4 Variable Range Hopping Conduction

4.1 Introduction

4.1.1 Room Temperature Conduction in Silicon Suboxides

In the last decade several studies on non-stoichiometric amorphous silicon oxides showed a monotonic decrease of the electrical conductivity at room temperature with increasing oxygen content, over several orders of magnitude, from the level of the semiconductor (unhydrogenated) amorphous silicon \( \sigma \sim 10^{-4} \, \Omega^{-1} \text{cm}^{-1} \) to the level of the electrical insulator silicon dioxide \( \sigma \sim 10^{-15} \, \Omega^{-1} \text{cm}^{-1} \) [49,53,111].

In the sputtered amorphous silicon suboxides (a-SiO\(_x\)) under investigation in this study, again a strong dependence of the electrical conductance on oxygen concentration is observed. In figure 1.1 on page 11 the dc conductivity of thin layers (0.5 \( \mu \text{m} \)) of a-SiO\(_x\), measured at room temperature in the co-planar configuration discussed in section 2.3.2, is plotted as a function of oxygen/silicon ratio \( x \). Indeed, the conductivity of these layers drops monotonically over more than ten orders of magnitude with the oxygen/silicon ratio \( x \) rising from 0 to 1.3.

4.1.2 Conduction by Free Carriers

Generally, together with an increase in (room temperature) resistivity, in silicon suboxides also a widening of the optical bandgap is observed, from approximately 1.8 eV in a-Si up to 8.9 eV in a-SiO\(_2\) [53,58,66,106,111,112]. In section 3.4 the observed increase in the optical bandgap is explained by theoretical calculations on the band structure of SiO\(_x\) [114]. Consequently, the simplest model used to explain the decrease in conductivity adopts a conduction mechanism based on the activation of carriers to free delocalized states beyond the bandgap (‘band conduction’), directly linking the conductivity with the size of the bandgap. However, we will demonstrate that this model does not apply to our material.

Theories on non-defective non-doped semiconductors show that the Fermi level is positioned around mid-gap to obey the condition of charge neutrality in the material [118]. In the case of band conduction in SiO\(_x\) this would lead to an
increase in activation energy with increasing $x$, from around 0.9 eV in a-Si up to around 1.5 eV for suboxides with $x \approx 1.5$. Indeed, an increase in activation energy has been observed in several studies on the conduction of different silicon suboxides [49,53,111]. In these studies the $x$ dependence of the (room temperature) resistivity of SiO$_x$ is easily explained in terms of an increased activation energy within a band conduction model.

Although this theory has proven to explain and predict the electrical characteristics of several silicon suboxides studied in the past [49,53,111], there is serious reason to doubt the application of this theory to our sputtered material. All Electron Spin Resonance (ESR) measurements, presented in section 3.3.2, show a strong signal of the paramagnetic electron of the neutral silicon dangling bond (Si:DB). Because of the neutral appearance of these Si:DB states, it is concluded that in the a-SiO$_x$ under investigation the chemical potential $\mu$ is positioned around the energy level of these neutral states. This energy level, equivalent to the Fermi level at $T= 0\, \text{K}$, is expected to resemble the level of the atomic Si:sp3 hybrid orbital, because of the unbonded nature of the dangling bond electrons. In section 3.4.2 it is suggested that this energy level, which is located around mid-gap in a-Si, remains at a more or less fixed position with respect to the conduction band edge of a-SiO$_x$ with $x < 2$. This position of the chemical potential, which is closer to the conduction band than to the valence band in all compounds but $x = 0$, suggests a prevalence of n-type band conduction over p-type band conduction. Moreover, due to the observed high concentration of neutral silicon dangling bonds and the assumed more or less fixed position of the Si:DB states with respect to the conduction band edge, the activation energy of this assumed n-type band conduction process is not expected to increase with increasing $x$. As a result, we do not expect a band conduction mechanism with an activation energy depending on $x$. Therefore, the model explaining the conduction in SiO$_x$ in terms of different activation energy with different $x$ is not applicable to the compounds discussed here. Indeed, measurements on the temperature dependence of the conductivity indicate a different mechanism of conduction.

### 4.1.3 Temperature Dependence of Conduction

In figure 4.1 the dc conductivity of 0.5 µm thick layers of SiO$_x$, measured in the co-planar configuration, is plotted as a function of temperature ($30\, \text{K} \leq T \leq 300\, \text{K}$) in an Arrhenius plot. Whereas a band conduction model predicts an Arrhenius temperature dependence of the conductivity, the deviating temperature dependence observed in our samples clearly reveals a different conduction mech-
4.1. INTRODUCTION

Figure 4.1: Conduction of a-SiO$_x$ versus temperature, plotted in an Arrhenius plot, for samples with different oxygen/silicon ratio $x$: (a) $x = 0.01$, (b) $x = 0.14$, (c) $x = 0.35$, (d) $x = 0.84$, (e) $x = 1.17$, (f) $x = 1.82$.

anism, at least at low temperatures up to room temperature.

Taking the slopes in the Arrhenius plots of figure 4.1 as activation energies results in values at room temperature increasing from 0.12 $\pm$ 0.01 eV to 0.35 $\pm$ 0.02 eV with $x$ increasing from 0 to 1.3. Although these values indeed rise with increasing $x$, they do not resemble 0.7 eV, as expected according to the hypothesis of a pinned chemical potential around the Si:DB states, as discussed in the last part of the previous section.

The measured values are much smaller and suggest that the electronic processes that are dominant in the conduction, at least up to room temperature, occur in a much narrower energy band around the level of the chemical potential. Because the electronic states in semiconductors around this level within the gap are localized, the transport of charge requires a conduction mechanism through localized states. This mechanism, which is known as hopping conduction, is observed in two well-known varieties, i.e. nearest neighbor hopping and variable range hopping. The latter conduction mechanism is distinguishable from other conduction mechanisms by its different temperature dependence: $\log \sigma \sim T^{-1/4}$ (see section 4.3.1, equation 4.23). In figure 4.2 the data of figure 4.1 is represented in a $\log \sigma$ versus $T^{-1/4}$ plot, clearly showing this temperature dependence over the
A log $\sigma \sim T^{-1/4}$ behavior does not necessarily imply a variable range hopping (vrh) conduction mechanism. According to calculations, also other conduction mechanisms, albeit using sometimes very specific presumptions, can show a temperature dependence similar to the $T^{-1/4}$ dependence [119–121]. However, theories on the vrh conduction, described in more detail in the next section, indicate a strong relation between the level of hopping conductance and the concentration of localized states around the chemical potential $\mu$. Since the SiO$_x$ layers under investigation in this work possess a large concentration of these states, as observed by ESR measurements, the dominance of vrh conduction in these materials seems plausible. Although this conduction mechanism is often observed in studies on semiconductors at lower temperatures (in fact, theory shows that the dominance of the vrh conduction mechanism is always expected at sufficiently low temperatures [20]), the clear observation of a log $\sigma \sim T^{-1/4}$ dependence in our compounds at all temperatures up to room temperature provides an excellent tool to examine the mechanism of hopping conduction, and in particular the variable range hopping conduction.
4.1.4 Outline

In 1968 Mott introduced the concept of a type of hopping conduction called variable range hopping (vrh) [19]. Although Mott’s original manuscript successfully described the empirically observed \( \log \sigma \sim T^{-1/4} \) dependence, the derivation of this relation proved rather unsatisfactory from a statistical point of view. Following Mott’s publication several different and more thorough approaches, each based on different mathematical techniques and assumptions, were used to describe the vrh mechanism [122–128]. Nevertheless, they all resulted in very similar expressions of temperature dependence. Since Mott’s formalism reveals a clear insight in the processes involved in the vrh conduction, an analytical description based on this formalism is presented here. Both the derivation of the \( \log \sigma \sim T^{-1/4} \) relation, valid at low electric field strengths (the ‘Ohmic’ regime), as well as an extension of the original model to the regimes of higher field strengths is presented in section 4.3. A discussion on the validity of the ‘Mott model’ and a comparison with other analytical studies concludes this section.

The essential difficulty of describing the effective hopping conduction in a system with randomly distributed localized states is precisely its randomness, which cannot be dealt with analytically without questionable methods of averaging. Whereas the analytical averaging is hindered by the large spread in the individual site-to-site hopping probabilities, percolation theory [81,129,130] on the other hand has proven to be very successful in dealing with these large differences. This led to the publication of several studies, in which the vrh process is expressed in terms of a percolation problem [131–139]. As in Mott’s analytical description, these publications put emphasis on the qualitative relations between the important parameters in the system, by applying ‘ready-made’ analytical solutions of general percolation problems [81] to the vrh process. Although this approach has proven to be successful in describing the vrh process in the Ohmic low-field regime [131–136], the convolution of the hopping process to a standard percolation problem appears less straightforward in the medium-field [137–139] and, in particular, the high-field regime [139].

In this study no attempts have been made to express the vrh process in terms of a standard percolation solution. Instead, a purely numerical description of the process is obtained by repeatedly solving the percolation problem in a system of randomly distributed localized states. Quantification of the relations between the important parameters in the vrh process is achieved by statistically averaging over the individual percolation solutions in different distributions of localized states.

In section 4.4 this procedure is elucidated, and its results are checked for con-
sistency with the existing models in the low field regime. In the second part of this section an extension of the model to the high field regime is presented, revealing a clear quantified description of the relation between current and field strength in this regime.

Section 4.5 discusses the assumptions made in both the analytical and numerical descriptions of the vrh process, and the applicability of these models to the case of vrh conduction in the a-SiO$_x$ films under investigation.

4.2 Hopping Probabilities

Assuming no correlations between the occupation probability of different localized states the net electron flow between these states is simply given by

$$I_{ij} = f_i(1 - f_j)w_{ij} - f_j(1 - f_i)w_{ji}, \quad (4.1)$$

with $f_i$ denoting the occupation probability of state $i$ and $w_{ij}$ the electron transition rate of the hopping process between the occupied state $i$ to the empty state $j$. Defining the chemical potential $\mu_i$ as the chemical potential at the position of state $i$, the occupation probability is given by the Fermi-Dirac distribution function

$$f_i = \frac{1}{\left[1 + \exp\left[\frac{(E_i - \mu_i)/k_BT}{2}\right]\right]} - 1. \quad (4.2)$$

The transition rate is related to a hopping probability by

$$w_{ij} = \gamma P_{ij}, \quad (4.3)$$

with $P_{ij}$ the probability of success in a hopping attempt between states $i$ and $j$ and $\gamma$ an unknown parameter related to a certain ‘attempt-frequency’. This ‘attempt frequency’ is discussed in more detail in section 4.3.

Since the hopping process originates from tunneling events the hopping transition rate is derived from the tunneling probability:

$$P_{\text{tunnel} i\rightarrow j} = \exp(-2\alpha|R_{ij}|) \quad (4.4)$$

with $R$ the physical distance separating the two localized states, and $\alpha$ the localization parameter of these states. In a mathematically simple one-dimensional system the $\alpha$ parameter corresponds with the exponential decay of a wavefunction in a potential barrier and is directly related to the height of the potential barrier. In systems of higher dimensions this relation is less obvious, and the $\alpha$ parameter is
characterized by an integration of all possible tunneling paths between two sites, viz. the $\alpha$ parameter reflects the ‘potential landscape’ surrounding the hopping sites.

From thermodynamic considerations and assuming detailed balance in hopping between two localized states, the transition rate of a carrier hopping from site $i$ with energy $E_i$ to site $j$ with energy $E_j \geq E_i$ is often described by [138,139]:

$$w_{ij} = \gamma \exp \left( -2\alpha |R_{ij}| \right) \left\{ \exp \left[ -\left( E_i - E_j \right) / k_B T \right] - 1 \right\}^{-1}, \quad (4.5)$$

with $\gamma$ depending on the phonon spectrum, the electron-phonon coupling strength and the energy difference between the two sites in order to keep $w_{ij}$ from diverging as $|E_i - E_j| \to 0$ [139].

Applying equations 4.2 and 4.5 to expression 4.1 results in the relation between the current and the potential difference ($\Delta \mu \equiv \mu_j - \mu_i$) between two hopping sites [139]:

$$I_{ij} \sim \gamma \exp \left( -2\alpha |R_{ij}| \right) \sinh \left[ \frac{\mu_j - \mu_i}{2k_B T} \right] \times$$

$$\left\{ \cosh \left[ \frac{E_i - \mu_i}{2k_B T} \right] \cosh \left[ \frac{E_j - \mu_j}{2k_B T} \right] \sinh \left[ \frac{|E_i - E_j|}{2k_B T} \right] \right\}^{-1} \quad (4.6)$$

In all theories leading to an analytical description of the vrh process [19,20,122–124,131,139] equation 4.6 is simplified by assuming all energy differences in the expression larger than or comparable to $k_B T$. In case of low electric field strengths, resulting in a small voltage drop over a single hopping distance ($\Delta \mu \ll k_B T$), this gives

$$\sigma_{ij} \equiv \frac{I_{ij}}{\Delta \mu} \sim \gamma \exp \left[ -2\alpha |R_{ij}| + \frac{|E_i - \mu_i| + |E_j - \mu_j| + |E_i - E_j|}{2k_B T} \right], \quad (4.7)$$

with $\mu \approx \mu_i \approx \mu_j$. This expression was introduced in 1960 by Miller and Abrahams [140] and is often referred to as the ‘Miller-Abrahams’ conductance.

In the limit of high electric field strengths, leading to a voltage drop over a single hopping distance in the order of or higher than $k_B T$, expression 4.6 is simplified by

$$I_{ij} \sim \gamma \exp \left[ -2\alpha |R_{ij}| + \frac{|E_i - \mu_i| + |E_j - \mu_j| + |E_i - E_j| - (\mu_i - \mu_j)}{2k_B T} \right]. \quad (4.8)$$

This situation is discussed in more detail in section 4.4.2.
4.3 Mott’s Formalism

In the formalism developed by Mott [19,20] the hopping process is even more simplified by assuming that the dominant contribution to the hopping current is through states within $k_B T$ of the chemical potential $\mu$, thereby eliminating the exact occupation probabilities of the states in the description. In this case the hopping probabilities are derived directly from equation 4.5, giving the probability of a carrier tunneling from a localized state $i$ with energy $E_i$ to an empty state $j$ with energy $E_j$:

$$P_{ij} \approx \begin{cases} \exp \left( -2\alpha R_{ij} - \frac{E_j - E_i}{k_B T} \right) & \text{if } E_j > E_i \\ \exp (-2\alpha R_{ij}) & \text{if } E_j \leq E_i \end{cases}$$

(4.9)

In this description again the approximation $|E_i - E_j| \geq k_B T$ is used, although the validity of this approximation is questionable. The implications of this assumption and results of a more thorough approach are discussed in section 4.3.5. It is noted that the ‘Miller-Abrahams’ conductance (equation 4.7) is restored by the product $f_i (1 - f_j) P_{ij}$.

Since the hopping probability depends on both the spatial and energetic separation of the hopping sites it is natural to describe the hopping processes in a four-dimensional hopping space [122,123], with three spatial coordinates and one energy coordinate. In this hopping space a range $R$ is defined as

$$R_{ij} = -\log P_{ij}$$

(4.10)

This range, given by the magnitude of the exponent in equation 4.9, represents a distance in four-dimensional hopping space, indicating the hopping probability.

In a system in which localized states are randomly distributed in both position and energy, the probability distribution function of all hops originating from one site is generally dominated by the hop to the nearest neighboring site in the four-dimensional hopping space, due to the exponential character of the hopping probabilities (equation 4.9). This site at closest range corresponds only with the spatially nearest neighbor if the first term on the right hand site of equation 4.9 is dominant. This is true if $\alpha R_0 \gg 1$, with $R_0$ the average spatial distance to the nearest neighboring empty localized state, that is in cases of strong localization and/or low concentration of localized states. The hopping distance $R$ is limited to the spatial nearest neighboring hopping site at average distance $R_0$, and the conduction mechanism is called nearest neighbor hopping. However, if $\alpha R_0$ is in the order or less than unity, or in all cases at sufficiently low temperatures, the second term on the right hand site of equation 4.9 contributes significantly to the
hopping probability and hops to sites that are further away in space but closer in energy might be preferable. This is the variable range hopping (vrh) process, which concept was introduced by Mott in 1968 [19].

It will be demonstrated that the hopping range in the vrh process depends on the material parameters $\alpha$ and $N_\mu$, and on the external parameters temperature $T$ and electric field $\vec{F}$. It is convenient to exclude the effect of the electric field, by writing the energy term of $R_{ij}$ as

$$\frac{E_j - E_i}{k_B T} = \frac{E_j' - E_i' - (-e)\vec{R}_{ij} \cdot \vec{F}}{k_B T} = \frac{W_{ij} + e\vec{R}_{ij} \cdot \vec{F}}{k_B T}$$

(4.11)

with $E_i'$ the energy of state $i$ compared to the chemical potential $\mu$ at position $i$, and $W_{ij} \equiv E_j' - E_i'$ the energy difference between the hopping sites in the absence of an electric field. Here hopping by electrons (charge -e) is considered; hopping by holes, however, is represented by the same expression.

Following equations 4.9 and 4.10 the hopping range is then expressed as

$$R_{ij} = \begin{cases} 
2\alpha R_{ij} + \frac{W_{ij} + e\vec{R}_{ij} \cdot \vec{F}}{k_B T} = R'_{ij} + \frac{e\vec{R}_{ij} \cdot \vec{F}}{k_B T} & \text{if } W_{ij} > -e\vec{R}_{ij} \cdot \vec{F} \\
2\alpha R_{ij} & \text{if } W_{ij} \leq -e\vec{R}_{ij} \cdot \vec{F}
\end{cases}$$

(4.12)

with $R'_{ij}$ the hopping range in the absence of an electric field.

Since the probability distribution function of all hops originating from one site is dominated by the hop to the site at closest range, the average hopping probability from this site $i$ is approximated by $P_i \approx \exp(-R_{i,nn})$, with $R_{i,nn}$ the range between state $i$ and its nearest neighboring state in the four-dimensional hopping space (the 'site at closest range'), i.e.

$$R_{i,nn} = \min (R_{ij}).$$

(4.13)

The drift of carriers under the influence of an electric field determines the conductivity. Because transport consists of a series of hops, the net conductivity depends on an average of the probabilities of sequential hops. As sequential probabilities multiply, the appropriate average is the geometric mean, i.e. [123]

$$\sigma \sim \langle P \rangle = \lim_{n \to \infty} \left[ \prod_i^n P_i \right]^{1/n} = \exp \left[ \lim_{n \to \infty} \frac{1}{n} \sum_i^n \ln P_i \right] \equiv \exp \left( -\overline{R}_{nn} \right).$$

(4.14)
Although $R_{i,n}$ depends on the randomly distributed sites around state $i$, it is possible to imagine an average nearest neighboring hopping range $\bar{R}_{nn}$. Assuming now that all individual hops are of range $\bar{R}_{nn}$ in the 4D hopping space, in real space these hops will be in random directions. However, for hops to sites with the same energy difference in the absence of an electric field (same $W_{ij}$), greater real distances will be hopped in the downfield direction than upfield (equation 4.12). So summing over all final states from initial state $i$ results in an average real forward distance hopped, $\bar{R}_F$.

Omitting now the direct use of equation 4.6, but following the simplified formalism used by Mott (equation 4.9), the effective current density in a vrh process in the presence of an electric field can be written as the product of the following factors:

- The number of charge carriers involved in the hopping process. This number is approximated by $2N_\mu k_B T$, with $N_\mu$ the density of localized states in volume and energy around $\mu$.

- The charge of the carriers: $-e$ for electrons.

- An attempt frequency $\nu_{ph}$, depending on the extent of electron-phonon interaction. In the following analytical description this frequency is supposed to be independent of temperature and hopping distance. The implications of this assumption are discussed at the end of the section.

- The average forward distance traveled per hop, $\bar{R}_F$.

- The average hopping probability $\bar{P} = \langle P \rangle \equiv \exp (\bar{R}_{nn})$, optimized to the closest hopping range for all individual hops (equation 4.13) and averaged over all hopping states.

Hence, the current density is approximated in Mott’s formalism by

$$j \sim \langle e \bar{R}_{ij} \cdot jN_\mu k_B T \nu_{ph} \exp (-R_{ij}) \rangle \approx e \bar{R}_F N_\mu k_B T \nu_{ph} \exp (-\bar{R}_{nn}) .$$

(4.15)

The critical factor in this equation is the determination of the average nearest hopping range $\bar{R}_{nn}$ since it has an exponential effect on the current. The description of this average nearest hopping range depends on the magnitude of the applied electric field.
4.3. MOTT’S FORMALISM

4.3.1 Low Electric Field Regime

If the contribution of the electric field $\frac{e\bar{R}F}{k_B T}$ to the hopping range $\bar{R}$ is small, that is if $|e\bar{R}F| \ll k_B T$, the effect of the electric field on the hopping current can be approximated by the difference in probability of hopping in or against the direction of the field. Using equations 4.12 and 4.15 to describe both the current in and against the direction of the field, this yields

$$j \sim 2e\bar{R}' N_\mu k_B T \nu_{ph} \exp \left(-\bar{R}'_{nn} \right) \sinh \left( \frac{e\bar{R}' F}{k_B T} \right),$$

(4.16)

with $\bar{R}'$ the average hopping distance in the absence of an electric field, and assuming $\bar{R}_F \propto \bar{R}'$.

The average nearest hopping range in the absence of an electric field, $\bar{R}'_{nn}$, is estimated using the following reasoning: Suppose that at temperature $T$ the carrier hops to a site within a sphere of radius $r(T)$. Statistically, this site is located on average at a distance $\bar{R} = \frac{3}{4} r$ from the original site. Furthermore, since we assume no correlation between position and energy of the site in the absence of an electric field, the energetically closest site within this sphere will on average have an energy difference with the original site

$$\bar{W} = \frac{3}{4\pi r^3 N_\mu} = \frac{3^4}{4^4\pi R^3 N_\mu},$$

(4.17)

assuming a constant density of states around $\mu$. Thus, the average range $\bar{R}'$ of this site is given by

$$\bar{R}' = 2\alpha \bar{R} + \frac{\bar{W}}{k_B T} = 2\alpha \bar{R} + \frac{3^4}{4^4\pi R^3 N_\mu k_B T}.$$  

(4.18)

Minimizing this equation with respect to $\bar{R}$ results in an optimal average hopping distance

$$\bar{R}' = \frac{3}{4} \left( \frac{3}{2\pi\alpha N_\mu k_B T} \right)^{1/4}.$$  

(4.19)

This expression is characteristic for the vrh mechanism, indicating an increasing hopping distance with decreasing temperature. The probability of this hop taking place, in terms of the average nearest hopping range in the absence of an electric field, is given by

$$\bar{R}'_{nn} = \left( \frac{T_0}{T} \right)^{1/4},$$

(4.20)
with

\[ T_0 = C_T \frac{\alpha^3}{k_B N_{\mu}} \]  

(4.21)

and the proportionality constant \( C_T \) given in this formalism by

\[ C_T = \frac{24}{\pi}. \]  

(4.22)

Combining equations 4.16, 4.19 and 4.20, and using \( \sinh(\frac{e\bar{R}F}{k_B T}) \approx \frac{e\bar{R}F}{k_B T} \) since \( |e\bar{R}F| \ll k_B T \), results in the expression

\[ \sigma = \frac{j}{F} = \sigma_0 \exp \left( -\frac{T_0}{T} \right)^{\frac{1}{4}}, \]  

(4.23)

with \( T_0 \) given by equation 4.21 and \( \sigma_0 \) defined in this formalism by

\[ \sigma_0 \sim v_{ph} \left( \frac{N_{\mu}}{\pi \alpha k_B T} \right)^\frac{1}{2}. \]  

(4.24)

Consequently, in the low electric field regime the vrh process is characterized by an Ohmic conduction behavior. The conductivity is dominated by the exponent in equation 4.23, resulting in a \( \log \sigma \sim T^{-1/4} \) temperature dependence. The condition for this low electric field regime is given by

\[ \frac{|e\bar{R}F|}{k_B T} \ll 1 \implies F \ll \frac{4}{3e} \left( \frac{2\pi \alpha N_{\mu}}{3} \right)^\frac{1}{2} (k_B T)^\frac{3}{4}, \]  

(4.25)

indicating that this regime extends to higher field strengths with higher temperature.

### 4.3.2 Medium Electric Field Regime

With increasing field strength the effect of the field on the current becomes more complicated. As long as \( |e\bar{R}F| \ll k_B T \) the effect of the field on the average hopping distance can be neglected, and the process is described by only considering the difference in hopping probability when hopping the average hopping distance in or against the direction of the field. In other words, the effect of the field is considered as a first order deviation from the optimized average hopping range \( \bar{R}_{nn} \) in the absence of an electric field.
When $|e\vec{RF}| \gg k_B T$, that is if the electric field is much larger than the expression on the right hand side of equation 4.25, this approximation no longer holds and the effect of the field on $\mathcal{R}_{ij}$ has to be considered before optimizing the average hopping range. Although the original Mott model does not include any field effects outside the Ohmic regime, we adopt its formalism here to reveal the important processes in the higher field regimes.

Assuming $|e\vec{RF}| < W$ and following equation 4.12, the probability of a hop taking place is written as

$$P_{ij} = \exp \left( -\mathcal{R}_{ij}' - \frac{e\vec{R} \cdot \vec{F}}{k_B T} \right).$$  

(4.26)

If $|eRF| \gg k_B T$ the probability of hops in the direction of the electric force (for electrons opposite to the direction of the field) is much larger than the probability of hops against this force. Consequently, the nearest hopping range is almost certainly associated with a hop in the direction of the electric force. Hence, the nearest hopping range is approximated by

$$\mathcal{R}_{nn} \approx \min \left( 2\alpha R + \frac{W - eRF}{k_B T} \right).$$  

(4.27)

In this equation $W$ again describes the energy difference between two sites in the absence of a field. Using equation 4.17 in minimizing equation 4.27 effectively the preferential direction of $\vec{R}$ in the direction of the field is neglected in the minimization routine, and only the effect of $\vec{F}$ on the magnitude of the average hopping distance is considered. Still, in first order approximation an average hopping distance can be deduced

$$\bar{R} \sim \left( \frac{3}{\pi N_\mu (2\alpha k_B T - eF)} \right)^{1/4}.$$  

(4.28)

and a corresponding optimized average hopping range

$$\mathcal{R}_{nn} \sim \left( 2\alpha - \frac{eF}{k_B T} \right) \bar{R} + \left( \frac{C}{N_\mu k_B T} \right) \bar{R}^{-3},$$  

(4.29)

with $C$ some numerical constant in the order of 1, depending on the shape of the volume considered in minimizing equation 4.27.

According to equations 4.15 the vrh current density in the electric field regime $k_B T \ll |eRF| < W$ can now be written as

$$j \sim \bar{R} \exp \left( -\mathcal{R}_{nn} \right).$$  

(4.30)
with $\bar{R}$ given by equation 4.28 and $\bar{R}_{nn}$ by equation 4.29.

The upper-limit of the medium-field regime is obtained from equations 4.28 and 4.17:

$$|e\bar{R}F| < \bar{W} \Rightarrow F < \frac{\alpha k_B}{2e} T.$$  \hfill (4.31)

### 4.3.3 High Electric Field Regime

At even higher field strengths, where $|eRF| \geq W$, a negative energy difference between initial and final hopping state is obtained. From equation 4.12 it is clear that the corresponding hopping probability is then defined by the spatial term of the hopping range only: $R = 2\alpha R$. Physically this means that the initial energy difference between the hopping states is completely compensated by the energy gain of the charge carrier hopping in the direction of the electric force. Hopping any further in the direction of this force results in a net surplus of energy, which does not increase the hopping probability. Therefore, the site at closest hopping range is expected to satisfy the condition $|e\bar{R}F| = \bar{W}$. Using equations 4.17 to describe $\bar{W}$ in terms of $\bar{R}$, this results in an expression for the average hopping distance:

$$\bar{R} = \frac{3}{4} (\pi e N, \mu F)^{-\frac{1}{4}}.$$  \hfill (4.32)

Again following equation 4.15, the current density is then approximated by

$$j \sim \exp \left( -\frac{F_0}{F} \right)^\frac{1}{4},$$  \hfill (4.33)

with

$$F_0 = C_F \frac{\alpha^4}{e N, \mu}.$$  \hfill (4.34)

and the proportionality constant $C_F$ denoted in this formalism by

$$C_F = \frac{81}{16\pi}.$$  \hfill (4.35)

Since the energy needed in the hopping process is provided by the electric field, no thermal activation is required anymore and a field induced tunneling current is expected. Indeed, equation 4.33 shows no temperature dependence (besides
4.3. MOTT’S FORMALISM

from a linear effect of the number of carriers participating in the hopping process, equation 4.15), yet an exponential dependence of the current on field strength.

So far, the influence of the electric field on the analytical description of the vrh current has been categorized in terms of the magnitude of this electric field. However, not the electric field but, more specific, the energy transfer of the electric field to the hopping carrier determines the influence of the field. This energy transfer is given by the product $e \vec{R} \cdot \vec{F}$. Since according to equations 4.19 and 4.28 the average hopping distance increases with decreasing temperature, this energy transfer also increases with decreasing temperature. Consequently, the low, medium and high electric field regimes are equally described as high, medium and low temperature regimes. The transition from the medium-field to the high-field temperature independent regime (equation 4.31) is given in terms of a transition temperature

$$T_{-T_{\text{indep}}} = \frac{2e}{\alpha k_B} F,$$  \hspace{1cm} (4.36)

which is, in contrast to most parameters in the vrh process, a function of $\alpha$ only, instead of a combination of $\alpha$ and $N_\mu$.

4.3.4 Numerical Evaluation

The analytical description of the vrh processes discussed so far is based on equation 4.15, describing the vrh current in terms of $\bar{R}_{nn}$ and $\bar{R}$. Although the derivation of the analytical expressions for these parameters requires the classification in different field strength and/or temperature regimes, numerical values for these parameters are readily obtained by expressing $\bar{R}$ as a function of $R$, $F$ and $T$, using equations 4.12 and 4.17, and minimizing this expression with respect to $\bar{R}$ numerically. Using these numerically obtained values for $\bar{R}_{nn}$ and $\bar{R}$ a quasi-analytical vrh current can be calculated as a function of $\alpha$, $N_\mu$, $\nu_{\text{ph}}$, $T$ and $\vec{F}$, without any additional classification in field strength or temperature.

Results of these calculations are plotted in figures 4.3 and 4.4, showing the net vrh current, that is the difference of the current in and against the direction of the field, through localized states with localization parameter $\alpha = 10^7$ cm$^{-1}$ and density $N_\mu = 10^{18}$ cm$^{-3}$ eV$^{-1}$ at different field strengths and temperatures. In these calculations $\nu_{\text{ph}}$ is supposed to be 1 THz, independent of temperature.

Clearly, the Ohmic regime with linear $j - F$ characteristics and $\log \sigma \sim T^{-1/4}$ temperature dependence can be distinguished at low field strengths and high temperature. Furthermore, the field induced tunneling regime, characterized by a
Figure 4.3: Calculated vrh current density through localized states with $\alpha = 10^7 \text{cm}^{-1}$ and $N_\mu = 10^{18} \text{cm}^{-3}\text{eV}^{-1}$, as a function of electric field strength and at different temperatures. (^) indicates the field limit to the Ohmic regime according to equation 4.25, (↓) shows the onset of the field induced tunneling regime according to equation 4.36.

$\log j \sim F^{-1/4}$ field dependence and very weak temperature dependence, is observed at high field strengths and low temperatures. In the plots the limits of the Ohmic regime to the field strength and temperature, given by equation 4.25, are indicated by the arrows pointing up. The arrows pointing down represent the critical field strengths and temperatures given by equation 4.36, indicating the onset of the field induced tunneling regime.

Comparing figures 4.3 and 4.4 with the measured data plotted in figures 5.1 and 5.2 (section 5.2.1), it is clear that at least qualitatively the analytical model agrees with measurements. However, it is necessary to make some critical remarks regarding this analytical description.

4.3.5 Discussion

Most criticism on Mott’s derivation of the $\log \sigma \sim -(T_0/T)^{1/4}$ relation focuses on the simplifying assumption of proportionality between mean hopping energy
and the inverse cube of the hopping distance (equation 4.17). Indeed, especially at higher field strengths, the spherical symmetry that is implicitly assumed in deducing equation 4.17 is certainly questionable. In addition, only the hopping probabilities of carriers at the level of the chemical potential $\mu$ are taken into account, thereby neglecting the presence and occupation probabilities of states above and below this level. A more thorough mathematical analysis on the four-dimensional quantity range [122–124], omitting the direct use of equation 4.17 and including states around $\mu$ occupied according to a Fermi-Dirac distribution, however, results in similar expressions of temperature and field dependence. With $\mu$ positioned in a constant DOS and at low electric field strength, again Ohmic conduction and a dominant $\log \sigma \sim -(T_0/T)^{1/4}$ temperature dependence of conduction is derived, with proportionality constant $T_0$ identical to the definition in equation 4.21. Furthermore, at high field strength a conduction mechanism independent of temperature and with field dependence $\log \sigma \sim -(F_0/F)^{1/4}$ is derived, with $F_0$ only differing from equation 4.34 in the dimensionless constant $C_F$ (according to this description $C_F = 64/\pi$). At medium field strengths a $\log \sigma \sim F^2$ is predicted.
Only slightly different results are obtained following another approach, in which the conductivity is expressed in terms of a Green function corresponding to the linearized rate equation (4.1) [125–128]. In this description the exact temperature and field dependencies appear to be related with possible directional constraints on the hopping current path. In the case of isotropic random motion of the hopping carrier in a constant DOS at low field strengths, again the
\[ \log \sigma \sim -\left(\frac{T_0}{T}\right)^{1/4} \]
relation is derived, with \( T_0 \) only differing from equation 4.21 in its proportionality constant \( C_T \) (here, \( C_T = 12/\pi \)). At medium field strengths again a \( \log \sigma \sim F^2 \) is predicted. However, if the electric field is assumed to be strong enough to direct the motion of the carriers in a general forward direction (‘directed’ motion), the conduction in the Ohmic regime is found identical to equations 4.23 and 4.21. In this case a weaker field dependence in the medium field regime is expected, i.e. \( \log \sigma \sim F \). The controversy between isotropic and directed hopping will be discussed in more detail in the following section using concepts of percolation theory.

### 4.4 Formalism Based on Percolation Theory

In modeling the vrh conduction mechanism, generally a set of sites is supposed to form a random resistors network, with impedances connecting all individual sites given by the inverse of the corresponding hopping probabilities (equation 4.9):

\[ Z_{ij} \propto \exp \left( R_{ij} \right) . \]  

(4.37)

The basic difficulty in quantitatively describing the overall impedance of this network in an analytical expression arises from the wide exponential spread in magnitude of the site-to-site resistors between randomly chosen hopping sites. Whereas this wide spread is obstructing the use of analytical averaging, it has proven to be beneficial when dealing with the problem using a numerical approach based on percolation theory. Following this theory [81,130] the network is characterized by a sub-set of interconnected sites, spanning the entire volume, with two-site connections \( Z_{ij} \leq \tilde{Z}_t \). In this formalism the threshold impedance \( Z_t \) is defined as the minimum impedance \( \tilde{Z}_t \) needed to ensure an infinitely large cluster of interconnected sites within an infinitely large network. Essentially, the percolation threshold describes the highest impedance of the most conducting percolation path through the system. The actual sub-set of sites participating in the conduction is expected to be slightly bigger than the most conducting percolation path, including more parallel paths with slightly higher resistance. The overall impedance of the system is described by an optimization between the most conductive percola-
tion path with threshold impedance \( Z_t \) and a slightly larger sub-set of sites with occasionally a slightly larger site-to-site impedance.

Seager and Pike [132] demonstrated that this optimization is increasingly more dominated by the threshold impedance \( Z_t \) with increased spread in the site-to-site impedances. By comparing the derived threshold impedance with the calculated resistance of in an array of 1000 sites, they showed that the threshold impedance accurately describes the overall resistance of the system if the average variation in the 5-6 smallest impedances originating from each site exceeds \( \sim 7 \) orders of magnitude. We explicitly verified whether this criterion was met in the simulations presented here, and found that only at the highest temperatures (500°C) in the most dense system considered (\( N_{\mu} = 10^{20} \text{ eV}^{-1} \text{ cm}^{-3} \) with \( \alpha = 10^6 \text{ cm}^{-1} \)) the average spread in the 6 smallest impedances originating from each site is in the order of \( 10^7 \). In the ‘typical’ system with \( N_{\mu} = 10^{20} \text{ eV}^{-1} \text{ cm}^{-3} \), \( \alpha = 10^7 \text{ cm}^{-1} \) and \( T = 300 \text{ K} \) this spread already exceeds 11 orders of magnitude, and runs up to 128 orders of magnitude in the most ‘diluted’ system at 16 K. Consequently, in our percolation description of the vrh process simply the threshold impedance is sufficient to accurately describe the impedance of the entire network. Physically this means that the impedance of the network is described as if the current through the system is completely characterized by the current carrying backbone of the percolation path, which in turn is characterized by its highest impedance. Although in reality the current will be carried by a larger cluster of sites with slightly higher maximum site-to-site impedance, the large spread in \( Z_{ij} \) allows us to effectively neglect these contributions in determining the conductivity of the system.

### 4.4.1 Analytical Solutions of the Percolation Problem

In general percolation theory the criterion of percolation is often expressed in terms of an expected number of connections to a single site needed to ensure a percolating cluster through the system [81,130]. The application of this description to the vrh process with site-to-site connections given by equation 4.37 has led to several publications in which the dependence of \( Z_t \) on \( \alpha, N_{\mu}, T \) and \( F \) is derived [131–139]. As in the analytical descriptions, these studies primarily focussed on the qualitative relations between the parameters in the system.

Although this more analytical approach has proven to be successful in describing the vrh process in the Ohmic low-field regime [131–136], the convolution of the hopping process into a standard percolation problem appears less straightforward in the medium-field [137–139] and, in particular, the high-field regime [139]. The differences between ‘standard’ percolation solutions and the hopping
process appear to concentrate on two issues, often referred to as the concepts of ‘directional constraints’ and ‘correlation between consecutive hops’.

- **Directional constraints.** Whereas a percolation problem is by definition characterized by a single threshold impedance independent of the size of the system, empirically the vrh resistance is found to vary linearly with the dimensions of the measured sample \( R = \rho \frac{L}{A} \), with \( A \) the cross sectional area and \( L \) the distance between the electrodes. This discrepancy has led to the introduction of the concept of ‘directional constraints’, restricting all individual hops in the current carrying path to the general forward direction \([133,137–139]\). Its concept is extraneous to the percolation problem, and comprises the view that the important conducting paths are not necessarily identical with the critical percolation paths. Essentially, it reflects the idea that the mere presence of an electric field might impose a straighter optimal path between the electrodes than the critical percolation path, which possibly meanders aimlessly through the material.

- **Correlation between consecutive hops.** By adopting a formalism, in which the percolation problem is defined in terms of an expected number of connections to a single site needed to ensure a percolating cluster, the individual connections are generally supposed to be uncorrelated. However, the actual site-to-site hopping events are most certainly correlated. Especially when the occupation probabilities of the sites are included, the energy of the common site between two consecutive hops strongly correlates the two events, since it determines the occupation probability of both the final site of the first hop and the initial site of the consecutive hop. A large percolating current is consequently less easily achieved, since optimal occupation requires a high probability of a vacancy in the first case, but a high probability of occupation in the latter case. Although this concept has successfully been included in some descriptions of the low-field Ohmic vrh conduction \([133,135,136]\), with increasing field strength a possible field-induced rearrangement of charge along a current carrying path \([120,139]\) appears to complicate the description significantly \([133,137–139]\). As a result, no quantitatively clear description of the vrh process in the high field regime has yet been reported.

### 4.4.2 Numerical Solutions of the Percolation Problem

In this study no attempts have been made to express the vrh process in terms of standard (analytical) percolation solutions. Instead, a purely numerical descrip-
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Quantification of the relations between the important parameters in the VRH process is achieved by statistically averaging over the individual percolation solutions in different distributions of localized states. Although this procedure does not give a clear insight in the processes involved in the hopping process, the circumvention of standard percolation solutions does yield some significant advantages.

Firstly, the use of a finite system size allows us to reject any extraneous ‘directional constraints’ in the percolation problem. The finite system size inevitably constrains the current to flow inside a macroscopically small channel. The criterion of percolation as a closed path between two opposite sides of this channel restrains the current carrying path from meandering aimlessly through the system, without restricting all individual hopping events to a forward direction. As a result the macroscopic current can be envisaged to flow through numerous of these parallel and in series positioned small channels, resulting in a size dependent conductivity of the entire (macroscopic) system. Essentially, these channels represent the density of individual threshold impedances that carry the macroscopic current. Still, the changes in the overall resistance of a macroscopic sample are presumed to be adequately described by the threshold impedance of a single channel alone, as long as these channels are large enough to contain a threshold impedance similar to the threshold impedance defined in the infinite system. Since we restrict ourselves in this numerical study to the changes in the VRH conduction at different temperatures and field strengths, only the effects on the threshold impedance need to be examined.

Furthermore, the procedure of prescribing an actual percolation path in a system automatically comprises the concept of correlation between the connecting site-to-site hopping events. Due to these correlations the site energies in the percolation path appear confined to a band around the chemical potential \( \mu \), in order to preserve a finite probability of both entering and leaving the site. The implications of these correlations in the low-field Ohmic regime are discussed in more detail later in this section. Also, the effects of charge rearrangements along a current carrying path in the high field regime are discussed at the end of this section.

Primary objective of this percolation study is a quantitative refinement of the analytically derived relations, more specifically the \( \log \sigma \sim -(T_0/T)^{1/4} \) relation at low electric field strengths and the \( \log I \sim (F_0/F)^{1/4} \) relation at high field strengths. Although several authors have reported on a percolation description
of the vrh conduction in the Ohmic and medium-field regime [131–136], only
few of them reveal a quantified description of the proportionality constant $C_T$
in a system in which both concepts of ‘directional constraints’ and ‘correlation
between consecutive hops’ are incorporated [135,136]. We will show that our
results are in excellent agreement with these studies, confirming the consistency
of our model with the existing description.

The high-field regime on the other hand appears much less documented. Al-
though Pollak et al.[139] did report on extending their model in the Ohmic regime
[133] to the medium- and high-field regimes, no emphasis was put on the ex-
act quantification of the derived relations. Moreover, their high field description
does not include any effects of a field induced charge rearrangements along the
current carrying path, whereas later studies do reveal a possible significance of
these rearrangements [141]. Consequently, no consensus on the proportionality
constant $C_F$ has been obtained. In the second part of this section we present
a purely numerical percolation description of the vrh process in the high field
regime, focussing on a quantification of the proportionality constant $C_F$ in a sys-
tem in which the field induced charge rearrangements along the current carrying
path are included.

The numerical results discussed here are all obtained using a constant system
size of $10^4$ hopping sites, randomly distributed in energy and position. The en-
ergies are distributed within a band of specified bandwidth ($\Delta E$, generally 1 eV)
around the chemical potential; the positions are randomly assigned within a cube
of volume $L^3$, with $L$ satisfying the specified density of states $N_\mu = 10^4/\Delta E L^3$.
The electric field is supposed in the $\hat{x}$-direction, perpendicular to two opposite
sides of the cube, $x = 0$ and $x = L$. Percolation is established when at least one
site in a cluster of interconnected sites is connected to the $x = 0$ plane and at least
one site is connected to the $x = L$ plane, with site-to-site and site-to-plane con-
nections $Z_{ij} \leq \tilde{Z}_t$. The percolation threshold $Z_t$ is defined as the minimum value
of $\tilde{Z}_t$ needed to ensure percolation over the cube in the direction of the electric
field. To test the validity and reproducibility of the obtained threshold impedances
several measurements on systems containing $10^5$ hopping sites were performed.
Although these calculations resulted in marginally smaller threshold impedances,
compared to the results in the systems of $10^4$ sites, the relative differences in
threshold impedances with changing $\alpha$, $N_\mu$, $T$ and/or $F$ appeared completely un-
affected by the change in system size between $10^4$ and $10^5$ hopping sites. This
indicates that the system of $10^4$ hopping sites is large enough to represent an infi-
nite system, as required by the definition of a percolation threshold.
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Figure 4.5: Numerically derived threshold impedance in a network of localized states versus temperature (16 - 625 K), using different values of localization and density of states. Solid lines are fits within a set of equal localization and density. (a) $\alpha = 10^6$ cm$^{-1}$, $N_\mu = 10^{18}$ cm$^{-3}$eV$^{-1}$, (b) $\alpha = 10^7$ cm$^{-1}$, $N_\mu = 10^{20}$ cm$^{-3}$eV$^{-1}$, (c) $\alpha = 10^7$ cm$^{-1}$, $N_\mu = 10^{19}$ cm$^{-3}$eV$^{-1}$, (d) $\alpha = 10^8$ cm$^{-1}$, $N_\mu = 10^{21}$ cm$^{-3}$eV$^{-1}$, (e) $\alpha = 10^8$ cm$^{-1}$, $N_\mu = 10^{20}$ cm$^{-3}$eV$^{-1}$.

Low Electric Field Regime

In section 4.2 it is demonstrated that in the low electric field limit $\Delta \mu \equiv \mu_j - \mu_i \rightarrow 0$ the two-site hopping current is linearly proportional to the applied potential difference $\Delta \mu$, i.e. the sinh $\frac{\mu_j - \mu_i}{2k_B T}$ term in equation 4.6 can be approximated by its argument. In the low field limit a two-site hopping impedance is then defined by

$$Z_{ij} \sim \cosh \left( \frac{E_i - \mu}{2k_B T} \right) \cosh \left( \frac{E_j - \mu}{2k_B T} \right) \exp \left[ 2\alpha |R_{ij}| + \frac{|E_i - E_j|}{2k_B T} \right],$$

(4.38)

again using the assumption that the energy differences are larger than $2k_B T$, i.e. $\sinh \frac{|E_i - E_j|}{2k_B T} \approx \frac{|E_i - E_j|}{2k_B T}$. The validity of this assumption is discussed in section 4.5.

In a network of sites linked by impedances $Z_{ij}$ and assuming a constant density of states around the chemical potential $\mu$, the overall impedance is deter-
mined by three parameters: the density of sites, the localization of the sites and the temperature of the system. Using the percolation model described above, this impedance is approximated by the threshold impedance $Z_t$ and is calculated numerically for various values of the parameters $N_\mu (10^{17} - 10^{21}\ \text{cm}^{-3}\text{eV}^{-1})$, $\alpha (10^6 - 10^8\ \text{cm}^{-1})$ and $T (16 - 625\ \text{K})$. In figure 4.5 some results of these calculations are plotted, showing the temperature dependence of the threshold impedance in a network of sites with different density and localization. Each data-point is the resulting average of ten calculations with different randomly distributed hopping sites. The errors correspond to the root-mean-square deviations within these ten calculations. The sets of data points corresponding with a specific combination of localization and density of states are fitted with a $-\log Z_t \sim -(T_0/T)^{1/4}$ temperature dependence, represented in figure 4.5 by the solid lines.

Clearly, the expected $\log \sigma \sim -\log Z_t \sim -(T_0/T)^{1/4}$ dependence is observed, with different $T_0$ for different $\alpha$ and/or $N_\mu$. Only in curve (e), corresponding with the conduction in a system with $\alpha = 10^8\ \text{cm}^{-1}$ and $N_\mu = 10^{20}\ \text{cm}^{-3}\text{eV}^{-1}$, a deviation from this dependence is observed at high temperatures. The deviating data points appear to coincide with hopping through states with energies near the edge of the considered energy band of 1 eV. Physically these points mark the transition to the nearest neighbor hopping regime. In practice the energy band will often be smaller than 1 eV and either the transition to nearest neighbor conduction or the dominance of a band conduction mechanism will be observed at even lower temperatures.

Considering the analytically expected dependence of $T_0$ on $\alpha$ and $N_\mu$ (equation 4.21), the input parameters were scaled to the single parameter $\alpha^3/N_\mu k_B T$ and plotted versus the calculated threshold impedance. Figure 4.6 shows the resulting scaling plot using all calculated data. Indeed, within the margin of error all calculations with different $\alpha$ and $N_\mu$ collapse onto a single line, indicating the $T_0 = C_T\alpha^3/k_B N_\mu$ dependence predicted by equation 4.21.

Comparing the slope of the points in the scaling plot, $C_{T,\text{num}} = 18.5 \pm 0.2$, with the analytically derived proportionality constant $C_{T,\text{ana}} = 24/\pi \approx 7.6$ (equation 4.22), it is clear that the numerically derived temperature dependence is stronger than analytically expected. However, the percolation description presented here differs on two points from Mott’s description: 1. In the Mott model the occupation probabilities of the hopping states are neglected in the exponential term of the hopping current and only incorporated as a pre-exponential factor considering the number of hopping carriers proportional to $k_B T$ (equation 4.15). 2. In the Mott model the individual hops are considered uncorrelated, whereas in our model consecutive hops are most certainly correlated due to the energy of the common site, determining the occupation probability of both the final site of a first
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Figure 4.6: Scaling plot showing the relation between the calculated threshold impedance and the value $(T_0/T)^{1/4}$, with $T_0$ given by equation 4.21. The threshold impedance is calculated using sets of localized states with $\alpha = 10^6$ - $10^8$ cm$^{-1}$ with $N_\mu = 10^{20}$ cm$^{-3}$eV$^{-1}$, and $N_\mu = 10^{17}$ - $10^{21}$ cm$^{-3}$eV$^{-1}$ with $\alpha = 10^7$ cm$^{-1}$, $T = 16$ - 625 K. A linear fit through the data, corresponding with $C_T = 18.5$, is indicated by the solid line.

hop and the initial site of the consecutive hop. Since the more thorough analytical analyses [122–128] in which the occupation of states around $\mu$ are included still result in a proportionality constant $C_{T,ana} = 24/\pi$, equivalent to Mott’s description, the effect of correlations seems to be the dominant one.

For comparison between the analytical expressions derived by Mott and our numerical calculations it is instructive to carry out the calculations without incorporating the occupation probabilities of the individual sites, that is with two-site impedances $Z_{ij}$ given by the inverse of the hopping probability $P_{ij}$ (equation 4.9) only. Consequently, the correlation between consecutive hops due to the energy of the common site is effectively removed. Following a similar procedure as described above, leading to the derivation of the numerical $C_{T,num} = 18.5$, these calculations result in the scaling plot depicted in figure 4.7. Again the $\log \sigma \sim -(T_0/T)^{1/4}$ relation with $T_0 = C_T \alpha^3/k_B N_\mu$ is observed, but with the proportionality constant $C_{T,num} = 6.45 \pm 0.06$ more in correspondence with the analytically derived value of 7.6. Apparently, the simplifying assumptions in Mott’s calculations, neglecting the influence of the occupation probabilities of
hopping states above and below the level of the chemical potential and assuming no correlation between consecutive hops, retain the essential characteristics of the vrh process. Yet an accurate quantitative description requires the inclusion of the correlation between consecutive hops due to the energy of the common site. This apparently results in a stronger temperature dependence of the vrh conduction, illustrated by the value $C_T = 18.5 \pm 0.2$.

Qualitatively, all analytical percolation studies on the vrh process in the Ohmic regime show a similar result, corresponding with the analytical $\log \sigma \sim -\left(\frac{T_0}{T}\right)^{1/4}$ relation derived by Mott (equation 4.23). Furthermore, although the analytical percolation studies show a wide spread in the proportionality constant $G_T$, roughly ranging from 10 to 27 [131–136], only two of these studies present a quantification of this constant with consideration of both concepts of ‘directional constraints’ and ‘correlation between consecutive hops’. The values of $G_T$ derived in these studies, i.e. 17.8 [135] and 19 [136], appear in excellent agreement with the value $18.5 \pm 0.2$ derived in our study, thereby confirming the consistency of our purely numerical procedure and the analytically derived expressions.
4.4. FORMALISM BASED ON PERCOLATION THEORY

High Electric Field Regime

With increasing field strength the voltage drop over a single hopping distance increases. If this voltage drop is in the order of $k_B T$ or larger, the ‘Miller-Abrahams’ approximation of the general two-site current-voltage characteristics of equation 4.6 no longer holds. Both the expansion of the $\sinh(\Delta \mu / 2k_B T)$ term to only its linear component and the use of a single chemical potential in the $\cosh(E - \mu / 2k_B T)$ terms are no longer acceptable. As a result the current between two hopping sites depends on the chemical potential of both sites, which in turn depend on the strength and direction of the applied electric field. Therefore, a percolation model based on site-to-site hopping currents instead of (Ohmic) impedances needs to be adopted.

Furthermore, whereas in a homogeneously conducting material the potential is supposed to drop linearly with the physical distance from the contacts, in an inhomogeneously conducting material the potential is supposed to drop more strongly over regions with higher resistance than in the more conducting regions. Since the conductivity in a percolation path is by definition extremely inhomogeneous, the arrangement of site potentials in a percolation model is not straightforward. Especially taking into account the fact that in the higher field regimes the two-site impedances itself are considered field dependent, the determination of the site potentials seems rather complicated. In the medium-field region this problem has been approached by Pollak and Riess [139], resulting in a dominant $\log I \sim T^{-1/4}$ temperature dependence and $\log I \sim eF/k_B T$ field dependence. More recently however, a study on the redistribution of charge on the hopping sites due to a steady-state current [141] suggests a different site occupation in the medium-field region. The effect of this on the medium-field conduction has not been made quantitative yet.

Fortunately, in the high electric field regime some simplifying assumptions can be made. Since this regime corresponds with the low temperature regime, the expression of the site-to-site hopping current in the low $T$ limit, equation 4.8, can be used. Furthermore, the presumption of temperature independence implies that the energy part of the hopping process is completely compensated by potential differences over the hopping sites. As a result only hops downward in energy need to be considered, i.e. $E_i \geq E_j$ and consequently $|E_i - E_j|$ in equation 4.8 can be written as $E_i - E_j$. An effective two-site hopping current is then defined as

$$I_{ij} = \exp \left[ -2\alpha |R_{ij}| + \frac{|E_i - \mu_i| + (E_i - \mu_i) + |E_j - \mu_j| - (E_j - \mu_j)}{2k_B T} \right].$$ (4.39)
The current appears to be characterized by the relative energies of the individual hopping sites compared to their site potentials, and not depending on the absolute potential or energy differences between the sites, which are functions of the electric field strength. Thus, the two-site current is solely determined by the spatial component and the occupation probabilities that are controlled by the site potentials. The only requirement on the electric field is given by the condition that all hops are in the energetically downward direction. Hops to, in the absence of an electric field, energetically higher states need to be accompanied by an equivalent voltage drop, in order to have the required energy supplied by the electric field instead of by phonons. The average field strength needed to accomplish this is characterized by the total voltage difference over the system, which is equivalent to the total drop in chemical potential over the current carrying path.

By imagining a network of sites connected with impedances proportional to $I_{ij}^{-1}$, with $I_{ij}$ given by equation 4.39, a percolation problem can be set up to find an imaginary ‘threshold current’ $I_t$ in the system. However, solving this problem seems not feasible due to the lack of knowledge on the site potentials. On the other hand, according to general percolation theory the critically percolating cluster of sites would comprise a current carrying backbone with at least one site-to-site current equal to the threshold value. But since a steady-state situation would prescribe a constant current throughout the whole current carrying backbone, all site-to-site currents in it need to be equal. In order to achieve this, charge will redistribute itself along the path, thereby changing the chemical site potentials. From equation 4.39 it is clear that this rearrangement can never increase the current between two sites above the value dictated by the tunneling probability, $I_{ij} \leq \exp(-2\alpha|R_{ij}|)$. Optimization of the current is therefore obtained when the site potentials are altered in such a way that the single hopping event with smallest tunneling probability is optimized, leaving only the tunneling probability in its two-site current expression. As a result the threshold current in the high field regime is identical to the threshold current in a system of sites with all connections given by

$$Z'_{ij} \equiv I'_{ij}^{-1} = \exp(2\alpha|R_{ij}|).$$ (4.40)

Due to the lack of an energy parameter the percolation in such a system is often referred to as R-percolation [137], in contrast to the R-$\varepsilon$ percolation [138] in the four-dimensional hopping space discussed so far.

In this procedure the implicit assumption is made, that both the backbone of the percolating cluster and the threshold current do not alter upon rearranging the site potentials. Potentially, the redistribution of charge could cause another two-
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Figure 4.8: Position of sites in a cluster interconnected to the $x = 0$ plane with connections $Z'_{ij} \leq Z'_{1}$, projected to the $x$-$y$ plane. Used parameters are: $\alpha = 10^{7}$ cm$^{-1}$, $N_{\mu} = 10^{20}$ cm$^{-3}$eV$^{-1}$, $T = 16$ K and a voltage difference of $-5.4$ V in the $\hat{x}$ direction. The solid line represents the most conductive current carrying path over the system.

site current along the backbone to drop below the smallest tunneling current, but due to the large spread in $I_{ij}$ this effect seems negligible.

In the following calculations a network of sites is constructed, randomly distributed within a cube of certain dimensions and within a specific energy range. This energy range is assumed much larger than the energetic band used in the low field regime, to allow for any possible variation in the site energies with respect to the ground potential caused by an arbitrary inhomogeneous electric field. Eventually, the actual voltage drop over the sites will restrict the number of actual hopping states to within a specific (smaller) bandwidth around the chemical potential.

All sites are imaginary connected with impedances given by Mott’s simplified expression of hopping probabilities, equation 4.9. This expression both reflects the assumed impedances to energetically lower states (equation 4.40) and limits the hops to energetically higher states by the exponential energetic term. Assuming a ground potential at the $x = 0$ side of the cube, an interconnected cluster of sites connected to this plane and with all internal connections $Z'_{ij} \leq Z'_{1}$ can be
Figure 4.9: Site energies of the cluster depicted in figure 4.8 versus \(x\) position. The solid line connects the site energies of the most conductive path over the system.

Identified. An example of such a cluster is plotted in figures 4.8 and 4.9, showing the projected \(y\)-position and the energy, respectively, of the sites in the cluster as a function of distance from the \(x = 0\) plane. In this example \(\alpha = 10^7\ \text{cm}^{-1}\), \(T = 16\ \text{K}\) and the dimensions of the cube and energy range match a site density \(N_{\mu} = 10^{18}\ \text{cm}^{-3}\text{eV}^{-1}\). Percolation in the \(\hat{x}\) direction is dominated by a backbone of the cluster, defined by the most conducting percolating path. This path is depicted in figures 4.8 and 4.9 by the solid line.

From both figures it is clear that:

a. the important current carrying hops in the backbone of the cluster are all in the forward direction, as expected in the high field limit even more than in the low- and medium field regimes, and

b. all consecutive hops are to energetically lower sites, due to the low temperature and its strong influence on the hopping probabilities (equation 4.9). Consequently, the sequence of hops in the current carrying backbone does not require any thermal activation and is therefore independent of temperature, in accordance with the high field description of the v rh process.

By allocating a value for the chemical potential to each site in the backbone of the cluster, the occupation probabilities of these sites can be expressed in terms of the Fermi-Dirac distribution function (equation 4.2), which can be incorporated in the expression on the two-site impedances according to equation 4.1. This
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Figure 4.10: Deviations of the site energies from the local chemical potential of the sites in the current carrying backbone indicated by the solid line in figures 4.8 and 4.9. The site potentials were derived by assuming a maximum uniform current through the path. The dotted line represents the hopping event with smallest tunneling probability (equation 4.40).

results in the effective two-site currents predicted by equation 4.39. Assuming no contact potentials at the electrodes at both ends of the path, i.e. $E_x=0, L = \mu_x=0, L$, the condition of maximum uniform current through the isolated backbone now uniquely defines all chemical potentials in the backbone.

Figure 4.10 shows the deviation of the site energy from the potentials of the sites in the current carrying backbone depicted in figures 4.8 and 4.9, as derived by the routine described above. Not surprisingly, the site potentials more or less resemble the site energies, due to the fact that the potential dictates both the occupation probability of a final state in the hop entering the site and the occupation probability of the initial state in the consecutive hop. The mean deviation of the energy of the sites in the backbone of figure 4.9 from their corresponding local chemical potential appears to be $\sim 3k_B T$, corresponding with only 4 meV.

Apparently, the local chemical potential of the sites in the current carrying path is determined by the current path itself, rather than vice versa. Charge is distributed along the path in such a way that the chemical potentials of all sites in the path closely resemble the site energies in order to obtain an optimal charge transport through the system. As a result, the voltage drops more or less gradually
over the percolation path, without large fluctuations in the voltage differences between consecutive hopping sites, in contrast to what was put forward in the beginning of this section. From the fact that in the high field regime all hops are in an energetically downward direction this might already have been expected, since hopping to an energetically lower state essentially is a pure tunneling event, which is supposed independent of voltage differences. Physically this means that a gradually dropping potential is favorable over sharp voltage drops, since the gain in hopping probability over these sharp voltage drops would be insignificant compared to the decrease in hopping probabilities in the remaining regions with weaker electric field.

In figure 4.10 the hop spanning the longest spatial distance in the current carrying path, corresponding with the critical impedance in the R-percolation system, is accentuated by the dotted line. Note that in this figure only one spatial coordinate is depicted, whereas the total hopping distance is in 3D space. The energies of the sites preceding this critical hop all appear lower than the corresponding site potentials, whereas the sites following this hop are positioned energetically slightly above their potentials. Physically, this effect arises from the fact that the critical link in the percolation path constitutes a bottleneck for the current, with the current filling the states preceding this link in analogy to the formation of lakes ahead of a dam, while the occupation probabilities at the downcurrent site of this link decrease [139].

Furthermore, because the initial site of the critical hop is positioned energetically below and the final site above their respective site potentials, these potentials do not contribute to the probability of the hop, leaving only the tunneling probability in the two-site current expression in this particular part of the path. Since the current is prescribed uniform throughout the whole path, this specific two-site tunneling probability characterizes the overall current in the path, and with it in the entire finite sized system of which the path is the current carrying backbone. Consequently, these calculations support the hypothesis that the maximum current in the high field regime corresponds with the critical impedance in the R-percolation problem with connections given by equation 4.40.

The corresponding average field strength is found by the quotient of the potential drop over the percolating path and the length of the path in the direction of the electric field. The first is accurately described by the drop in site energies, because the sites at both ends of the path correspond to metallic states of the electrodes; the latter is given by the system size used in the percolation problem. In the system described by figures 4.8 to 4.10 the voltage drop was assumed 5.4 V, corresponding to an average electric field strength of 1 MV/cm in the negative $\hat{x}$.
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Figure 4.11: Numerically derived threshold currents in a network of localized states in the high field regime as a function of average electric field strength ($10^5 - 10^7$ V/cm, $T = 16$ K), using different values of localization and density of states. Solid lines are fits within a set of equal localization and density in the high field limit. (a) $\alpha = 10^6 \text{ cm}^{-1}$, $N_\mu = 10^{18} \text{ cm}^{-3} \text{eV}^{-1}$, (b) $\alpha = 10^7 \text{ cm}^{-1}$, $N_\mu = 10^{20} \text{ cm}^{-3} \text{eV}^{-1}$, (c) $\alpha = 10^7 \text{ cm}^{-1}$, $N_\mu = 10^{19} \text{ cm}^{-3} \text{eV}^{-1}$, (d) $\alpha = 10^8 \text{ cm}^{-1}$, $N_\mu = 10^{21} \text{ cm}^{-3} \text{eV}^{-1}$, (e) $\alpha = 10^8 \text{ cm}^{-1}$, $N_\mu = 10^{20} \text{ cm}^{-3} \text{eV}^{-1}$.

direction. By assuming a smaller voltage drop over the system, the current carrying path would be restricted to hops with less loss of energy, which would limit the R-percolation and consequently the maximum current through the system, as expected. Therefore, varying the limit on the voltage drop over the system results in an I-F characteristic in the high field regime. The results of these calculations with various combination of localization and density of states are plotted in figure 4.11.

To provide an equal system size at all field strengths, and since the site potentials in the current carrying backbone were found to drop rather gradually over the system, a limited range (typically 4 eV) of the energy of states around the level of a linearly dropping potential was included in these calculations. It should be noted that this range does not correspond with any physical bandwidth of sites involved in the hopping process; it merely reflects the fact that the voltage drop over the system is expected not to deviate more than 2 eV from the level of linearly dropping potential.
Figure 4.12: Scaling plot showing the relation between the calculated threshold current in the high field regime and the value \((F_0/F)^{1/4}\), with \(F_0\) given by equation 4.34. A linear fit through the data, corresponding with \(C_F = 9.6\), is indicated by the solid line.

In figure 4.11 each data point again represents the average of ten independent calculations, with the error marking the root-mean-square deviation within these ten calculations. The sets of data points corresponding with a specific combination of localization and density of states are fitted with a \(\log I_t \sim -(F_0/F)^{1/4}\) field dependence, represented in figure 4.11 by the solid lines.

Clearly, the expected \(\log I \sim -(F_0/F)^{1/4}\) dependence is observed, with \(F_0\) depending on \(\alpha\) and \(N_\mu\). The deviations at low field strengths in the bottom two sets of data seem to correspond with the transition to the medium-field regime. Indeed, an analysis on the corresponding percolation paths show individual hopping events to energetically higher states, indicating a temperature dependence in the conduction.

Considering the analytical description of \(F_0\) (equation 4.34), again a scaling plot is constructed with the input parameters converted into a single parameter \(\alpha^4/eN_\mu F\). The result is plotted in figure 4.12, showing calculations on the threshold current with different values of the parameters \(N_\mu\) \((10^{17} - 10^{21} \text{cm}^{-3} \text{eV}^{-1})\), \(\alpha\) \((10^6 - 10^8 \text{cm}^{-1})\) and \(F\) \((10^5 - 10^7 \text{V/cm})\). The calculated threshold currents were found to be independent of the temperature used in the simulations, providing that
the criterion on the temperature in the high field regime was met (equation 4.36). In these calculations a temperature of 16 K was used, which appeared sufficiently low to secure a temperature independent current in all calculations.

Within the margin of error all calculations with different $\alpha$ and $N_\mu$ converge to a single line, supporting the expected $F_0 = C_F \alpha^4 / eN_\mu$ dependence. Fitting the data with this dependence results in the quantification of the proportionality constant $C_{F,\text{num}} = 9.6 \pm 0.2$.

Analytically, this proportionality constant is quantified in equation 4.35 by $81/16\pi \approx 1.6$, assuming Mott’s simplified expression on site energies (equation 4.17), and in the mathematically more thorough analyses [122–124] by $64/\pi \approx 20.4$. Both numbers are derived without taking into account the correlation between successive hops and therefore cannot be considered exact. Their inconsistency reflects the uncertainty in the exact value of $C_F$.

Numerically, the quantification of this proportionality constant has been studied only rarely. A quasi-numerical study based on percolation theory shows a value of $61$ [139], but in this case the site potentials were supposed to drop linearly over the system, without quantifying the effect of deviations from this behavior. Another often quoted study [142] reports on the relation between $T_0$ and $F_0$:

$$F_0 = a k_B T_0 / e,$$

with $a$ some undefined constant in the order of unity. Indeed, combining equations 4.21 and 4.34 shows the validity of this relation, with $a = C_F / C_T$. Using the values of $C_F$ and $C_T$ obtained from our percolation study we are able to define the value of $a$ as $a = 0.520 \pm 0.013$.

## 4.5 Discussion

Regarding the theoretical assumptions made in Mott’s description on the vrh process, most criticism focuses on the likelihood of a constant density of states around the chemical potential $\mu$. Although at sufficiently low temperatures the energy width of the band of states involved in the hopping process might become sufficiently narrow to assume a more or less constant DOS, at higher temperatures this band width, estimated by the average hopping energy, can be up to several tenths of an eV. When considering vrh through states in (exponential) band tails, surely the approximation of constant $N_\mu$ over this energy range is not valid, but also in the case of vrh conduction through localized states around mid-gap, the energy range of supposed constant density of states seems rather large. On the other hand,
the high average hopping energies do justify the assumed \( \sinh \frac{|E_i - E_j|}{2k_B T} \approx \frac{|E_i - E_j|}{2k_B T} \) relation underlying equations 4.7 and 4.8.

In this study on a-SiO\(_x\), the energy band of states involved in the hopping process is estimated using figure 4.1. Since the optimization of the hopping distance, characteristic for the vrh process, tends to decrease the temperature dependence of the conduction, the slopes of the conductivity plotted in an Arrhenius plot can be considered as lower-limits of the average hopping energy. This results in a minimum bandwidth of the localized states involved in the vrh process at room temperature of 0.12 ± 0.01 eV in the a-Si sample up to 0.35 ± 0.02 eV when \( x = 1.3 \). Indeed, these bandwidths seem rather large for a constant \( N_\mu \), nevertheless a clear \( \log \sigma \sim T^{-1/4} \) dependence is observed.

Assuming a non-uniform DOS around \( \mu \), \( N(E) = N_\mu E^n \), several studies using different techniques (Green function formalism [125,126], numerical approach [133,143,144]) show a general

\[
\log \sigma \sim -\left( \frac{E}{\mu} \right)^\nu, \quad \nu = \frac{n+1}{n+4}
\]

(4.42)
temperature dependence of the conduction in the Ohmic regime, retaining the \( T^{-1/4} \) dependence in a constant DOS \( (n=0) \). However, the application of these non-uniform DOS’s, with such a strong dip around \( E = \mu \), is often limited to the case of strong electron-electron interactions, resulting in a parabolic Coulomb gap around the position of the chemical potential. The resulting process will be addressed shortly at the end of this section.

The use of a single value of \( \alpha \) in calculations on hopping processes in disordered materials seems questionable due to similar arguments. The \( \alpha \) parameter, which describes the attenuation length of the wave function of an electron in the localized state, is characterized by the nature and surroundings of the localized state. With a spread in energy of the involved localized states of several tenths of an eV it is likely to assume that these hopping sites are composed of by different types of localized states or at least by states with different surroundings. Therefore, a similar localization parameter for all these states does not seem feasible. Considering the strong influence of \( \alpha \) on \( T_0 \) and \( F_0 \), which characterizes the temperature and field dependence of the conduction, it is clear that even a small spread in \( \alpha \) cannot be neglected easily.

An analytical description of the effect of such a spread is not readily obtained, but the effect of a spread in \( \alpha \) can be calculated numerically using the percolation model described in the previous section. By adding a different localization parameter to the characteristics of every single site in the system, the effective tunneling
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Figure 4.13: Calculated threshold resistance in the low field limit in a system with different site localization, as a function of temperature (16 - 625 K). (a) corresponds with a non-uniform flat distribution of the localization parameter $\alpha \in [5 \times 10^6; 1.5 \times 10^7]$ cm$^{-1}$. (b), (c) and (d) correspond with a system with uniform localization parameter $\alpha = 5 \times 10^6$, $1 \times 10^7$ and $1.5 \times 10^7$ cm$^{-1}$, respectively. The density of states in all calculations equals $N_\mu = 10^{20}$ cm$^{-3}$ eV$^{-1}$.

The probability is altered according to

$$P_{\text{tunnel } i \rightarrow j} = \exp \left[ - (\alpha_i + \alpha_j) |R_{ij}| \right].$$

Consequently, the $2\alpha|R_{ij}|$ terms in the connecting impedances of the percolation description (equation 4.38 in the low field limit and equations 4.39 and 4.40 in the high field regime) need to be altered to $(\alpha_i + \alpha_j) |R_{ij}|$. Using these impedances the threshold values in both high and low field regimes are easily obtained, assuming a specific distribution of the localization parameter. In figures 4.13 and 4.14 the calculated $\sigma$-$T$ and $I$-$F$ characteristics of a network of sites with density $N_\mu = 10^{20}$ cm$^{-3}$ eV$^{-1}$ are plotted. The localization parameters $\alpha$ of the individual sites in these calculations were chosen randomly within a band of $1.0 \times 10^7$ cm$^{-1}$ around the average localization parameter $\bar{\alpha} = 1.0 \times 10^7$ cm$^{-1}$. For comparison, also the characteristics of the system with uniform localization parameter $\alpha = 5 \times 10^6$, $1 \times 10^7$ and $1.5 \times 10^7$ cm$^{-1}$ are depicted.

The calculations with non-uniform localization parameter again show the expected $T^{-1/4}$ and $F^{-1/4}$ dependencies. The corresponding proportionality con-
Figure 4.14: Calculated threshold current in the high field regime in a system with different site localization, as a function of electric field strength ($F = 10^5 - 10^7$ V/cm). (a) corresponds with a non-uniform flat distribution of the localization parameter $\alpha \epsilon [5 \times 10^6; 1.5 \times 10^7]$ cm$^{-1}$. (b), (c) and (d) correspond with a system with uniform localization parameter $\alpha = 5 \times 10^6, 1 \times 10^7$ and $1.5 \times 10^7$ cm$^{-1}$, respectively. $N_\mu = 10^{20}$ cm$^{-3}$ eV$^{-1}$ and $T = 16$ K.

Constants $T_0$ and $F_0$ coincide with the calculated values in a system with a uniform localization parameter $\alpha = 8.4 \times 10^6$ and $8.9 \times 10^6$ cm$^{-1}$, respectively. These values are slightly below the average localization parameter in the non-uniform case, $\alpha = 1 \times 10^7$ cm$^{-1}$, which shows that the effect of the more extended states overcompensates the effect of the more localized sites.

To conclude this section some additional remarks need to be mentioned. In the theoretical studies on the vrh process discussed so far, charge is supposed to be transported via a single-phonon-induced tunneling process, assuming $h\omega_0 \gg k_B T$, with $\omega_0$ the mean phonon frequency. The interaction of the phonons in the solid with the hopping electrons are taken into account using grand-canonical statistics in the hopping probabilities and a so-called attempt frequency ($t_{ph}$ in equation 4.15 or $\gamma$ in equation 4.3) in the pre-exponential factor. This frequency, which is supposed to be independent of temperature and hopping distance and energy, is however strongly related to the electron-phonon coupling strength and
the phonon density of states. Nevertheless, in most studies the use of a constant attempt frequency is justified [131] by assuming that the temperature and field effects on this frequency are much smaller than the exponential factors shown explicitly, resulting in the $\log \sigma \sim T^{-1/4}$ and $\sim F^{-1/4}$ dependencies. On the other hand, especially in hopping events that need to be accompanied by a large exchange of energy, as in the case of carriers hopping in the direction of a very high field, this interaction could strongly limit the hopping probability. This could result in a lower current at high field strengths than theoretically expected.

More generally, the legitimacy of the $\hbar \omega_0 \gg k_B T$ assumption, and with it the application in most practical hopping cases of the Miller-Abrahams conductance (equation 4.8), has been questioned [120,145]. This has led to a description of a multiphonon assisted tunneling process [120]. Taking into account the deformation of the surroundings induced by the carriers, this description has been extended to a low T single phonon and a high T multiphonon assisted small polaron hopping conduction [135]. Although this description is not postulated on the Miller-Abrahams two-site hopping rates (equation 4.8), still the resulting general temperature dependence in the Ohmic regime is consistent with equations 4.42 and 4.21, in both the single phonon and multiphonon hopping case.

Moreover, the effect of electron-electron interactions on the vrh conduction has been subject to several studies. Most of these studies consider the effects of a Coulomb gap in the DOS of localized electronic states [144,146]. Basically, the results of these studies are consistent with equation 4.42 assuming a parabolic Coulomb gap, showing a $\log \sigma \sim T^{-3+1/2} = T^{-1/2}$ temperature dependence of conduction. The relevance of the electronic interactions on the vrh conduction appears to increase with decreasing temperature, depending on the relative magnitude of the hopping energy and Coulomb gap.

The effects of the occupation of surrounding sites on the hopping process, considering the fluctuating effects on the site energies [147] or the possibility of a simultaneous and correlated motion of carriers [148], are supposed to be only relevant at even lower temperatures. Calculations show that in most common semiconductors (a-Si, a-Ge) the effect of electronic interactions can be neglected down to $T \approx 10 K$ [131], in which temperature region indeed a $\log \sigma \sim T^{-1/2}$ temperature dependence has been observed [149,150]. Since in this study on SiO$_x$ no measurements were performed below 30 K and, more specifically, the $\log \sigma \sim T^{-1/2}$ dependence does not fit our data, the effects of these interactions were neglected.
4.6 Conclusions

The temperature dependence of the conductivity observed in the investigated SiO\textsubscript{x} films, \(\log \sigma \sim T^{-1/4}\), suggests a dominant variable range hopping (vrh) conduction mechanism in these films. In this chapter the vrh conduction mechanism is modeled in terms of the following parameters: \(N_\mu\), the density of localized states around the chemical potential \(\mu\), \(\alpha\), a parameter indicative for the localization of these states, \(T\), the temperature of the phonon spectrum and \(F\), the electrical field.

In the first part of this chapter the qualitative relations between these parameters were demonstrated, following the simplified but transparent formalism introduced by Mott [19]. At low field strengths and/or relatively high temperatures this model predicts an Ohmic conduction mechanism with a \(\log \sigma \sim -(T_0/T)^{1/4}\) temperature dependence of the conductivity. On the other hand, at high field strengths and/or low temperatures a temperature independent conduction mechanism is expected, with a characteristic \(\log I \sim -(F_0/F)^{1/4}\) current-field dependence. Both parameters \(T_0\) and \(F_0\) appear functions of the material properties \(N_\mu\) and \(\alpha\): \(T_0 \sim \frac{\alpha^3}{k_B N_\mu}\) and \(F_0 \sim \frac{\alpha^4}{e N_\mu}\).

In the second part of this section a purely numerical model based on percolation theory is presented. In the low field regime the validity of the model is confirmed by a comparison with the above mentioned \(\log \sigma \sim -(T_0/T)^{1/4}\) relation, with \(T_0 = C_T \frac{\alpha^3}{k_B N_\mu}\). The derived value of the proportionality constant \(C_T = 18.5 \pm 0.2\) is in good agreement with values reported in analytical percolation studies on the same subject [135,136]. Next, the model is adapted to the high field regime, in which the \(\log I \sim -(F_0/F)^{1/4}\) relation is confirmed. We use this model to estimate the proportionality constant \(C_F\) in the \(F_0 = C_F \frac{\alpha^4}{e N_\mu}\) relation by \(C_F = 9.6 \pm 0.2\). Due to the complex nature of the vrh process in the high field regime and the significant differences of this process with analytical percolation systems, we feel that the numerical study presented in this chapter comprises a more reliable quantified description of the process than the reported quantitatively different analytical results [123,139]. It is noted that, using the quantified expression of \(T_0\) and \(F_0\), values of \(N_\mu\) and \(\alpha\) can be derived unambiguously from the observed temperature and field dependencies of the conductivity in a system.

Finally, the numerical models in both the low field and high field regimes are adapted to a more realistic system of sites with a diverse localization. It is observed that in such a system the conductivity is dominated by the contribution of states with small localization parameter, i.e. the more delocalized states.