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Tunneling-based charge percolation transport in a random network of semi-conductive nanoclusters embedded in a dielectric matrix

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ABSTRACT

The percolating tunneling transport of electrons in a random network of nanoclusters made of semi-conductive material and embedded in a dielectric matrix is studied in a simple model. Despite some strong assumptions, the model is able to reproduce results already reported in the literature, like the critical behavior of the current density at small volume fractions of nanoclusters. Due to its simplicity (e.g. contribution to the local conduction only from nearest neighbors), the model predicts a near-critical variation of the conductance which is rather close to the universal power-law behavior of a direct-contact composite material. In addition, the method can also compute total average numbers of electrons and their spatial distribution established in the sample operated in stationary regimes. Using such features of the model, optimal device configurations can be designed for optoelectronic applications.

1. Introduction

Composites obtained by mixing materials of different properties have long been considered as best solutions for various practical problems and, therefore, have been under intense investigation [1–4]. One of the current applications of such complex materials is obtaining active media in optoelectronics by embedding conductive nanoclusters (NCs) of convenient sizes in dielectric host matrices [5]. Various procedures for preparing random networks of (semi-) conductive NCs, with controlled diameters, in dielectric host materials have been developed to date [6–9]. When the background material for such photonic devices is silicon, the possibility of integrating them in usual, silicon-based, microelectronic chips becomes, technologically, very attractive [5]. Excitonic states confined in the NCs (whose band gaps are direct and larger than in the corresponding bulk versions) lead to intense photo-luminescent responses through optical transitions [6]. The morphologic features of NCs are obviously crucial in obtaining high-rate optical recombinations. However, when integrating such devices on microelectronic chips one may need to induce the excitonic states by electric stimulation and this operation mode implies processes of charge transfer between neighboring NCs. Therefore, understanding the whole picture of these electro-luminescence phenomena includes detailed clarification of charge propagation through the network of NCs. When their density in the host dielectric becomes large enough, but not sufficient for establishing electrical contacts, tunneling charge transport will clearly dominate. Ideally, the embedded NCs could be treated as a regular network for describing the related transport issues [8]. However, from the practical point of view, no significant regularity may be expected and their ensemble should be more accurately treated as random. Charge transport in such a random lattice is percolating in nature and should display the characteristic features of the related statistical phenomena [3,4,10,11]. Percolating charge transport is itself a vast and well covered field of research [10–12]. Among the multiple aspects within its range, the charge percolation through quantum tunneling between neighbor nodes of the random network show peculiar behavior and recently attracted considerable interest in the specialized literature [3,4,13–29]. The present research focuses on the charge tunneling percolation (TP) phenomena as the main transport mechanism in a random network of semi-conductive NCs embedded in a dielectric host matrix. More precisely, the NCs act as nodes of such a random network, where radiative recombination processes are also assumed to occur. To get a working idea of how to optimize the structural and functional parameters of a light emitting device based on such a composite structure [8] it is therefore important to have a detailed image of NCs population with mobile (i.e. tunneling) charges of both signs under various conditions. As this is a project that would entail rather large computing effort, it was split in stages dealing separately with TP of electrons, of holes and their interaction on NCs through recombination processes. In the present paper, only TP electron transport is considered and the related results are reported which can be then easily translated into a hole-only TP transport picture. The system will be assumed in a stationary state under a constant external bias. Also, in order to keep the computing time at reasonable levels and to focus only on transport phenomena, several important simplifications had to be considered. The used

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approximations will be detailed and discussed in the following sections. Despite the relatively simple model adopted, many features of the electron TP are revealed, in accordance with theoretical and experimental results reported previously in the literature. In addition, the model allows one to straightforwardly relate these peculiar features to the spatial charge distribution in a particular operation regime of the sample. Besides being a useful method of analysis in itself, the proposed model proves to be a solid basis for a further detailed description of a TP-based light emitting device.

2. Model description

A randomly positioned network of *identical spherical* NCs is considered as being embedded in a sample of dielectric material shaped as a rectangular parallelepiped (Fig. 1). Charge (electron) transport through it is assumed to occur through sequential quantum tunneling processes. Thus, when a *stationary flow* of charge is established, each NC contains a certain stable (on the average) amount of electrons. Fractional *stationary* values of these NC charges should be regarded as time averages of rapidly fluctuating (integer) numbers which actually define the *instantaneous* NC charge [30,31]. The electron flux is injected into the sample through its bottom plane, where a grounded cathode is attached. The upper side of the sample is kept at a certain positive potential V by another electrode. Both the injection of electrons into the sample and their exit are assumed to take place through quantum tunneling effects. The assumed structure of each individual NC consists of an inner core, of diameter D_{in} (containing the conductive or semi-conducting material), enclosed in a dielectric outer shell, of diameter D, which is essentially a substoichiometric compound of the material of the NC with that of the host matrix [6,7]. At usual bias voltages, the tunneling probability of an electron between two NCs will be considered as vanishingly small if they are separated by distances larger than $D - D_{in}$ (the host material is assumed with even larger band gap than the NC shells, so tunneling trough this dielectric is essentially prohibited) [20]. On the other hand, $D - D_{in}$ is also the minimum distance between two distinct NCs and will be actually the tunneling distance for electrons. Generic values for the dimensional parameters of NCs are $D = 5$ nm and $D_{in} = 3.6$ nm. Such values are consistent, for example, to size parameters of already obtained random networks of silicon nanoparticles embedded in silicon oxide matrices [5–7], thus forming composite materials of major importance in various optoelectronic applications [5,8]. The sample can be further partitioned in a regular network of cubes of edge length D, where NCs may be eventually placed according to a uniform probability distribution. The external bias is applied along the z-axis. The sample is assumed as a rectangular parallelepiped, with a squared base in the x-y plane. The height of the sample (along the z-axis) will be denoted by H and the lengths of the basis edges by L. To facilitate the analysis, the sample is split in slabs parallel to the x-y plane, each of height D. In this arrangement, the electrons can tunnel only between NCs occupying adjacent cells either "vertically" (that is along the z-axis) or in their own "horizontal" slab (Fig. 1).

The applied bias should produce a "macroscopic" uniform electric field in the sample, along the z-axis: $F = \Delta V/H$, where ΔV is the voltage drop over the whole composite material. Nevertheless, the presence of the conductive NCs must influence the local electric field strength in the dielectric host. Also, the local field in each NC's neighborhood should be more complex: it should depend on the NC position in the sample and should not be always directed along the axis of the "macroscopic" field. However, in order to get a tractable model, such a complicated picture should be drastically simplified, e.g. by a mean field description. Similar approaches are frequently used in the literature, either in the form of effective tunneling conductivities [17,18,21,24] or by introducing a mean field in a Fowler-Nordheim tunneling equation [25]. We have taken a different (slightly more detailed) approach in our computations by first assuming that, on the average, the electric field is identical in each NC shell, both in value and in its orientation (along the z-axis). It follows that the "in-slab" tunneling occurs through a simple rectangular potential barrier and that, for the "vertical" tunneling, one should consider identical trapezoidal barriers. Moreover, to compute the field strength in the NC shell, we considered that, given the small size of each NC, it may be regarded (the shell included) as embedded in a uniform composite dielectric environment formed by the sample's host matrix combined with the spatial random spread of NCs. The textbook example of a dielectric sphere in a uniform external field [32] can then be easily extended for our NC-shell-composite dielectric case. Thus, assuming that the field is uniform at large distances from the NC and that the space charge vanishes in the vicinity of the shell boundaries (in order to simplify the field connection conditions at these boundaries), one may straightforwardly apply electrostatics to obtain the following form of the field strength in the shell at its frontier with the NC:

$$F_{eff} = \frac{9}{\Lambda}\frac{K_{nc}}{K_s}\frac{\Delta V}{H}, \tag{1}$$

where $\Lambda = \left(2+\frac{K_s}{K_c}\right)\left(2+\frac{K_{nc}}{K_s}\right)+2\left(1-\frac{K_s}{K_c}\right)\left(1-\frac{K_{nc}}{K_s}\right)\left(\frac{D_{in}}{D}\right)^3$. We have denoted by K_{nc}, K_s and K_c the dielectric constants of the NC, of its shell and of the composite, respectively. To estimate ΔV, one may assume

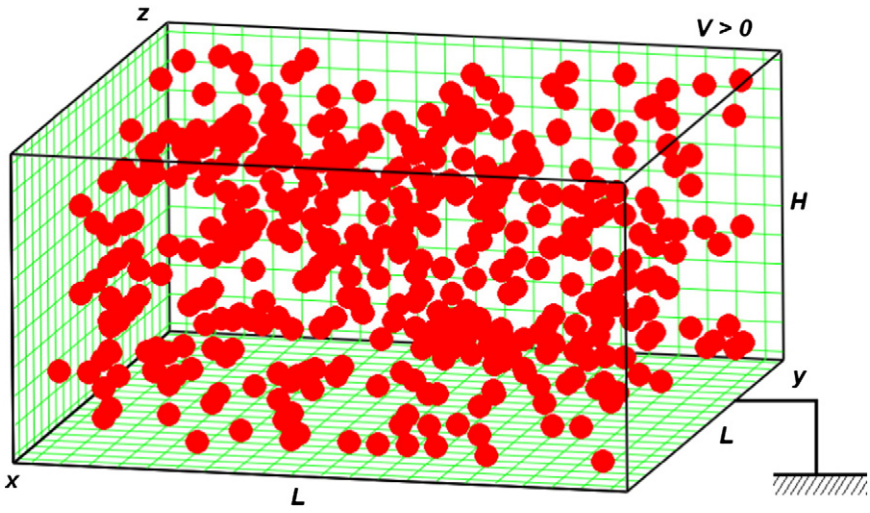

Fig. 1. Schematic representation of the piece of composite material considered in the model: The sample is a rectangular parallelepiped with height H and a square basis of side L. The embedded NCs are identical and form a random network. The external bias is applied between the lower basis (which is grounded) and the upper one.