, N$) peaks, Δ_n decreases, $\Delta_n = 2(\beta_1^z) (\cos \frac{\pi n}{N+1} - \cos \frac{\pi(n+1)}{N+1})$, the step-like current structure in multilayer heterostructures with large N can hardly be observed.

(b) **Two molecular states.** Usually, the high-lying electron states in molecular systems are characterized by larger values of parameters which determine the intermolecular electron transfer. Therefore, in calculations of the I-V dependence for the two-level model we assumed that α_2 and β_2^σ are considerably larger, than α_1 and β_1^σ . At the same time, the intermolecular interaction in the LB film should be much smaller, than the difference between the π electron molecular levels, i.e., $\alpha_\mu, \beta_\mu^\sigma \ll |E_2 - E_1|$. Under these conditions, the level E_2 , which is opened at higher voltages, reveals itself in the I-V characteristic as an abrupt structureless current increase, as shown in Fig. 1b. The threshold voltage is strongly dependent not only on the relative position of molecular levels but also on the coupling parameter α_2 (responsible for the resonance width) and parameters of intermolecular interaction, primarily β_2^σ (responsible for the resonance splitting). As a result, with the increase of the monolayer number the threshold voltage will be shifted towards lower values.

Unfortunately, the characteristic parameters of heterojunctions studied in [4] are practically unknown. Therefore, in the choice of parameters, we have been mainly guided by the best qualitative correspondence between the calculated I-V curve (see Fig. 1b) and the current behavior, which was observed in [4] for the symmetric heterojunction consisting of two monolayers. The theory fits the best experimental results for the following set of parameters: $\alpha_1 = 0.02$, $\alpha_2 = 5\alpha_1$, $\beta_1^z = \beta_1^\perp = 0.005$, $\beta_2^z = \beta_2^\perp = 6\beta_1^z$, $|E_2 - E_1| = 0.155$. Since in accordance with the present model the shape of the I-V curve observed should be very sensitive to the number of monolayers, measurements of this characteristic in heterostructures with the different number of monolayers but otherwise identical will provide a reliable verification of the suggested model. In this connection, it seems helpful to outline once more the

role of characteristic parameters in formation of the I-V curve structure.

Under the condition that the electron (hole) conduction bands are much narrower, than that in metal, and that the interaction, which determines the metal-monolayer electron transfer, is much weaker in comparison with the interatomic interaction responsible for the electron mobility in metal, the interlayer interaction gives rise to the step-like current-versus-voltage dependence associated with the resonant tunneling through a molecular level. The number of steps produced in the I-V characteristic by one "conducting" level (HOMO or LUMO) is equal to the number of monolayers in the LB film. The equality $eV = 4\beta_\mu^z$ gives an estimate of the voltage interval needed to reveal all steps originated from the HOMO (or LUMO) level. The further increase of the applied potential can open the next level (HOMO-1 or LUMO+1) which gives similar step-like dependence but at higher voltages. The relative position of the second series of steps with respect to the first one is determined by the energy difference $|E_2 - E_1|$ and also by parameters of the intermolecular interaction, $\alpha_{1(2)}$ and $\beta_{1(2)}^z$ (see above). Depending on particular values of these parameters (β_μ^\perp plays minor role under the condition $\beta_\mu^\perp \ll E_\mu$), the two series of steps can be either well separated or overlapped. What we see in Fig. 1b are the two steps produced by the molecular level nearest to the Fermi energy, with the second step partly smeared (compare with the long-dashed curve in Fig. 1a) due to the opening of the next level.

In conclusion, it is shown that the step-like structure in the current-versus-voltage dependence is an inherent feature of LB film based heterojunctions, where the electron transfer from metal to the LB film with narrow conduction bands is weak.

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