Interdependence of resistance and optical transmission in conductive nanowire networks

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Abstract

Metallic nanowire networks show great potential for use in transparent conductive displays. The coupled relationship between the principal materials properties of interest for such applications, optical transmittance and sheet resistance, is known to be affected by both nanowire dimensions and area coverage. Existing theory to describe the observed interdependence requires consideration of both bulk and surface phases.

Here, we present an analysis of structural variables in these materials confirming that bulk considerations do not typically apply. Accordingly, we develop a model using statistical theory for random line networks that requires consideration of a surface phase only. The resultant simple expression relates sheet resistance and optical transmission of heterogeneous nanowire assemblies in terms of nanowire dimensions. Comparison of our model with experimental and simulation data from the literature shows excellent agreement. In closing, we provide theoretical insights into the observed influence on sheet resistance of poly-disperse nanowire lengths and of structural variability.

Background

As industrial and societal demand for transparent conducting materials used in displays, solar cells, etc., increases, there is a considerable focus on the identification of suitable material systems to replace the current material of choice, indium-tin oxide, which is not well suited to flexible displays, and is a finite and rapidly depleting resource [1]. Among the candidate systems to replace doped metal oxides are metal nanowire networks, an example of which is shown in Figure 1; these consist of sparse random arrays of metal nanowires with conductivity and optical transmission determined by the number of nanowires deposited per unit area and nanowire dimensions, see e.g. [2, 3].

The review of Langley et al. [1] provides an excellent overview of experimental and theoretical developments in our understanding of the factors affecting optical and electrical properties of silver.

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nanowire networks and related systems. Here we focus on the literature describing key behaviours since these inform our development of a theoretical model capturing the dependencies of optical and electrical properties on nanowire and network variables.

Mutiso et al. [4] used simulation to investigate the effect of nanowire length and the number of nanowires per unit area on sheet resistance, $R_s$ ($\Omega/\square$) for nanowires of fixed diameter. Their simulation generated planar random networks of inter-penetrating rods and assumed all resistance to occur at the junctions between them. Constant values of resistance were assigned to each junction, regardless of their area, and Kirchoff’s current laws solved for the resultant network of resistors. The simulations showed $R_s$ to decrease with increasing nanowire aspect ratio for a given fractional coverage of the area by nanowires. Further, for networks of nanowires with bi-disperse lengths, the sheet resistance was dominated by the contribution of longer nanowires. Using realistic values of junction resistance as a free-parameter, the simulation results of Mutiso et al. [4] compared favourably to their experimental data obtained for networks of nanowires with aspect ratio around 200 to 300. In a subsequent Monte-Carlo study, da Rocha et al. [5] generated computational resistance networks from micrographs of silver nanowire networks and accounted for the intrinsic resistance of nanowires such that a given sheet resistance was obtained with much lower values of junction resistance. The importance of the result is that the relative magnitudes of junction resistance and wire resistance have a strong influence on strategies to optimise sheet resistance through choice of materials and processing routes.

De et al. [6] note, as might be expected, that figures of merit (FoMs) coupling sheet resistance with optical transmittance often make use of Beer-Lambert dependencies, such that the transmittance, $T$, of a nanowire film with thickness, $t$, is given by

$$ T = e^{-\alpha t} , 
$$

where $\alpha$ (m$^{-1}$) is an absorption coefficient. Khanarian et al. [7] note that in typical regimes of interest, the thickness of nanowire films is comparable to the diameters of the constituent nanowires, and thus is difficult to measure. They proceeded to show that transmission was well characterised by the expression

$$ T = e^{-n C_{ext}} , 
$$

Figure 1: Left: Micrograph of a network of silver nanowires with mean coverage approximately 5 times the percolation threshold. Nanowires shown have mean length of around 20 $\mu$m and mean width of around 60 nm. Right: Graphical representation of a random network of lines each with uniform length 20 $\mu$m.
where $n$ is the expected number of nanowires per unit area and $C_{\text{ext}}$ is the extinction coefficient at normal incidence obtained from Mie theory. A semi-empirical extension of this exponential dependency is provided by Large et al. [8]. We note also that Bergin et al. [2], Ahn et al. [9] and Khanarian et al. [7] all show a linear decrease of transmittance, $T$, on the fraction of the network covered by nanowires. In the theoretical treatment that follows, we provide a structural basis for these observed dependencies.

The standard reference structure for heterogeneous fibrous materials is a random fibre network, where fibre centres are distributed according to a point Poisson process in two dimensions and the orientation of fibre axes has a uniform distribution [10]. Theoretical relationships derived for such structures have been used to inform structure-property dependencies for a range of materials including paper [11], battery separators [12] and electrospun polymer scaffolds for application in tissue engineering [13]. These models allow network structure to be described in terms of fibre geometries, network porosity and a dimensionless discrete random variable called coverage, $c$, which gives the number of fibres covering points in the plane of support of the network, i.e. for a given point in the plane, the coverage is the number of nanowires with cross-section intersecting a line perpendicular to the plane at that point. For the systems considered here, the extended objects of interest are nanowires rather than fibres and the same dependencies can be assumed to persist. A graphical representation of a sparse random network of lines with uniform length is shown on the right of Figure 1.

For a random network of nanowires with mean coverage, $\bar{c}$, the probability that a point has coverage, $c$, is given by the Poisson distribution\[14\]:

$$P(c) = \frac{e^{-\bar{c}} \bar{c}^c}{c!} \quad \text{for } c = 0, 1, 2, 3, \ldots$$

If the expected number of nanowires per unit area is $n$, then for a network of nanowires each with length, $\lambda$, and width, $\omega$, the total length of nanowires per unit area, $\tau = n \lambda$ and the mean coverage is given by [10]

$$\bar{c} = n \lambda \omega$$

$$= \tau \omega .$$

For completeness, we note also that $\bar{c}$ can be calculated as the ratio of the mass per unit area of the network to that of the nanowires. Assuming circular cross-section, this latter parameter is given by $\pi \omega \rho/4$, where $\rho$ is the density of the material and $\rho = 10.5 \ g \ cm^{-3}$ for silver.

In their seminal Monte-Carlo study of percolation and conductivity, Pike and Seager [15] showed that the percolation threshold, i.e. the lowest mean coverage at which a conducting path across the network exists, is determined only by the aspect ratio of the nanowires, $A = \lambda/\omega$, such that

$$\bar{c}^* = \frac{k}{A} = \frac{k \omega}{\lambda} .$$

From Pike and Seager we have $k = 5.71$; more recently, Li and coworkers [16, 17] obtained $k = 5.64$; the experimental data of Khanarian et al. [7] yield $k = 5.67$. We expect the aspect ratio of nanowires to be of order 100, so we have the rule-of-thumb that networks may be considered be percolated for $\bar{c}$ greater than about 0.05.

De et al. [6,18] propose that the conductance of nanowire networks can be modelled as following the behaviours of ‘percolative regime’ for sparse networks and exhibiting ‘bulk-like’ behaviours for film thicknesses greater than around 160 nm for their networks of nanowires with diameter 84 nm,
this thickness corresponding to an areal density of around 70 mg m\(^{-2}\). From nanowire dimensions, we calculate that this corresponds to a mean coverage, \(\bar{c} = 0.04\), which is consistent with our estimates of the percolation threshold.

De et al. [18] report bulk-like behaviour for networks with areal density 233 mg m\(^{-2}\), which corresponds to a mean coverage, \(\bar{c} = 0.33\). Now, all regions of the network with coverage 1 and 2 represent network surface only; if we consider nanowires not in the surface to be in the bulk of the network, then this can exist only in regions with coverage 3 or more. Indeed, Kallmes and Corte [11] defined two-dimensional networks as those where the fraction with coverage greater than 3 was less than 1 %. From Equation (3), we can calculate the fraction of the network with coverage greater than 3: for a network with \(\bar{c} = 0.33\), as found to exhibit bulk-like behaviour by De et al. this fraction is less than 0.04 %; considering only that part of the network covered by nanowires, it is around 0.1 %. So, although the two-regime model proposed by De et al. provides good predictions of network behaviour in the range of mean coverages of practical interest, these are not sufficiently high for bulk structural characteristics to be significant and hence for there to be a transition between regimes.

In what follows, we show that established relationships from the literature modelling the structure of random fibrous networks can be extended to predict the interdependence of sheet resistance and transmittance in nanowire networks without the requirement for a transition between percolative and bulk-like behaviours. The treatment accounts for the influence of nanowire dimensions and network variables to yield insights into how the resistance-transmittance parameter space can be controlled by informed choice of materials.

**Theory**

We model the resistance of a random network of nanowires as a system of parallel resistors, each with resistance, \(r_{p,i}\). The resistance, \(R\), of a network of \(n_r\) parallel resistors is given by

\[
\frac{1}{R} = \sum_{i=1}^{n_r} \frac{1}{r_{p,i}}.
\]

(6)

Let the resistance of a given resistor \(r_p\) be that of a single path through a network with mean coverage at the percolation threshold, \(\bar{c}^*\). In any such path, the number of junctions, \(n_j\), will be one fewer than the number of constituent nanowires, \(n_w\), such that \(n_j \approx n_w\) for \(n_w \gg 1\). Further, since any single path can be modelled as the resistances of junctions and nanowires in series, then the mean resistance of a path is proportional to the mean number of nanowires per conducting path, \(\bar{n}_p\) such that

\[
\bar{r}_p \propto \bar{n}_p (r_j + r_w),
\]

(7)

where \(r_j\) and \(r_w\) are the resistances of junctions and nanowires respectively.

We expect the mean number of nanowires per conducting path to be proportional to the expected number of nanowires per unit area required for percolation, \(\bar{n}^*\). From Equations (4) and (5), this is given by

\[
\bar{n}^* = \frac{\bar{c}^*}{\lambda \omega} = \frac{k}{\lambda^2}.
\]

(8)

So we have

\[
\bar{r}_p \propto \bar{n}^* (r_j + r_w)
\]
Further, if the variance of \( r_p \) is small, then to a first approximation, \( r_p = \bar{r}_p \), such that Equation (6) yields

\[
R = \frac{\bar{r}_p}{n_r} .
\]  

(10)

Kallmes and Corte [11] show that for thin networks, \( i.e. \) those with mean coverage less than about 1, the expected number of junctions per unit area is

\[
n_c = \frac{\bar{c}^2}{\pi \omega^2} \lambda^2 (r_j + r_w) .
\]  

(11)

If we assume that the junctions in any of our parallel resistors contribute to the resistance of that path only, then the number of parallel resistors in our model is proportional to the number of junctions per unit area in the network, \( i.e. \) \( n_r \propto n_c \). Accordingly, we combine Equations (9), (10) and (11) to yield

\[
R_s \propto k \frac{\pi \omega^2}{\bar{c}^2} (r_j + r_w) \lambda^2
\]  

(12)

\[
= K \frac{\omega^2}{\bar{c}^2} \lambda^2
\]  

(13)

\[
= K \frac{\bar{c}^2}{\lambda^2} A^2 ,
\]

where \( K \) collects all constants and thus should have no dependence on \( \omega, \lambda \) or \( \bar{c} \), but should depend on the resistances of junctions and the intrinsic resistance of the constituent nanowires, \( r_j \) and \( r_w \) respectively. Note the introduction of the subscript, ‘s’ such that Equation (13) gives the sheet resistance, \( R_s \); this being a consequence of the dependence of the number of junctions per unit area, \( n_c \).

Now, Equation (13) predicts that a plot of \( \sqrt{R_s} \) against \( 1/(\bar{c} \lambda) \) will be linear with gradient, \( \sqrt{K} \omega \).

Figure 2 shows such a plot for the data of Mutiso et al. [4]. We observe that the data arising from simulations for idealised random networks of nanowires with fixed width, \( \omega \) and constant junction resistance form a single group with constant gradient. The steeper gradients of the experimental data can be attributed to nanowire diameter, the intrinsic resistance of nanowires, which was assumed zero in the simulation, and higher junction resistance than assumed for the simulations. Full regression data associated with Figure 2 are provided in Table 1.

We expect that transmission of light through a nanowire network will depend on the fraction of the network covered with nanowires and the extent to which light is refracted at their edges; this phenomenon is termed ‘hazing’. From Equation (3), we obtain the fraction of the network that is not covered by nanowires as the probability of coverage, \( c = 0, \ i.e. \)

\[
\epsilon = P(0) = e^{-e} .
\]  

(14)

Further, we note that hazing will occur at the perimeters of these open areas such that \( T \propto \epsilon \). For completeness, we note that for full partitioning of a plane by random lines, the total perimeter per unit open area can be obtained from the result of Miles [20] as \( 2 \tau \), as expected, so the relative contribution of hazing to transmission is expected to increase with mean coverage; for the low mean coverages in the region of interest for transparent displays, such influences are likely to be negligible, so will not be accounted for in our subsequent analysis. In the introduction we noted the observation that \( T \)
Figure 2: Plot of $\sqrt{R_s}$ against $1/(\bar{c} \lambda)$ for the data of Mutiso et al. [4]. Linear regressions passing through the origin have coefficients of determination greater than 0.95 for each data set, confirming excellent agreement between these data and Equation (13). For simulated data, generated using constant parameters for all variables other than nanowire aspect ratio, the gradient is effectively constant. For experimental data, the higher gradient can be attributed to the different diameters of the constituent nanowires, their finite resistance, and different values of junction resistance from those used in the simulations.

<table>
<thead>
<tr>
<th>$A$ (nm)</th>
<th>Gradient ($\sqrt{\Omega/\mu m}$)</th>
<th>$r^2$</th>
</tr>
</thead>
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<tr>
<td>Simulation</td>
<td>50</td>
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</tr>
<tr>
<td></td>
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<td></td>
<td>600</td>
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<td></td>
<td>800</td>
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<td>27.7</td>
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<tr>
<td></td>
<td>275</td>
<td>23.4</td>
</tr>
</tbody>
</table>

Table 1: Regression data for linearisation of the data for Mutiso et al. [4] as plotted in Figure 2.


Table 2: Regression data for linearisation of the data for Sorel et al. [3] and Bergin et al. [2] as plotted in Figures 3 and 4, respectively

<table>
<thead>
<tr>
<th></th>
<th>( \lambda ) (( \mu )m)</th>
<th>( \omega ) (nm)</th>
<th>Gradient ( \sqrt{\Omega/\Box} ) ( \mu )m</th>
<th>Intercept ( \sqrt{\Omega/\Box} )</th>
<th>( r^2 )</th>
</tr>
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<td>Sorel et al. [3]</td>
<td>4.0</td>
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<td>4.7</td>
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<td>0.952</td>
</tr>
<tr>
<td></td>
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<td>2.7</td>
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<td></td>
<td>4.4</td>
<td>88</td>
<td>7.3</td>
<td>-0.63</td>
<td>0.925</td>
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<td></td>
<td>8.7</td>
<td>127</td>
<td>10.5</td>
<td>0.94</td>
<td>0.861</td>
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<td>Bergin et al. [2]</td>
<td>25.0</td>
<td>85</td>
<td>39.5</td>
<td>-2.85</td>
<td>0.665</td>
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<tr>
<td></td>
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<td></td>
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For experimental data recovered from the literature, we find that plots of \( \sqrt{R_s} \) against \( 1/(\log(1/T) \lambda) \) always exhibit a non-zero intercept on the ordinate. We interpret this as either a systematic calibration error in the measurement of \( T \) or as a contribution of a backing substrate to light absorption. Figure 3 shows a least-squares fit of Equation (15) to the data of Sorel et al. [3], for nanowires of different widths; here Equation (15) was modified such that \( T \to (T - \beta) \), and \( \beta \) and \( K \) are therefore the free parameters for fitting. The inset figures show the predicted linear relationship between \( \sqrt{R_s} \) and \( 1/(\log(1/T) \lambda) \). Figure 4 shows this modified form of Equation (15) fitted to the data of Bergin et al. [2] for networks of nanowires with differing length and width. Regression data for the linear relationships shown in the inset plots in Figures 3 and 4 are provided in Table 2. Recall that we expect the gradient of our linearised plot to be proportional to the nanowire diameter, \( \omega \); this dependence is essentially captured in the regression on the data of Sorel et al. [3], as reported in Table 2.

**Polydisperse nanowire lengths**

Khanarian et al. [7] and Large et al. [8] report that the lengths of nanowires are well described by lognormal distributions. For nanowires from different suppliers, Khanarian et al. report coefficients of variation of nanowire length between 0.046 and 1. Large et al. used ultrasonication to reduce the
Figure 3: Plots of transmittance, $T$ against $R_s$ for the data of Sorel et al. [3]. Broken lines show fit of Equation (15) to the data, assuming $T \rightarrow (T - \beta)$; inset figures show linear dependence between $\sqrt{R_s}$ and $1/(\log(1/T) \lambda)$ as predicted by Equation (15). Regression data are provided in Table 2.
Figure 4: Plots of transmittance, $T$ against $R_s$ for the data of Bergin et al. [2]. Broken lines show fit of Equation (15) to the data, assuming $T \rightarrow (T - \beta)$; inset figures show linear dependence between $\sqrt{R_s}$ and $1/\log(1/T)\lambda$ as predicted by Equation (15). Regression data are provided in Table 2.
length of nanowires and found a plot of standard deviation of nanowire length against the mean passed
through the origin with gradient 0.5, suggesting that ultrasonication reduces nanowire length whilst
preserving an effectively constant coefficient of variation, \( CV(\lambda) \approx 0.5 \) for their process. Further,
they show that using the length-weighted nanowire length computed from their data as \( \lambda_w = \bar{\lambda}^2 / \lambda \)
in their figure of merit accounts for the effect of nanowire length distribution well. We note that the
lognormal distribution arises as a consequence of the Central Limit Theorem for stochastic attrition
processes, and thus might be expected to characterise nanowire breakage due to, *e.g.* ultrasonication.

In the Supplementary Information, we show that for a lognormal distribution of nanowire lengths
with coefficient of variation \( CV(\lambda) \), the length-weighted average length \( \lambda_w = (1 + CV^2(\lambda)) \bar{\lambda} \). Thus,
for \( CV(\lambda) \approx 0.5 \) we have \( \lambda_w \approx 1.25 \bar{\lambda} \). Noting that Equation (13) gives \( R_s \propto 1/\lambda^2 \) for a network of
nanowires with uniform length, it follows that for a lognormal distribution of lengths

\[
R_s \propto \frac{1}{\lambda_w^2} \propto \frac{1}{(1 + CV^2(\lambda))^2 \bar{\lambda}^2}.
\]

By definition \( CV(\lambda) \geq 0 \), so we may state that the sheet resistance of a network of nanowires with a
lognormal distribution of lengths is less than that of a network of nanowires with uniform length by
a factor \( 1/(1 + CV^2(\lambda))^2 \). For completeness, we note that for \( CV(\lambda) = 0.5 \), as observed by Large *et al.* [8], this factor is about 0.6. The result is consistent with the observation of Mutiso *et al.* [4] that
the resistance of networks with bi-disperse lengths was dominated by the contribution of the longer
nanowires.

**Network uniformity**

As is evident on first inspection of Figure 1, an inherent property of stochastic processes is that they
exhibit non-uniformity. Accordingly, we expect non-uniformity in the structure of nanowire networks
to manifest itself in non-uniformity of transport and optical properties. Indeed, Khanarian *et al.*
observed significant spatial variability in their measurements of sheet resistance, \( R_s \) and reported that
this variability increased as mean coverage decreased towards the percolation threshold [7]. Whilst
not discussed, the same phenomenon can be observed in the error bars on the sheet resistance data of
Bergin *et al.* [2]; these reveal also smaller variance of sheet resistance for networks of shorter nanowires.
We shall discuss these phenomena in detail elsewhere; for now we note that a natural extension of
Equation (13) is that spatial variability of \( R_s \) will depend on the local averages of coverage, \( c \). Further,
for a point Poisson process of coverage as considered here, the coefficient of variation of coverage is
\( CV(c) = 1/\sqrt{\bar{c}} \), so increases as mean coverage decreases, this being consistent with the observed
dependence of variability of sheet resistance on mean coverage.

**Conclusions**

We have presented a theoretical model for the effect of nanowire dimensions and coverage on the
coupled relationship between sheet resistance and transmission in conductive nanowire networks. Our
model uses statistical theory to parametrise the resistance of parallel resistors and assumes the trans-
mission of light through the network to be proportional to its fractional open area. On this basis, we
predict that sheet resistance is proportional to the square of nanowire diameter and inversely proportional to the square of nanowire length and network coverage. Although current flow in a nanowire assembly is considerably more complex than that assumed for modelling purposes, comparison of our model with families of data from the literature arising from simulations and from experiment yields excellent agreement. Using the example of the often-observed lognormal distribution for nanowire lengths, we have provided also a theoretical basis for the observation that the sheet resistance of networks of nanowires with a distribution of lengths is dominated by the contribution of longer nanowires. We show also that the known theoretical dependence of network uniformity on mean coverage, coupled with our theory, provides qualitative agreement with the observed influence of mean coverage on the variability of sheet resistance.

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Author contributions

CAA carried out the literature review and developed the first versions of the theory under the supervision of BD & WWS. CAA carried out preliminary data analysis and curve fitting; WWS refined the model and prepared the first draft of the manuscript. All authors contributed to the final version of the manuscript.

References


Supplementary Information

Length-weighted nanowire length distribution

A lognormal distribution of nanowire lengths, $\lambda$ has probability density given by

$$f(\lambda) = \frac{1}{\sqrt{2\pi} \lambda s} e^{-\frac{(m - \log(\lambda))^2}{2s^2}}$$  \hspace{1cm} (16)

with mean $\bar{\lambda} = e^{m + \frac{s^2}{2}}$ and variance, $\sigma^2(\lambda) = \left(e^{s^2} - 1\right)e^{2m + s^2}$. It follows that the coefficient of variation of $\lambda$ is

$$CV(\lambda) = \frac{\sigma(\lambda)}{\lambda} = \sqrt{e^{s^2} - 1}.$$  \hspace{1cm} (17)

The length-weighted distribution of nanowire length is

$$g(\lambda) = \frac{\lambda f(\lambda) d\lambda}{\int_0^\infty \lambda f(\lambda) d\lambda} = \frac{1}{\sqrt{2\pi} s} e^{-m + \frac{s^2}{2} + \frac{(m - \log(\lambda))^2}{2s^2}}$$  \hspace{1cm} (18)

and has mean

$$\bar{\lambda}_w = \int_0^\infty \lambda g(\lambda) d\lambda = e^{m + \frac{s^2}{2}}$$

$$= (1 + CV^2(\lambda)) \bar{\lambda}.$$  \hspace{1cm} (19)