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The interplay between Arrhenius and hopping conduction mechanisms in a percolating nanowire network

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Abstract

This study investigates the influence of different transport mechanisms on the conductance/resistance of devices based on percolating networks of semiconducting nanowires. We simulated systems such as random resistor networks where both Arrhenius and variable-range hopping mechanisms take place at the same time, and compared the results with experimental ones. Our assumption was that each mechanism represents only a fraction of the nanowires in the system and that the network resistance is given by the direct sum of the contribution of the mechanisms. An unexpected behavior observed in the experimental measurements led us to propose this approach, and the numerical results found in our simulations suggest that this model can explain the experiment.

Keywords: percolation, nanowires, transport mechanism

(Some figures may appear in colour only in the online journal)

1. Introduction

Self-assembled nanowires and nanobelts have attracted much attention in recent years due to their peculiar electronic and optical properties from the point of view of fundamental physics and technological applications [1–5]. The nanowires' growth is based on the well-established vapor–liquid–solid mechanism (VLS) in which the precursors in the vapor phase are carried to a region of constant temperature where the vapor is adsorbed by catalytic drops which start the growth. The catalyst acts as the energetically favored site for vapor-phase reactant adsorption and the nucleation site for crystallization when supersaturated [6]. For the investigation of the electronic properties of these systems, many authors have used temperature-dependent resistance measurements, which is a standard technique for probing electron transport mechanisms in different systems. Usually, the resistance in semiconductors can be described by an Arrhenius temperature dependence (thermally activated) as shown by equation (1)

$$\rho(T) = \rho_0 \exp\left(\frac{E_G}{2k_B T}\right), \quad (1)$$

where ρ_0 is a pre-exponential factor, E_G is the activation energy (usually the energy gap), and k_B is the Boltzmann constant. However, the presence of some degree of disorder in such nanostructures, which unintentionally appears in the nanowire, drastically affects the injection of current through the nanostructure [7, 8]. Usually, the disorder leads to carriers localization and it is possible to observe a transition from a simple thermal excitation mechanism to a more complex one (such as a variable-range hopping (VRH) mechanism [9]). The VRH mechanism arises when there is a sufficient amount of disorder states causing the random component of the crystalline potential to be large enough to localize the electron's wave functions near the band edges [10, 11]. The resistance in this case is written as

$$\rho(T) = \rho_0 \exp\left[\left(\frac{T_0}{T}\right)^m\right], \quad (2)$$

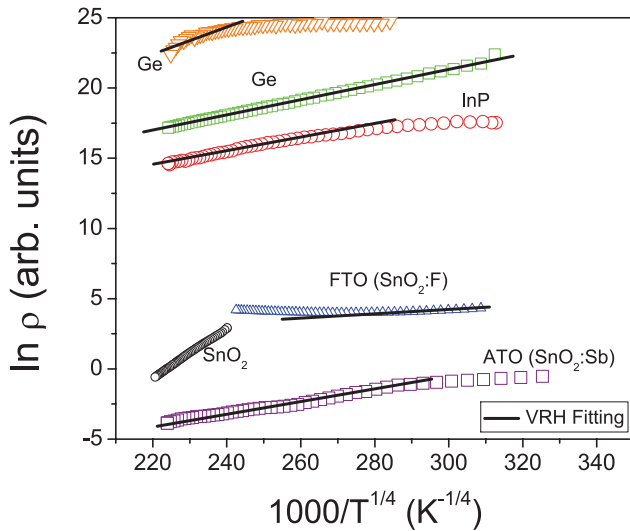


Figure 1. Temperature-dependent resistivity performed in devices based on different nanowires. VRH fitting shows, for some materials, that there is more than one mechanism acting on the electronic transport.

where T_0 is a constant that depends on the localization length and the density of states at the Fermi level. The VRH mechanism normally occurs only in the temperature region wherein the energy is insufficient to excite the charge carrier across the Coulomb gap between two sites. Hence, conduction takes place by hopping of small region ($k_B T$) in the vicinity of the Fermi level where the density of states remains almost a constant ($m = 1/d + 1$), where d is the dimension of the system. This condition is fulfilled when the temperature is sufficiently small or when the energy states are uniformly distributed [9].

Both resistance behaviors such as those described above are observed in nanowires produced by the VLS mechanism: there is no way to separate those that obey the Arrhenius law from those characterized by the hopping mechanism. Then, the electronic behavior of a device based on VLS nanowires will only be known after it has been built. As found in many papers in the literature [12, 13], this picture agrees with both single and multiple nanowire devices (network devices).

As an example, figure 1 shows experimental temperature-dependent resistance measurements for different materials. It is possible to observe that some of them (with the exception of Ge and SnO₂) cannot be described by a simple thermal excitation mechanism or the VRH mechanism either.

Devices based on a percolating network of nanowires are very promising due to the enhancement of the signal-to-noise response when subjected to different environments. This feature makes percolating devices useful for the development of different sensors, and here we will study the electron transport in these systems as a function of the combination of a random two-dimensional dispersion of nanowires characterized by distinct transport mechanisms.

We used percolation theory in the framework of Monte Carlo methods to simulate the electronic transport in an ensemble of nanowires, looking for the relative contributions of Arrhenius and hopping mechanisms to the net conductivity of the ensemble. In this scenario, Monte Carlo methods are

useful because they allow us to test a large number of ensembles and analyze networks where the analytic problem is impossible to solve. Using this approach we found that the mixture of these mechanisms can change the slope of the resistance-versus-temperature curves as seen in the experimental results in figure 1, which explains the presence of more than one transport mechanism.

This paper begins by giving a brief overview of percolation theory and its use in random resistor networks. After that, we introduce the methodology used to solve the problem mentioned above. Next, we present the validation of our model in the context of percolation theory, the results for different mixing of the mechanisms and the results which reproduce the behavior that is observed experimentally. Finally we draw conclusions about our findings.

2. Theory

Percolation theory can be used to study carrier transport in complex systems such as multiple-nanowire devices. In this model, electrical conductance is expressed by a power-law dependence [14] as shown by equation (3)

$$G = G_0(n - n_c)^\alpha, \quad (3)$$

where n is the density of elements, $n_c = 1/\pi(4.236/L)^2$ is the percolation threshold and α is the critical exponent. For 2D networks, theory predicts that $\alpha = 1.33$.

In order to simulate percolating networks, we used Monte Carlo methods to study a random arrangement of one-dimensional sticks. Networks composed by such elements were considered as ideal two-dimensional thin films over an insulating substrate. This assumption is reasonable because the nanowire's cross section is negligible when compared to its length [15]. The first step of our computational simulation was to randomly place each stick with length L and orientation angle θ (with $-90^\circ \leq \theta \leq 90^\circ$) over the substrate. As nanowires are grown by a self-organized mechanism, their length and width can vary within a range of values. Hence, we choose to use a normal distribution equation (4) to provide the stick length that we used in the simulations:

$$f(L, \mu, \sigma) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(L - \mu)^2}{2\sigma^2}\right], \quad (4)$$

where L is a statistical variable of the stick length, μ is the mean of the distribution and σ is the standard deviation.

The next step was to find a percolation pathway in the network. This pathway is composed of sticks that are connected and make a spanning cluster through the system. To calculate the value of G in equation (3) a percolation pathway must exist between the electrical contacts where the conductance is measured. A cluster-based mechanism was used to identify percolation pathways which were analyzed as a random resistor network, considering connections between two or more nanowires and connections between nanowires and

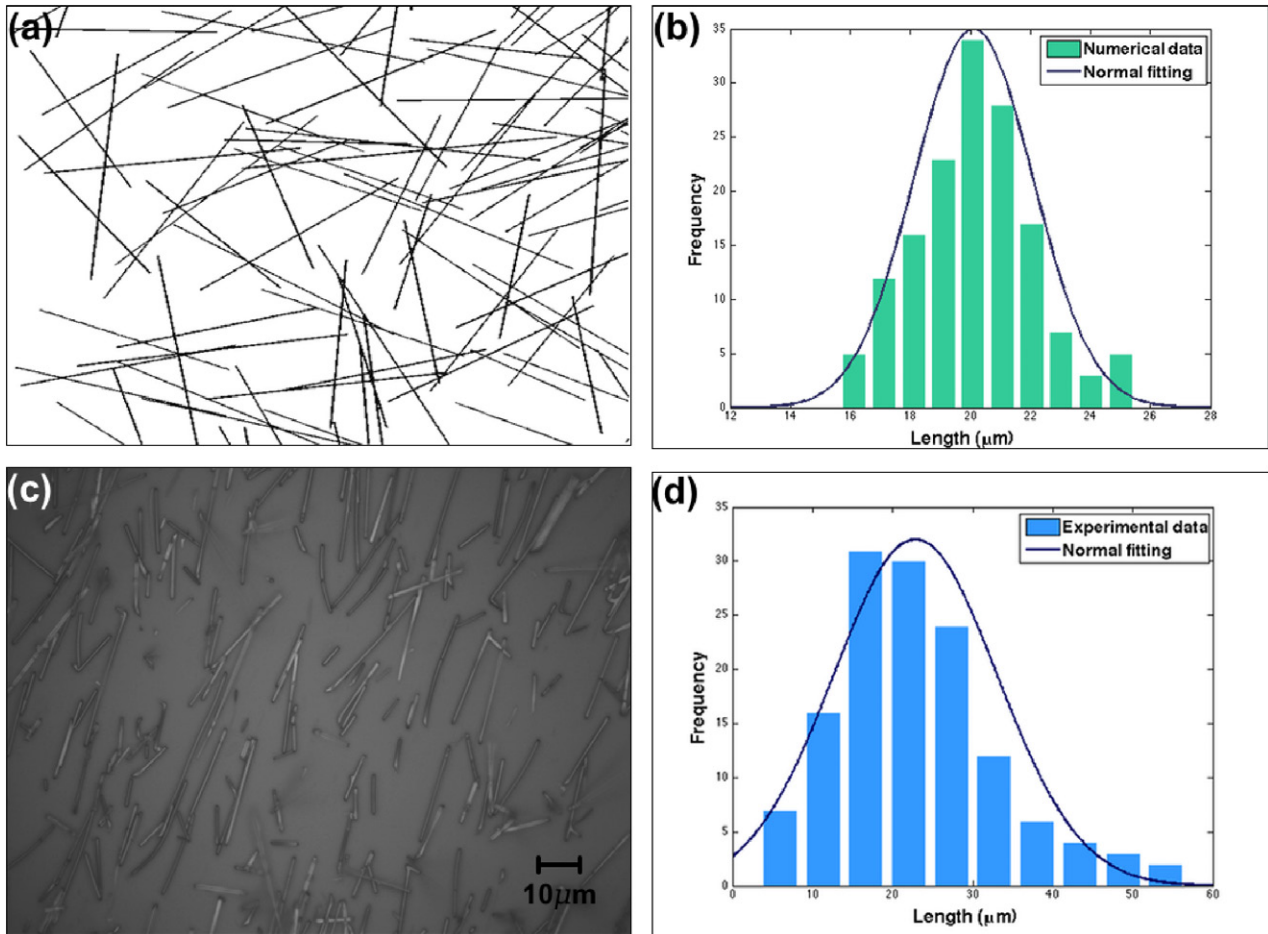


Figure 2. (a) Simulation of a network with randomly positioned and oriented sticks. (b) Nanowire length distribution obtained using equation (4). (c) SEM image of a substrate covered with a random dispersion of SnO₂ multiple nanowires. (d) Nanowire length distribution from the experimental data in (c).

electrical contacts (positioned on the top and on the bottom of the system). Therefore, the algorithm runs over all nodes, junctions between two or more sticks, and determines which are connected. All identified connections are stored in a sparse matrix which will be used in further calculations.

Finally, a node-elimination algorithm [16] was implemented to solve Kirchhoff's current law for each junction in the network. Each node is identified as internal or external. The former define the network itself and the latter are the electrical contacts of the device. In this method, the internal nodes are removed in sequence and new connections are created between their neighbors to update the network conductance. This process is repeated until all internal nodes are removed and only the external nodes, where the voltage is known, are left. Then, the nodes are reintroduced into the network in a reverse process, i.e. from the last node to the first one. However, the conductance of the last node is known, because it was calculated in the last step of the forward process, and it allows us to calculate its voltage. Therefore, it is possible to calculate the voltage in the previous node and so on.

As mentioned above, both Arrhenius and hopping mechanisms of thermal activation are equally probable. Thus, the electronic behavior of a device based on VLS-grown nanowires should take into account these mechanism, at least. In our

study, we considered that each stick in the network follows an individual transport mechanisms given either by Arrhenius or hopping laws, equations (1) and (2), respectively. The question here is how to decide the amount of different nanowires with distinct transport mechanisms which contribute to the whole conductance/resistance. Moreover, we studied systems with different proportions of nanowires that have both mechanisms of transport and analyzed their effects on device resistance. In order to take account of these different contributions, we supposed a simple relationship between the overall resistance and the individual contributions from both Arrhenius and hopping mechanisms, as shown by equation (5).

$$\rho_T(T) = x\rho_{AR}(T) + y\rho_{VHR}(T), \quad (5)$$

where $x + y = 1$, $\rho_{AR}(T)$ is the resistance contribution due to the Arrhenius law, given by equation (1) and $\rho_{VHR}(T)$ is the resistance contribution due to the hopping law, given by equation (2).

3. Results and discussion

Here, we performed numerical calculations for the electronic transport based on nanowires and devices built in our

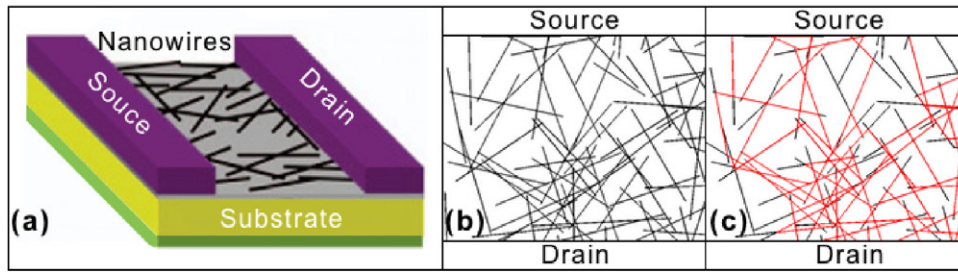


Figure 3. (a) Sketch of a network of nanowire devices with two electrical contacts (drain and source). Adapted from [21]. (b) Network simulation with sticks randomly positioned and (c) percolation pathway found in the network (red).

laboratory [17–20]. The synthesis of nanowires was based on the well-known VLS growth method [6]. In this approach, a catalyst seed in the liquid phase is used to act as a preferential site for the adsorption of material vapor. The seeds also offers better control over the process since the lateral nanowire dimensions are driven by the size of the growth seeds. The seeds were prepared by thermal annealing from a gold layer (1–3 nm thick) deposited over silicon substrates. In order to perform the synthesis a quartz crucible loaded with precursors (powders of the materials of interest) and silicon substrates were placed into a tube furnace (Lindberg/Blue M). Prior to the heating process, the tube was evacuated (10^{-2} Torr) and purged by using a 10% H_2/He flux (purity > 99.998) in order to avoid the undesirable presence of oxygen (this step is not used for metal oxide samples). Next, the H_2/He flux was adjusted between 10 and 30 sccm and the furnace temperature was continuously raised until it reached the ideal value for the synthesis process. After the sample's growth, the external heater was turned off and the furnace was left to cool down to the ambient temperature.

The devices built with these nanowires were fully experimentally characterized and provided important parameters for the simulations, for instance, film length and nanowire mean length. Figure 2(a) shows a simulation result considering random position and orientation for the nanowires; figure 2(b) shows the distribution of nanowire length obtained in our simulation; figure 2(c) shows an image of a real device composed of multiple semiconducting nanowires over an insulating substrate and figure 2(d) shows the length distribution for the sample in (c). For the experimental data, the length distribution can be fitted with a Gaussian curve and for this set of nanowires the mean length is $22.8 \mu\text{m}$ and the standard deviation is $10 \mu\text{m}$. From the images above, it is possible to see that both randomness and Gaussian length distribution are well described by simulations. Hence, we can affirm that realistic characteristics of the system can be reproduced by computational simulations using the methodology already described.

Figure 3(a) depicts a sketch of the structures which were studied: a random dispersion of nanowires on the surface of an insulating substrate where two electrical contacts were previously prepared (source and drain). An actual result of the stick's network simulation is shown in figure 3(b). Each connection between two or more sticks was considered as an electrical contact and thus contributes to the overall resistance. However, not every stick participates in the electrical

conduction, as clearly shown in figure 3(c) where only the sticks involved in the conduction process were highlighted (in red). The red sticks represent the percolation pathway found in this network and they are fully responsible for the conduction of carriers. When the pathway is found in the network, the algorithm looks for sticks that do not belong to the cluster and removes them. Moreover, the pathway is trimmed in order to eliminate 'dead-ends' that do not contribute to conduction.

In our investigation we considered two sources of resistance: R_{NW} for the nanowires and R_j for the junctions. R_{NW} can assume each one of the mechanisms given by equations (1) and (2), relying on the type of nanowire, which is randomly chosen. For R_j we used different possibilities, which will be discussed later. To verify the exponential law characteristic of the percolation behavior, we ran 30 simulations for random sets of films, varying the density from 0.3 to $0.8 \text{ NW } \mu\text{m}^{-2}$. The mean length (L) of the nanowires and the length (W) of the film was given by the devices built in our laboratory. In our simulations we used the sticks' mean length $L = 4 \mu\text{m}$ and film length $W = 40 \mu\text{m}$. Figure 4 shows the average conductance as a function of density for 30 randomly selected networks. In figure 4(a) we considered only the hopping mechanism; in figure 4(b) we considered only the Arrhenius mechanism and in figure 4(c) we assumed a mixture of both mechanisms, with half of each one. For the critical exponent, we found, $\alpha = 1.34$, $\alpha = 1.33$ and $\alpha = 1.30$, respectively. These values are in agreement with the theoretical value for 2D systems, which is $\alpha = 1.33$. Moreover, this last result shows that the exponential law for conductance in percolation theory is valid even for a mixture of mechanisms, which have not been reported in literature yet.

For all simulations reported here we considered that between two nanowires there is a source of resistance (R_j) due, mainly, to an oxide layer that can exist around the nanowires and can create a barrier that contributes to the network resistance [8, 22]. We studied two different possibilities for the contact resistance: (i) R_j constant and (ii) $R_j = R_j(T)$. In this last case we used a model from [20]. Due to the barrier between the nanowires, we supposed that $R_j > R_{NW}$.

After the theoretical verification of our model, we used the elimination algorithm [16] to calculate the network conductance for the temperature range from 77 to 300 K, which is a characteristic range used for temperature-dependent resistance measurements. In these simulations we considered the Arrhenius and hopping mechanisms separately and different

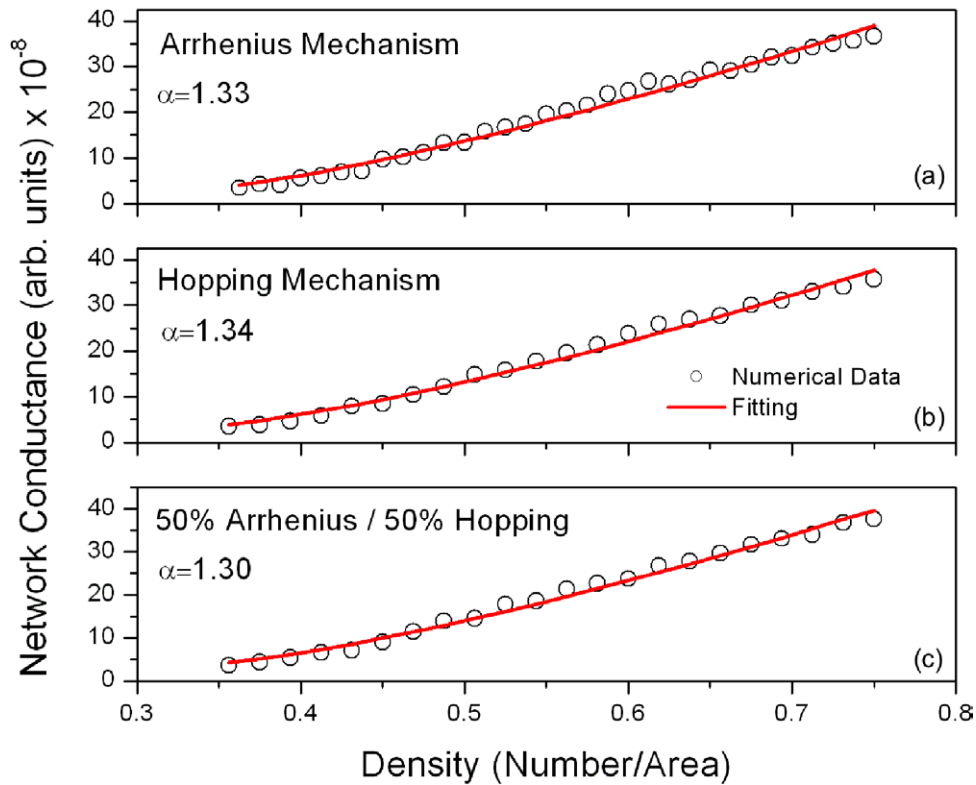


Figure 4. Mean value of network conductance versus nanowire density for a set of 30 randomly generated films. In (a) we considered only the Arrhenius mechanism; in (b) we considered only the VRH mechanism and in (c) we mixed both mechanisms. The red line is a fitting of the percolation theory that gives the critical exponent for the networks.

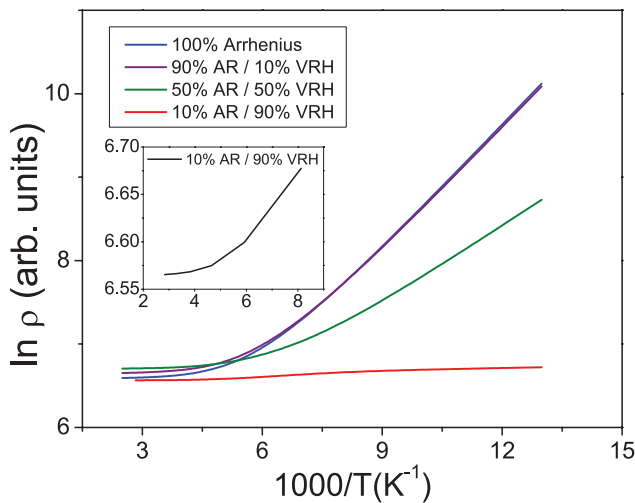


Figure 5. Numerical results for electrical resistivity versus the reciprocal of temperature. Different proportions of nanowires of both transport mechanisms were considered in these simulations. Inset: predominance of the VRH mechanism showing that this curve is not linear with respect to T^{-1} .

mixtures of them were used. The parameters (n , L , W and R_j) used here are the same as those mentioned above. The results of our simulations are shown in figure 5, and show that our assumption has some impact on the electrical behavior of the device: the resistance-versus-temperature curves bend as the mixtures of mechanisms vary; more specifically, when the Arrhenius regime becomes dominant. This change in

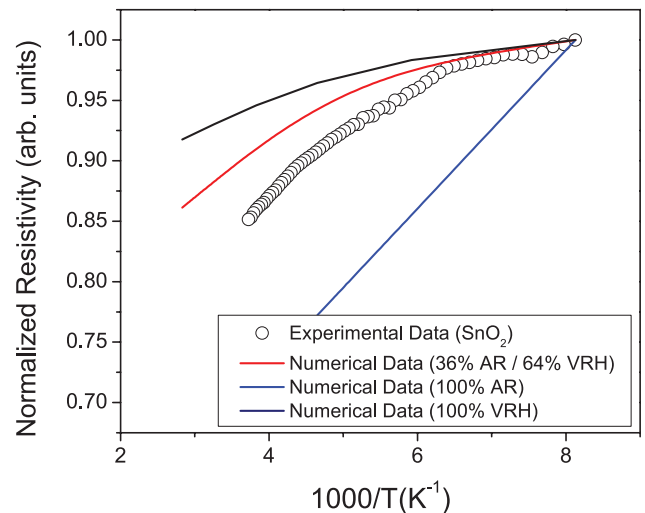


Figure 6. Electrical resistivity versus the reciprocal of temperature for a simulation (red line) and an experimental measurement (black circles) of SnO_2 nanowires. The drop in the resistivity cannot be fitted by only one transport mechanism; however, this behavior could be reproduced numerically with the assumption of two mechanisms. Black and blue lines represent only Arrhenius and VRH, respectively, which shows that this experimental result cannot be explained by either of them alone. However, the mix of these two processes approaches the experimental data.

the curvature is the same as the one observed in the experimental results in figure 1, where some curves does not adjust completely to the VRH fitting. Our results actually show that

when nanowire networks are described by different transport mechanisms, we can have different behaviors that do not necessarily depend on each nanowire, but on how they interact to form the device. With this confirmation, we move forward trying to use these results to numerically reproduce an experimental curve. In order to achieve this, we did several simulations mixing both mechanisms.

The devices used in the comparison with the simulations were built by direct evaporation of patterned metallic electrodes on the as-grown samples such as those used in figure 1. The experimental data were obtained from different SnO₂ devices: they were built trying out different metals for the electrodes, among which Ti and Ni exhibited an unvarying ohmic behavior, suited for temperature-dependent resistance measurements. In order to study the electrical conduction, 2-probe and 4-probe resistance measurements were carried out, varying the temperature from 100 to 400 K in a closed-cycle helium cryostat at pressures lower than 10⁻⁶ mbar.

Figure 6 shows the electrical resistivity as a function of the reciprocal of temperature for one experimental data set and for three numerical results. For these calculations we used a nanowire density of 0.625 NW μm⁻² and a mixing concentration that seems to be closer to the experiment was 36% of the Arrhenius mechanism and 64% of the VRH mechanism. Moreover, we considered that the junction resistance depends on the temperature, i.e. $R_j = R_j(T)$, and is given by the following expression [20]:

$$R^{-1} = G \propto \frac{q\mu_0 N_d (D - W_d)^2}{l} \exp\left(-\frac{qV_s}{kT}\right) \quad (6)$$

where q is the elementary charge, μ_0 is the crystal electron mobility, N_d is the donor concentration, D is the size of the nanostructure, W_d is the depletion region, l is the size between electrodes, V_s is the surface potential and k is the Boltzmann constant. We studied the effect of the contact resistance considering different situations: for the results in figure 4, we assumed the simplest case where R_j was constant and equal to 1 MΩ. It is possible to see that this assumption satisfies the theoretical curve. We also analyzed R_j in the range of 1 kΩ–10 MΩ. However, the best results are the ones we show here. For the results in figure 6 we used a more complex model given by equation (6), where R_j depends on structural parameters and on the temperature.

From figure 6 it is possible to observe that, qualitatively, the behavior of the experimental data and the numerical result represented by the red curve are very close, showing that more than one transport mechanism participates in the network resistance. Although many experimental properties of the systems were taken in account when running the simulations, the randomness of the networks plays an important role in the results. Therefore, the difference between the curves may be due to several factors. First of all, the geometric parameters such as position and angle of orientation of the nanowires are totally random, which means that it is impossible to generate two identical systems and hence

accurately reproduce the same electrical measurement in two different devices. Furthermore, there are other variables involved in the simulations, for instance, the kind of material, the number of nanowires, the resistance between them and others that could have an effect on the results. Moreover, as mentioned above, our goal was to explain the behavior that is observed experimentally and cannot be justified by only one transport mechanism and this was reproduced successfully by our simulations.

4. Conclusion

In this work we proposed a model to explain an odd behavior that is observed in experimental results of electrical measurements in random networks of semiconducting nanowires. We supposed that more than one mechanism participates in the electronic transport through the network. Furthermore, we supposed that between the nanowires there is a source of resistance that influences the electrical behavior of the system. Using computational simulations, we tested the validity of our model in the framework of percolation theory and showed that different mixing concentrations could lead to different network responses. Moreover, we showed that combinations of different amounts of nanowires with either Arrhenius or hopping dominant conduction mechanisms could reasonably reproduce experimental results.

Acknowledgments

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