ELECTRONIC TRANSFER BETWEEN NANOSTRUCTURES. NEGATIVE DIFFERENTIAL RESISTANCE IN CONDUCTIVE POLYMERS

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Abstract

The effect of negative differential resistance can be detected experimentally e.g. in some material systems based on polymers. These observations are sometimes explained being due to the presence of certain carrier traps which can capture the carriers of the electric current. In the present theoretical work we are going to show that besides of this carrier trapping, the origin of the negative differential resistance there can also be caused by an intrinsic mechanism. Namely, instead of the traps, the electron-phonon interaction can be expected to lead to a cooperation of atomic lattice vibrations with the charge carriers, when they tunnel between the localized states, which can in such a way provide the effect the negative differential resistance. A key feature in the present approach is that the electron-phonon interaction is included in a non-perturbative way. The theory will be briefly summarized and numerical calculations will be presented.

Keywords: Electron transfer, conductive polymer, nanostructures, quantum dots, negative differential resistance

1.   INTRODUCTION

The effort of the current basic and applied research towards the miniaturization of the electronic circuits, electronic elements and devices, which lasts already for several decades, has achieved the device characteristic dimensions of nanometers and the current technology is at present able to prepare samples suitable for experimental determination of their physical properties. The characteristic device size of the order of nanometers, or tens of nanometers, means that the lengths of the mean free path of the charge carriers can be longer than the device lateral size.

Among the interesting microelectronic elements there are such that display the negative differential resistance in the current-voltage dependence [1]. Although the effort to comprehend the question of the negative differential resistance (NDR) in nanostructures has been given already a considerable attention, we cannot say at present that the origin of NDR in various nanostructures has been fully understood [2,3].

It is interesting to consider the possible effect of the negative differential resistance in a certain class of bulk materials in which the charge carriers can occupy certain localized states, among which the charges can be irreversibly transferred by the action of the applied electric field. One such possibility can be realized upon using semiconductor quantum dots dispersed within a matrix material [4]. The charge carriers are then supposed to be transferred between the neighboring quantum dots and this kind of the electronic transfer could display the negative differential resistance effect. There is also another possibility of how to realize NDR, namely to use certain organic polymers to which suitable molecular groups are connected, in which molecular groups the charge carriers are supposed to be localized and among which the charge carriers can be transferred by the influence of the applied electric field [1]. Even in this case the charge carriers may display the NDR effect. In the two latter cases [1,4] treated experimentally, the quasi-zero-dimensional nanostructures, at which the charge carriers may be localized, are interacting with the reservoir of the atomic lattice vibrations, be it either the matrix material in which the quantum dots are deposited, or the basic molecular chain of the

polymer. Let us remark that this contact with the reservoir is taken into account when developing the theoretical formula making us able to calculate the current-voltage dependence for the model we consider.

The main purpose of the present work is to demonstrate, that the effect of the negative differential resistance can be expected to occur in the quantum dot aggregates, or in certain polymer materials, already when we take into consideration only the interaction of the charge carriers with the atomic lattice vibrations. Although we are interested mainly in the NDR effect in polymers, it is for us easier to represent the localized electronic states in a conductive polymer by those in quantum dots. In addition to it, in the numerical evaluation we choose the material parameters of ZnO. The negative differential resistance was indicated recently in experiments performed on samples containing ZnO nanoparticles [5,6], which represents another interesting system in the present context.

In the next chapter we shall specify the model with help of which we are going to specify some of the main properties of the quantum dot ensembles [7] or of some conductive polymers [8]. Then we shall specify the Hamiltonian with which we describe the physical model and describe the approximations leading to a formula allowing to calculate the electronic transfer between the quasi-zero-dimensional (Q0D) nanostructures. The numerical calculations of the rate of the transfer of the charge carrier from one Q0D nanostructure to another will be performed for the special case in which we assume that each Q0D nanostructure is approximated by a cubic quantum dot with the material properties of ZnO.

2. THE MODEL

As we have said in the Introduction we wish to study theoretically a material in which the charge carriers are localized in certain quasi-zero-dimensional sites. These sites can be represented for example by certain molecules adjoined to an otherwise nonconductive polymer molecule, or by quantum dots which may be assumed as distributed with some density inside a matrix material. Between the sites the charge carriers are supposed to be transferred by the applied electric field. Although the charge carriers can move in the space of the wave functions of all the Q0D sites of the sample under study, we can make a simplifying assumption by saying that with a good approximation the charge carrier's motion is sufficiently well specified when we consider only two neighborin Q0D sites, namely those between which the charge carrier is transferred by the electric field. Under this approximation our system is reduced to just two such Q0D sites. We assume that even the effect of the negative differential resistance can be manifested well enough already when using this simple double site model. Each one of these two sites is assumed to be connected to the reservoir so that we can then eventually speak about the temperature of the thermodynamic equilibrium system of their atomic lattice vibrations.

We are dealing with the electronic conduction of our system. In some cases, as are those of some conducting organic polymers, the effect of the electric conductivity is provided by the transport of holes. In order that we simplify the exposition of the present topic we shall simply speak only about electrons, having in mind that similar processes may occur also in the hole transport.

In order to be specific in the determination of the properties of the individual sites, we decide that the electronic states of the Q0D sites are represented by electronic eigenstates of a model quantum dot. The model quantum dot is assumed to have an infinitely deep rectangular electrostatic potential of a cubic shape quantum dot, with a certain electronic effective mass m_{eff}. We shall confine ourselves to only a single state given by the lowest energy state of the electronic states of the model quantum dot. Interacting with the applied electric field the electron is supposed to make a transition between the two quantum dots by the effect of the quantum mechanical tunneling. The electron is supposed to be coupled to the vibrations of the atomic lattices of the individual quantum dots. Out of all these vibrational modes we select dispersionless optical vibrations of the atomic lattice, which are assumed to be identical with the bulk modes of the optical vibrations of the material, which is, as we have said, the ZnO crystalline material. In order to keep our approach simple we confine the

electron-phonon interaction to its so called transverse part. The reader is referred to our earlier paper [9], where more details about the present formal approach are given. For example, we can select those optical vibration modes which correspond to the volume of the quantum dot by introducing the suitable form-factor [9] into the Hamiltonian of the whole system we consider.

3. FORMULA FOR CURRENT-VOLTAGE DEPENDENCE

The electronic distribution in our double-dot model is assumed to be homogeneous. This means that both quantum dots have the same electronic occupation densities N_0 and N_1, where $i = 0,1$ are indexes numbering the two sites. In the present paper we show the results computed for $N_0 = N_1 = 0.05$. We assume that the charge carrier first occupies the site with index $i = 0$, with the occupation probability as specified above, and we wish to calculate the rate with which the electron is being transferred to the neighboring site $i = 1$. Because at this process the system is at a state of non-equilibrium, we develop the transfer rate formula with help of the non-equilibrium Green's functions [10].

In the course of the derivation of the rate formula we first perform the so called Lang-Firsov (see [9] for references) transformation. In this way we include the electron-phonon interaction in an exact way. In the next steps, we neglect completely the quantities in the transformed Hamiltonian which have the meaning of the energy of the polaron well in the individual quantum dots. Also, the electronic quantum mechanical tunneling operator, which is considered as weak, and which gets a more complicated form after the Lang-Firsov, is simplified in the present theoretical approach. Namely, we confine the new tunneling operator to only such terms which are of the first order in powers of phonon operators. Also, we neglect that part of this transformed tunneling operator, which does not depend on the phonon particle operators at all. This latter approximation amounts to neglecting the electronic energy level splitting during the electronic transfer and due to this approximation the transfer rate formula may regarded to correspond to an incoherent electronic transfer. This latter approximation has in fact been undertaken by the classical researchers deriving the Marcus transfer rate theory or Förster's theory for exciton transfer (see [9] for references).

The resulting formula (see [10] for general approach) for the electronic transfer rate has the form of a convolution of the energy dependent spectral densities of the electron at the both sites $i = 0,1$. The two convoluted spectral densities come out shifted with respect to each other by the optical phonon energy. These spectral densities are determined from the Green's functions, which are given by the self energies determined self-consistently for the system of the electron moving in the space of two localized states interacting with phonons. The electron-phonon interaction is included in the self-consistent Born approximation (a nonperturbative approximation).

The self-consistent Born approximation for the inclusion of the electron-phonon interaction does for us a similar help as was done earlier by the macroscopic fluctuating parameter introduced in the electron transfer theory by Marcus [11]. We can understand this parameter's role in the following way: The electron, having a sufficiently long mean free path, reflects at the boundaries of the Q0D nanostructures and therefore finds conditions for coherent processes of multiple scattering with the phonon modes. During these coherent multiple collisions virtual optical multiphonon states can be assumed to be produced. These coherent phonon excitations can be then viewed as some macroscopic oscillations of the atomic lattice. As such the atomic lattice represents an outer force field, which depends explicitly on time. The effective Hamiltonian for the electron then depends on time and similarly as in classical systems we can regard the single electron energy concept in the system as somewhat restricted. In this way we can understand why the transfer rate formula does not depend on the energy conserving delta-function. Let us say at this point that we can rather appreciate Marcus's intuitive introducing of his macroscopic fluctuating parameter into the electron transfer theory [11].

The transfer rate formula for our present approach is specified in a larger detail in our earlier paper [9] to which the reader is referred.

4.   NUMERICAL RESULTS

The numerical calculations are performed for two coupled cubic shape quantum dots. These quantum dots have the lateral size of 12 nm each. The material of the quantum dots is the crystalline compound ZnO, in which the optical phonons have the excitation energy of 72 meV. As said above, the occupation of the dots is 0.05 of electron in each quantum dot. The parameter characterizing the electron tunneling is dependent on the distance of the separation of the quantum dots in space. We assume a situation, or such a density of the distribution of the Q0D electron sites in the volume of the sample, which corresponds to the magnitude of the tunneling parameter of 10 meV. Other parameters especially those enabling us to specify the magnitude of the electron-optical phonon coupling (Fröhlich's coupling) are those of ZnO. The electron occupation transfer rate is calculated as a function of the electric field assumed to be applied to the pair of the coupled dots. The electric field is simulated by assuming electronic orbital energy shift of the site number 1 with respect to the orbital energy of the state $i = 0$. This energy difference is at the x-axis in **Figure 1**.
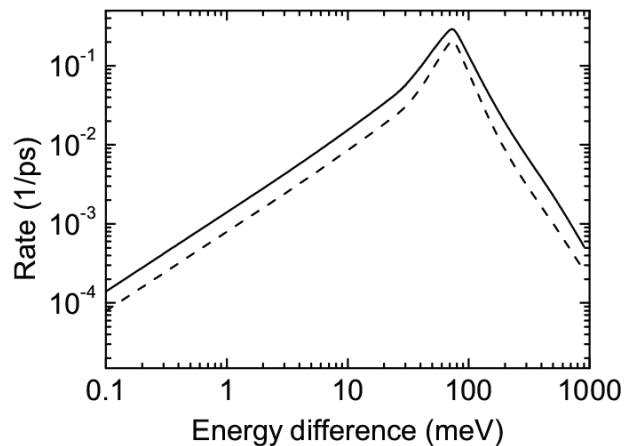
Figure 1 Rate of electron transfer between two ZnO quantum dots, at the atomic lattice temperature T_{LO} equal to 300 K (full) or 70 K (dash)

We see that the current-voltage dependence in this Figure has partly a nearly power law dependence of the straight line parts of the electric current dependence on the electron potential difference. This shape of the transfer rate is quite similar to the dependencies found in experiment on polymers [1]. The calculated rate is shown for two temperatures, 300 K and 70 K. Both the dependences have similar overall shape. The quantitative difference between these two curves is not significant. Both curves have a maximum at the electric field potential approximately equal to the optical phonon energy. The electric field potential difference larger than the optical phonon energy corresponds to the electric field at which the system shows the negative differential resistance.

The present simple model does not show the electronic rate increasing at the side of the large electric field values. We regard this absence of the increasing rate to our simple model. We might expect that assuming the presence of an optical phonon branch with larger energy could provide such a feature in the calculated dependence of **Figure 1**.

The property of the negative differential resistance thus may show us the significance of the nonadiabaticity of the electron-phonon interaction. The nonadiabatic effect of the electron-phonon calculation is introduced into the present calculation upon by determining the electron self-energy in an approximation which goes beyond the limits of any finite order perturbation calculation. From this point of view it may be useful to compare our nonperturbative approach with the recent theoretical analysis [12] of similar questions in conductive polymers.

5.   CONCLUSIONS

We have presented the model system which shows that the tunneling of electron between two quasi-zero dimensional nanosystems, in cooperation with electron-phonon interaction, included into the calculation in a nonperturbative way, can display the negative differential resistance works in the nanostructure systems, in

particular in conductive polymers. We can understand this finding as a possible interpretation of the negative differential resistance in conductive polymers. We suggest to regard this theoretically shown mechanism to be a manifestation of the electron-phonon nonadiabaticity in quasi-zero-dimensional structures. We admit that the mechanism, which we have suggested, can probably coexist with other possible mechanisms. We also conclude that the present model deserves further generalizations for the purpose of getting the theory which allows for a closer comparison with the real systems in experiment. The comparison of the calculated results with experiment appears interesting. Nevertheless, as for the future work, it would be enjoying to obtain from quantum chemical calculations some realistic single electron wave functions, electron energies of localized states and realistic values of the electron-phonon coupling constants for a real conductive polymer material, and perform then with such input data the negative differential resistance calculations.

ACKNOWLEDGEMENTS

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