Ultimate conductivity performance in metallic nanowire networks†

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In this work, we introduce a combined experimental and computational approach to describe the conductivity of metallic nanowire networks. Due to their highly disordered nature, these materials are typically described by simplified models in which network junctions control the overall conductivity. Here, we introduce a combined experimental and simulation approach that involves a wire-by-wire junction-by-junction simulation of an actual network. Rather than dealing with computer-generated networks, we use a computational approach that captures the precise spatial distribution of wires from an SEM analysis of a real network. In this way, we fully account for all geometric aspects of the network, i.e., for the properties of the junctions and wire segments. Our model predicts characteristic junction resistances that are smaller than those found by earlier simplified models. The model outputs characteristic values that depend on the detailed connectivity of the network, which can be used to compare the performance of different networks and to predict the optimum performance of any network and its scope for improvement.

Introduction

The unique behaviour displayed by nanoscale-sized materials is responsible for numerous scientific and technological breakthroughs. In comparison to their bulk counterparts, nanomaterials often reveal superior physical properties. Nonetheless, despite the unprecedented level of control that is currently possible over their structure, the manipulation of individual nanoscale components is still extremely laborious. For this reason, industry and academia have sought to exploit these functionalities without the need for precise nanomaterial placement. Candidates of particular interest are films comprised of randomly dispersed nanowires, commonly known as nanowire networks (NWNs).

NWNs are promising alternatives for a wide range of applications including flexible transparent conductors,1–3 thin-film solar cells,4 field-effect phototransistors5 and sensor6 devices, to name but a few. Formed by randomly dispersed conducting wires, NWNs may function as conducting materials depending on the degree of connectivity of the network as well as on the quality of the junctions formed between neighbouring wires. Effective signal transmission through the wires depends on the nature of coating layers or surface functionalization on these wires. Because these coatings are typically dielectric in nature, NWNs can be thought of as an array of randomly dispersed conducting wires connected by capacitive junctions which will only conduct current if the voltage drop across a junction exceeds its characteristic threshold voltage.7 Once this occurs, charge flows across the network through percolative paths formed by wires connected by resistive junctions.

The conduction properties of NWNs is dictated by a multitude of parameters such as the wire length and diameter distribution,8 interwire contact resistance, inner-wire resistance, wire density as well as their connectivity profile. With so many possible variables, such a study is best carried out through computer simulations. One way of simulating this percolative transport problem9,10 is to map the network into a node voltage problem: each wire is represented by a circuit node at a common voltage connected to other wires by a certain number of junctions and wire segments. Within this representation, it is then straightforward to obtain the overall conductance of a network by merely applying Ohm’s and Kirchhoff’s current laws.11,12 However, this approach involves an implicit assumption, hereafter referred to as the junction-dominated assumption (JDA), that the most significant contribution to the overall...
conductivity comes exclusively from the interwire junction resistances. This assumption is the basis for most earlier descriptions of NWNs, including a recent theoretical calculation to describe the sheet resistance and the optical transmittance of Ag NWNs \(^\text{13}\) where the characteristic junction resistance was then adjusted to match available experimental data.\(^\text{11}\)

The JDA is perfectly safe when the junction resistance is significantly larger than any other characteristic resistances within the network. This indeed is the case of NWNs comprised of carbon nanotubes.\(^\text{14,15}\) However, the demands for increasingly conductive films, driven by efforts to reduce the junction resistances, will ultimately undermine the validity of the JDA due to its neglect of the inner resistances of the wires.\(^\text{16}\) By relaxing the JDA, we can account not only for the geometric aspects of the network but also for the material properties of its components. Furthermore, by extending this picture to the limit of vanishingly small junction resistances we can provide an upper bound for the conductivity of the NWNs and reveal how much room there is to improve the conductivity of a film. Rather than working with computer-generated random networks, it is desirable to establish the upper bound for the conductivity of real networks. When conductivity measurements of such networks are compared with their respective upper bounds, one has a clear indication of how close to the optimum value they are. This calls for a computational tool capable of capturing the geometry of real networks combined with the ability to calculate the sheet resistance of the corresponding array of inter- and inner-wire resistors.

In this manuscript, in addition to relaxing the JDA as described above, we present for the first time a set of simulations that obtain the sheet resistance of networks with defined geometries through SEM image analysis of real samples (\textit{cf.} Fig. 1). In this way, we have a one-to-one correspondence between simulation and experiment and can simulate both the actual and ultimate network conductivity, the latter assuming the junction can be further optimized. Networks to be simulated were built from real experimental images of sparse and dense samples with wire densities \((n)\) ranging from 0.15–0.6 wires per \(\mu m^2\). This approach avoids the need for spatial configurational averaging highlighted in a recent paper in reference \(\text{12}\). Instead, our simulated network captures exactly the same spatial arrangement of the network displayed on the SEM images. The inner-wire resistance was included using a novel node-voltage approach capable of describing the transport properties of NWNs that also accounts for the wires resistivity. The model uses a new mapping scheme in which the wires of the network are described by a multi-nodal representation (MNR); the network topology is mapped as a graph carrying information about the wire junction connections and their respective separations. Critically, the model outputs for each network a set of characteristic values that are determined by the network connectivity and that allow a direct comparison between distinct networks. Such explicit examination of NWNs would not be possible throughout traditional configurational averaging approaches.

**Experimental and computational methods**

**Experimental procedure**

Ag nanowires (NWs) were purchased from Seashell Technology, LLC with an average length (diameter) of 6.7 \(\mu m\) (50 nm) (\textit{cf.} ESI†). Suitable single NWs were selected for contacting by electron beam lithography (EBL) after drop casting of NW/isopropanol dispersion (12.5 \(\mu g\) ml\(^{-1}\)) on clean Si substrates (1 \(\mu m\) thermal oxide) with pre-defined Ti/Au contact pads (5/25 nm). Isolated nanowire networks were formed by spray deposition...
of NW/isopropanol dispersion into EBL defined openings (120 μm × 20 μm) in bi-layer MMA (methyl methacrylate) and PMMA (poly methyl methacrylate) e-beam resists. Post-spraying, wires on the resist were removed by acetone lift off; wires gathered into the openings formed the isolated nanowire networks. EBL was used to define contacts to single Ag NWs and isolated networks such that each item could be interrogated by four co-linear electrodes (cf. ESI†). All contacts were metalized with Ag (120 nm).

Each section of the network bounded by adjacent electrodes was electrically stressed. Devices underwent electroforming by applying multiple 0–5 V dual sweeps stressing the network at increasing current compliance from the nA to mA range. The high current chosen ensures that the network conductivity is maximized with the vast majority of junction resistances optimized. This procedure has previously been shown to produce low resistance networks while avoiding potentially damaging high-temperature annealing steps.7,17 Following this optimization step, a Kelvin (4-wire) resistance measurement was recorded. Current is sourced across the outer two electrodes and the drop in voltage is measured across the two innermost electrodes. This removes the contact resistance from the measurement and provides a true sheet resistance of the network. The resistivity for 15 single wire samples was also extracted using 4-probe resistance measurements. Wire diameters and channel lengths, including the electrodes’ width18 were measured using SEM (cf. ESI†). All electrical measurements were carried out at ambient conditions using Keithley 4200 SCS. Imaging of nanowire networks was performed on a Zeiss Supra 40 SEM.

Simulations
Initially, we processed SEM images of 30 Ag NWN samples with distinct wire densities.19 This was done by opening the image files on an interactive canvas widget that allowed us to characterize each NWN on a wire-by-wire basis. The data is converted into Cartesian coordinates that are subsequently used as inputs for solving the resistor network problem. Examples are depicted on Fig. 1: micrograph images of real networks (left panels) are converted into mathematical objects (sticks) illustrated on the right panels. In instances of curved wires, we break the wire into smaller segments that approximately outline the wire curvature.

The standard way (JDA) of obtaining the transport characteristics of a given network containing N wires is to represent each wire by a node. The whole network is hence mapped into a voltage grid system of N nodes. Intersecting wires are represented by nearest-node neighbours connected by resistors that emulate active junctions (cf. Fig. 2). Note that the spatial location of these nodes is irrelevant within JDA. From the connectivity profile of the network, one can build the resistance matrix (MNR) of the system as described in ref. 12 and solve Kirchhoff’s circuit equation written in matrix form, MNRU = I, where the vectors U and I are the potential at each wire and the current injected/drain ed out of the circuit, respectively.20 The sheet resistance (Rs) is then obtained by evaluating

\[ R_s = \frac{I(U_{in} - U_{out})}{U_{in} - U_{out}} \]

where \( U_{in} \) and \( U_{out} \) is the potential on the left (right) electrode. The matrix MNR carries the resistance values assigned to each interwire junction (\( R_j \)), which is assumed to be homogeneous throughout the network. It is worth pointing out that our main findings are not changed when we relax this assumption and allow \( R_j \) to follow a normal distribution. The role played by a normal dispersion on the junction resistance distributions can be found in the ESI†.

The JDA scheme described above is attractive due to the ease of computational implementation. While it can provide an adequate qualitative interpretation about the conducting properties of networks, it lacks critical ingredients that must be taken into account. JDA description assumes that charge carriers hop ballistically from junction to junction without scattering by the wire material. As mentioned previously, this method fails whenever \( R_j \approx R_{in} \), where \( R_{in} \) is the typical value for inner-wire resistance. Previous Monte Carlo simulations21–24 on homogeneous networks above their percolation threshold have demonstrated that their transport properties are highly dependent on the ratio \( R_j/R_{in} \). To move beyond JDA, we must introduce a new voltage-node mapping that is capable of including the inner-wire resistance.

The resistance of an isolated wire is given by \( R_{in} = \rho L/A_x \) where \( \rho \) is the wire resistivity, \( L \) its length and \( A_x \) the cross section area. In networks however, the wire resistance must be partitioned according to its number of intersections; a wire making \( k \) connections is partitioned into \( k + 1 \) segments of length \( I \), each one of them carrying an inner resistance of \( R_{in}' = \rho /A_x \) where \( i = 1, \ldots, k + 1 \). Therefore, the novel voltage grid scheme must map the interwire connection points and not the wires, as done within JDA. This is illustrated in Fig. 2; one can see that nodes are attributed to all connection points in all wires. This gives a total number of nodes of \( 2N_w \) where \( N_w \) is the number of interwire connections of the network. This new mapping scheme generates a network that is topologically different from JDA and will be referred to as multi-nodal representation (MNR) since the wires can be described by multiple nodes. Note that in this scheme, the position of the
nodes matters. If two nodes share the same set of (x, y) coordinates, they characterize an interwire connection with junction resistance $R_j$. If two nodes belong to the same wire and are nearest neighbours, they feature an inner-wire segment which consequently has a resistance associated to it. Note also that the computational implementation of our approach does not require the use of 3D objects (e.g. cylinders) to order to account for the wire thickness. The networks can be still described by sticks dispersed on a plane since the diameter of wires is incorporated in the inner-wire resistances.

The determination of nearest nodes is done by viewing the whole network as a graph composed of vertices (junction points) and edges (wire segments). An adapted breadth-first search algorithm was implemented to inspect the whole network – represented as a graph – and to determine its complete chart of neighbouring node pairs. In this way, one can construct a new resistance matrix $M_{R_n}$ which is plugged into Kirchhoff’s circuit law to obtain the sheet resistance of the samples. Results obtained via both models (JDA and MNR) are compared in the following section.

**Discussion and results**

To implement MNR, we used a resistivity value of $\rho = 22.6 \pm 2.3 \ \text{n}\Omega\text{m}$ determined from room temperature resistance measurements of a distribution of 15 Ag nanowires with diameters of $D = 50 \pm 13 \ \text{nm}$ based on a SEM analysis of 101 Ag NWs. It is important to note that surface scattering effects will depend on wire diameter and temperature so that wire resistance measurements must be performed on representative wires and under the appropriate temperature conditions before this model can be applied more generally. These values were employed in all 30 NWN samples mapped from micrograph images. Fig. 3 shows the results obtained when JDA and MNR methods are applied on network #1 shown in Fig. 1a and b. This sample exhibits wire density of $n = 0.28 \ \mu\text{m}^{-2}$ and a measured sheet resistance of $R_{\text{exp}} = 84.42 \ \Omega$. The sheet resistance calculated as a function of the junction resistance $R_j$ is plotted for JDA (black dashed line) and MNR (blue solid line). The horizontal dotted line corresponds to $R_{\text{exp}}$. As expected, the sheet resistance grows linearly with $R_j$ for both descriptions (JDA and MNR). The models however differ in specific ways: JDA predicts that $R_s = a_0 R_j$, whereas MNR finds $R_s = a_0 R_j + R_0$, where $a_0$ is the slope and $R_0$ is the resistance that the network would have if all interwire contacts were perfect. Thus the $R_0$ shift between JDA and MNR models accounts for the influence of the inner-wire resistance on the overall sheet resistance and it is purely determined by the network geometry and its detailed connectivity. One immediate consequence of this shift is that the JDA tends to overestimate the junction resistances. The diamond and the circle on Fig. 3 identify the value of $R_{\text{exp}}$ in the JDA and MNR respectively that corresponds to the measured sheet resistance $R_{\text{exp}}$. The JDA-estimate for $R_{\text{exp}}$ is found to be approximately 40 $\Omega$ higher than for the MNR for this particular sample, and $R_0 = 46.43 \ \Omega$. With such a large contribution from the resistance of the network skeleton, it is not surprising that $R_j$ is overestimated by the same order of magnitude. In fact, recent attempts to obtain the junction resistances of NWNs within JDA have reported values of the order of 2 k$\Omega$, which is substantially larger than the values measured across individual junctions. The risk of an overestimation in $R_s$ is that it might raise false hopes that the junctions of a network can be further optimized. Once again, it is worth reiterating that the JDA model is only valid when the transport is dominated by junction resistances, i.e. when $R_{\text{exp}} \gg R_0$ and so the inclusion of the inner-wire resistance contributions will cause minor changes to the estimated values of $R_s$.

Another interesting consequence of relaxing the JDA is that by defining a quantity $\Delta = R_{\text{exp}} - R_0$, we can estimate how close (or far) a particular sample is from operating at its minimum resistance state $R_0$. For this particular sample $\Delta = 37.99 \ \Omega$, which means that the sheet resistance is about 38 $\Omega$ above its minimum resistance state. A more descriptive quantity that establishes how much room for improvement a network has is given by $\gamma = 1 - R_0/R_{\text{exp}}$. This dimensionless quantity, named optimization-capacity coefficient, ranges from 0 to 1. Values of $\gamma$ close to 1 represent networks whose conductivities can be considerably improved since their sheet resistances are far from the optimal value $R_0$. When $\gamma$ approaches 0, on the other hand, the network is close to its optimum conductivity and is unlikely that it can be further optimized. The ability to establish how much potential for optimization a network has serves as a useful guide in the search for networks with continuously larger conductivity values.

The characteristic values outputted by the model allow us to compare different networks. Table 1 shows the $\gamma$ values for the three networks that are discussed in detail here, together with the corresponding values of $n$, $R_0$, $R_{\text{exp}}$, $\Delta$, and $\Delta/a_0$ ($R_{\text{exp}}$) obtained within MNR. We note $\Delta/a_0 = R_{\text{exp}} - a_0 R_{\text{exp}} + R_0$. The complete table containing the characteristic values for

![Fig. 3](Color online) Sheet resistance ($R_s$) versus junction resistance ($R_j$) analysis performed on sample #1 using JDA (black dashed line) and MNR (blue solid line) models. Horizontal dotted line (red) marks the measured sheet resistance value ($R_{\text{exp}} = 84.42 \ \Omega$). Circle and diamond dots indicate the estimated junction resistance within MNR and JDA, respectively. Fitting line expressions used to obtain $a_0$ and $R_0$ values are added on top of each numerical curve.
all 30 samples can be found in the ESI.† No obvious correlation is seen between the optimization-capacity coefficient and either of these quantities, suggesting that γ may contain a rather non-trivial dependence. However, when γ is compared against the ratio Δ/a₀ for all 30 networks, a clear trend is observed. As shown in Fig. 4, a plot of γ as a function of Δ/a₀ displays a monotonic behaviour that spans the entire range of possible values for the optimization-capacity coefficient which is not very surprising given Δ/a₀ can be thought of as the estimated characteristic junction resistance. In spite of that, the fact that the diverse range of networks in Table S1† falls onto such a smooth curve suggests a very robust, if not universal, trend that is likely to be followed by all networks.

Besides determining the optimization-capacity coefficient for different networks, this quantity can also be used to assess how one specific network evolves as it is electrically stressed. Consecutive voltage sweeps are known to increase the conductivity of the network from completely inactive all the way to its fully optimized state. The quantity R₀ is determined by the geometry of the network (and will not change with the consecutive voltage sweeps) but the measured values of R*exp change as the network is stressed. The inset of Fig. 4 shows γ after a sequence of voltage sweeps. Note that it starts with a relatively large value of γ but it decays continuously indicating that the network is evolving towards its optimum value. Once again, γ appears as a useful quantity that can be employed to assess how much room there is to increase the conductivity of the NWNs.

Comparisons between networks

To highlight the advantage of using image processing techniques to reproduce the exact spatial distribution of real networks, we have selected to discuss the peculiar case of two samples shown in Fig. 1c–f that exhibit very distinct characteristic values (Δ/a₀, R₀, and γ) but rather similar sheet resistances and same wire density (0.16 wires per μm²). In this example, the simple intuitive relationship between density and sheet resistance fails to account for the critical role of connectivity in the performance of sparse films. The characteristic values within our model capture differences in connectivity for networks of similar densities. To demonstrate this, we present the image analysis of two samples labelled here as #2 and #3 (cf. Fig. 1c–f) and their characteristic values can be found on Table 1. Although both samples have the same wire density, their connectivity profiles differ remarkably. Sample #2 has fewer paths connecting one electrode to another compared with sample #3. Therefore, the distinct characteristic Δ/a₀, R₀, and γ values of each sample carry information about the inherent features of the networks that are hidden when analyzing global quantities such as sheet resistance versus density trends. An analysis of Fig. 1d reveals that the performance of network #2 relies basically on 2 junctions identified by the gray arrows. Those junctions are the main bridges connecting the electrodes. Since all the networks are mapped as a graph, we can quantify their importance by calculating their betweenness centrality28 degree. This critical property quantifies the number of times a node must be visited to connect the shortest path between two other nodes. Those two junctions are the ones with the highest betweenness levels and they play a major impact on the current propagation across the network. Critically, this kind of information can only be accessed via our approach where the network is mapped wire-by-wire, junction-by-junction. This method turns out to be extremely important for sparse networks such as samples #2 and #3 where each wire and each junction makes an important contribution to the conductivity.

Conclusions

We have introduced a novel computational method that exactly reproduces the spatial arrangement of experimentally generated NWNs through image analysis, so as to include the contribution of the inner-wire resistance in the calculation of the conductivity of these materials. Often neglected when the conductivity is dominated by junction resistances, the inner-wire resistances may play a significant role in the overall conductivity of NWNs. When the inner-wire resistances are neglected, results for the junction resistance tend to be overestimated. Regarding the prospects for optimization of the network
conductivity, it is important to have a realistic estimate of the quality of the junctions. If junction resistances are small (large), it is unlikely (likely) that they can be further improved. It is thus essential to be able to estimate them accurately. Furthermore, by including the inner-wire resistance contribution in our calculations we can establish an upper bound for the conductivity of NWNs by simply imposing ideal lossless junctions. A simple comparison of measured values of sheet resistances with the corresponding optimum values can tell how realistic the chances of further improving the network conductivity are. Rather than providing a qualitative assessment of the chances for improvement, we quantify the ease of improvement by introducing the optimization-capacity coefficient $\gamma$. This allows us to compare different networks, identifying those which can be further improved. Similar analysis can be used to study the evolution of one specific network as it is electrically stressed. Our model explicitly avoids the use of configurational averaging over the spatial distribution of wires in computer-generated networks, which is known to cause significant fluctuations in the calculated values of sheet resistance especially in the case of sparse samples. It also provides unique insights about the network's connectivity. Networks with similar wire densities and sheet resistances may have rather distinct connectivity profiles which are imprinted on the characteristic values determined within our model, providing insights that are simply not accessible using conventional configurational averaging approaches.

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**Notes and references**

19. ESL†