Electrical Transport in Nanoparticle Thin Films of Gold and Indium Tin Oxide

BY

JESPER EDERTH

Abstract

Electrical transport properties of nanoparticle gold films made by the gas evaporation method were analysed using resistivity measurements. Low temperature electrical transport measurements showed a cross-over from a temperature range dominated by inelastic scattering to a temperature range dominated by elastic scattering, presumably by grain boundaries. This cross-over shifted towards lower temperatures with increasing grain size.

High temperature in-situ electrical transport measurements were carried out in isothermal annealing experiments. Four types of samples, prepared at different deposition rates, were analysed. Samples prepared at low deposition rate displayed a higher thermal stability than samples prepared at high deposition rate. A relaxation model was fitted to the in-situ electrical transport data. The model included an activation energy, which was found to increase with increasing annealing temperature for all samples, thus pointing at the presence of pinning mechanisms in the samples.

Optical properties of nanoparticle gold films were investigated in the $0.3 < \lambda < 12.5 \, \mu m$ wavelength range. A model taking grain boundary scattering into account was successfully fitted to the experimental data and it was shown that the infrared reflectance decreased with decreasing grain size as a consequence of increased grain boundary scattering.

Nanoparticle tin-doped indium oxide films were made by spin-coating a dispersion containing the nanoparticles onto a substrate. The tin-doped indium oxide particles were prepared by a wet-chemical method. Optical properties were investigated in the $0.3 < \lambda < 30 \, \mu m$ wavelength range by reflectance and transmittance measurements. Effective medium theory was employed in the analyses of the optical data and information regarding film porosity and charge carrier concentration and mobility within the individual nanoparticles was obtained. It was found that ionized impurity scattering of the conduction electrons dominates within the particles. The temperature-dependent film resistivity was found to be governed by insulating barriers between clusters containing a large number of nanoparticles, thereby giving a negative temperature coefficient of resistivity.

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1. Introduction

Nanotechnology is a rapidly growing area of importance and interest, incorporating a wide range of research fields. These fields range from manipulating individual nanoparticles, and even molecules, by scanning probe microscopy to growing nanocrystalline and nanostructured materials by different deposition techniques; see review papers, e.g. Refs. 1,2. Electron beam lithography makes it possible to produce structures a few nanometers in size.3,4

Small particles have been of interest to researchers for a long time. It was in the second half of 19th century that scientists started to systematically investigate the collective properties of small particles, such as light scattering which was investigated by Lord Rayleigh and Tyndall. Later, at the beginning of the 20th century, Einstein published his work on the Brownian motion of small particles. In the 1940’s to the 1960’s, research groups in Japan made a considerable effort in the field of ultra-fine particles. Uyeda and Kimoto studied ultra-fine particles using electron microscopy and employing electron diffraction.5 Kubo presented his theory on the electronic properties of metallic fine particles6 wherein he discussed how the level spacing of the quantized electronic states affects the thermodynamic properties of a material, for example giving a decreased heat capacity. The first real breakthrough for applied research on ultra-fine particles came in the early 1970’s when magnetic alloy particles were used in recording tape. Tasaki et al.7 showed at this time that ultra-fine particles of Fe, with a few atomic layers of oxide, are resistant to further oxidization. In 1976 Granqvist and Buhrman8 published pioneering work on isolated ultra-fine particles. A systematic investigation of the size distribution of a number of different materials was presented. The generally occurring log-normal size distribution was studied, and differences in the properties between ultra-fine particles and bulk material were discussed. During the 1980’s the designation of the small particles was more or less changed from being referred to as ultra-fine particles to nanoparticles and research on nanoparticles and materials consisting of nanoparticles is today a large branch of nanotechnology. Nanostructured materials in general have been reviewed by, for example, Gleiter9 and Siegel.10-12
1.1 Nanoparticles

As the physical size of a material is reduced to a diameter of approximately less than 30 nm, i.e. nanoparticles are formed, a number of new properties are exhibited. For example, in a metal nanoparticle with the mean free path of the conduction electrons exceeding the particle diameter, the energy levels become discrete\(^{13}\) and the free-electron like behavior is no longer prevalent. The mean free path is the distance between scattering events, which is \(\sim 42\) nm in the case of bulk gold at \(273\) K.\(^{14}\) Discrete energy levels may be found in colloidal systems of metal nanoparticles where adjacent particles are separated by insulating barriers. Another important property of nanoparticles is the high surface to bulk ratio, which makes thin films of nanoparticles of significant interest for gas sensor applications. Furthermore, it has been found that the melting point of free metal nanoparticles is inversely proportional to particle size\(^{15}\) and that semiconducting nanoparticles display a blueshift of the band gap as the particle size is decreased. This is due to the quantum confinement effect.\(^{16}\)

1.2 Nanocrystalline Materials

Nanocrystalline (nc) materials (here also referred to as nanoparticle (n) films) make up a group of materials attracting a great deal of interest both from a fundamental and from an applied point of view. This is due to the fact that these materials display a large surface to bulk ratio, which distinguishes them from bulk materials. A nanocrystalline material contains a high concentration of grain boundaries or in the case of porous films, a large internal surface compared to the case of a bulk material. These properties are of considerable importance for electrical transport, optical, and mechanical properties.\(^{17-20}\) For example, n-Au films produced by the gas deposition method, with a grain size of \(\sim 10\) nm, display a Vickers microhardness that is \(6 – 7\) times higher than the hardness of n-Au films with a grain size of \(\sim 100\) nm.\(^{21}\)

Thin films of metal nanoparticles connected in a percolating network display high optical absorption in the infrared wavelength range\(^{22,23}\) due to the small size of the individual metal particles.

When it comes to the electrical transport properties of nc-materials, especially in nc-metals and heavily doped semiconductors, the electrical dc conductivity is very much affected by the microstructure and mainly by the grain boundaries.

Thermal stability is another property that has been widely studied in nc-materials.\(^{24-27}\) Nanocrystalline gold prepared by the gas deposition technique
exhibits remarkable thermal stability.\textsuperscript{28,29} Table 1.1 presents some basic properties of nanoparticles or nanocrystalline materials and their applications.

<table>
<thead>
<tr>
<th>Property</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength selective optical absorption</td>
<td>Solar collectors</td>
</tr>
<tr>
<td>High flow stress</td>
<td>Jet engines</td>
</tr>
<tr>
<td>Giant magnetoresistance</td>
<td>Reader heads in computers</td>
</tr>
<tr>
<td>High magnetic coercive force</td>
<td>Data storage</td>
</tr>
<tr>
<td>Large surface-to-bulk ratio</td>
<td>Sensors</td>
</tr>
</tbody>
</table>

1.3 General Aims of this Work

This thesis focuses on the electrical transport and optical properties of thin nanoparticle films of gold and tin-doped indium oxide (known as indium tin oxide or ITO). In the case of n-Au films this work is carried out from a fundamental perspective with a focus on electrical transport and grain boundary scattering. As regards n-ITO films, the work is focused mainly on optical properties, but also on electrical properties. Indium tin oxide is a very interesting material from an applied research point of view. High visible transmittance in addition to good electrical conductance makes ITO a very attractive material to be used, for example, as transparent electrodes for switching devices\textsuperscript{30} and light emitting diodes,\textsuperscript{31} as well as for solar cells.\textsuperscript{32}
2. Review of Nanoparticle Gold and Tin-Doped Indium Oxide Films

2.1 General Properties of Gold and Tin-Doped Indium Oxide

2.1.1 Gold

Gold has a face-centered cubic (fcc) structure with a lattice parameter of 0.40786 nm.\textsuperscript{33} Gold has a single \textit{s}-electron in the valence band with the outer shell configuration in the ground state given by: 5d\textsuperscript{10}6s\textsuperscript{1}. A high free electron concentration, 5.9x10\textsuperscript{22} cm\textsuperscript{-3},\textsuperscript{14} in addition to a mean free path\textsuperscript{14} of 42 nm at room temperature, makes gold a very good electrical conductor, with a Fermi velocity of 1.4x10\textsuperscript{6} cm/s.\textsuperscript{14} Because of its good electrical properties, gold is a highly reflecting material, with a plasma frequency at approximately 9 eV. However, strong absorption is present at energies much lower than the plasma frequency, due to interband transitions. For example, at 1.94 and 2.5 eV there are transitions from the \textit{d}-band to the Fermi surface.\textsuperscript{34} The \textit{d}-bands lie below the \textit{s}-band, which is the conduction band, in gold.

2.1.2 Indium Oxide and Tin-Doped Indium Oxide

The crystal structure of In\textsubscript{2}O\textsubscript{3} at normal pressure and room temperature is a fluorite-related cubic bixbyte type with 80 atoms in the unit cell. One fourth of the anions are missing. The lattice parameter is 1.0118 nm.\textsuperscript{35} Figure 2.1 presents the crystal structure of In\textsubscript{2}O\textsubscript{3}. The two non-equivalent In\textsuperscript{3+} ion positions have six-fold symmetry. The O\textsuperscript{2-} ions are arranged in fourfold symmetry.
In$_2$O$_3$ may be intrinsically doped by introducing oxygen vacancies ($V''_o$) in the lattice. Each oxygen vacancy contributes with two electrons to the conduction band. Kröger introduced a notation for doping, and an oxygen vacancy doped indium oxide structure may be written as \( \text{In}_2\text{O}_{3-x} (V''_o), e', \) where \( e' \) denotes a free electron.

It is possible to increase the charge carrier concentration further by extrinsic doping, for example in indium oxide doped with tin. The tin atoms may enter the indium oxide lattice substitutionally by \( \text{Sn}^{4+} \) replacing the \( \text{In}^{3+} \) at the cation site. This may be written, using Kröger notation, as \( \text{In}_2\text{O}_{3-x} (V''_o), e', \text{Sn}^{4+} \), but only if the degree of tin doping is so large that the oxygen vacancy doping can be neglected. The tin atom may also enter interstitially, thereby providing a more distorted lattice. Increasing the charge carrier concentration results in decreased mobility in the material mainly due to charged impurity scattering. Thus doping as a way of increasing the conductivity is a trade-off between charge carrier concentration and mobility. It has been found that in thin films the tin content should be in the range 4 – 6 at\%\textsuperscript{,}\textsuperscript{37,38} A higher degree of doping tends to decrease the charge carrier concentration due to the formation of neutral tin-oxygen complexes. Work done by Frank and Köstlin\textsuperscript{39} leads to the proposal of three different tin-
oxygen complexes: (Sn_2O_3)^+, \,(Sn_2O_5)^+, \, (Sn_2O_4)^+ \,(Sn_2O_3)^-. The first complex is strongly bound with two Sn^{4+} ions surrounded by three nearest neighbor O^{2-} ions, plus one O^{2-} in an empty quasi-anion site. The second complex is a loosely bound O^{2-} located interstitially between two Sn^{4+} ions located not necessarily on nearest neighbor In^{3+} sites. The last complex is a mix of the previous two described above.

Indium oxide has a direct band gap of ~3.75 eV.\(^{40}\) However, an indirect band gap\(^{40}\) has been observed in single crystals of indium oxide. Few band structure calculations have been performed on indium oxide, mainly because of the many atoms in the unit cell. However, Odaka et al.\(^{41}\) and Mizuno et al.\(^{42}\) have performed first-principles and molecular orbital calculations, respectively, on indium oxide. Their results disagree. Odaka et al.\(^{41}\) found that the conduction band consists of indium 5s-like states, with free-electron like character, and that the valence band originates from strong hybridization between oxygen 2p and indium 5s states, whereas Mizuno et al. found that the valence band originates from oxygen 2p states and the conduction band from oxygen 2p and indium 5p states.

Odaka et al.\(^{43}\) have performed first-principles band structure calculations on tin-doped indium oxide. The tin atoms create s-like symmetry impurity bands and there is no difference if the Sn^{4+} ion is located in the b or d-site. Mryasov and Freeman\(^{44}\) performed local density full-potential linear muffin-tin orbital electronic band structure calculations for Sn-doped In\(_2\)O\(_3\). They found that the lowest conduction band is split with Sn doping, due to strong hybridization with dopant s-type states.

2.2 Properties of Gold Nanoparticle Films

Properties of solids are strongly dependent on the microstructure, such as the atomic arrangement and chemical composition.\(^{16}\) Dislocations and defects in a crystalline structure are of considerable importance to, for example, electrical transport properties and mechanical properties.\(^{17-21}\) Below are some results on mechanical, thermal, and electrical properties of n-Au.

2.2.1 Mechanical Properties

As the mechanical hardness increases with decreasing grain size, i.e. following the Hall-Petch relation (the yield stress is linearly proportional to the square root of the reciprocal grain size), the elastic modulus is expected to decrease drastically. However, this is not the case for n-Au films produced by the gas deposition process,\(^{19}\) where the elastic modulii are found to be
higher than 94% of the bulk value. The density of these samples is comparable to that of bulk gold. These results hold for temperatures below approximately 200 K. At temperatures above this value, the elastic modulus decreases rapidly with temperature. It was suggested that a certain atomic process in the grain boundary region is responsible for the anelastic process present above 200 K. The grain boundary microstructure in materials produced by the gas deposition method is believed to be different from that in the polycrystalline counterpart, and it is estimated that the grain boundary thickness is \( \sim 2 - 3 \) times larger than in conventional materials.

2.2.2 Thermal Stability

In almost all applications one must consider the microstructural stability, especially if a material is subjected to high temperature. Grain growth and other microstructural atomic rearrangements are usually thermally activated processes. Of significant importance is the thermal stability in nc-materials, for which the concentration of grain boundary structure is considerably higher than in their polycrystalline counterpart. Excess energy stored in the grain boundaries is the main driving force for grain growth in nc-materials. This is a process associated with the diffusion of atoms primarily within grain boundaries. Scientists have studied the activation energies for grain growth and compared such data with those due to grain boundary diffusion. Malow and Koch\(^{25}\) carried out grain growth experiments of numerous materials and found good agreement between the activation energies of the grain growth process and those pertinent to grain boundary diffusion. Grain growth has also been studied by a number of other groups.\(^{25-28}\) Samples produced by the gas deposition process display superior results concerning thermal stability and grain growth. Okuda and Tang\(^{29}\) published results on n-Au, with a grain size of \( \sim 10 \) nm, exhibiting unusually high thermal stability. Grain growth was not detected up to 900 K upon annealing for 1 min in vacuum at a heating rate of 10 K/min. They argued that the presence of ultrafine pores, rather than a highly disordered interfacial structure, is responsible for the unique properties of n-Au produced by the gas deposition process, but this has not yet been confirmed experimentally.

2.2.3 Electrical Transport Properties

In nc-materials, and especially nc-metals, the electrical dc conductivity is very much affected by the microstructure; this is a consequence of the large area to bulk ratio of the individual grains. The length scale of the microstructure is comparable to the mean free path of conduction electrons, which makes the grain boundaries a significant source of scattering of the
conduction electrons. The effect of grain boundary scattering has often been described in the literature as conduction electrons tunneling through the grain boundaries, modeled as potential barriers associated with a transmission probability.45-48

2.3 Properties of Tin-Doped Indium Oxide Nanoparticle Films

2.3.1 Deposition Techniques

Tin-doped indium oxide is a material that has been widely studied for many years. For the past fifteen years a number of papers have been published on production processes of ITO nanocomposites.49-59 Among these processes we find ball milling60 and gas evaporation61 for producing highly transparent thin films with low electrical conductivity. Chemical techniques, such as sol-gel processes, are able to give samples with low resistivity, 2 to \(4 \times 10^{-4} \ \Omega \text{cm, and good optical properties.}^{49,54,57}

2.3.2 Post-Deposition Treatments

Several research groups have studied post-deposition heat treatments of ITO nanocomposites.55,59,60,62,63 The performance of the thin ITO film may be optimized upon judicious heat treatments to produce good optical and electrical properties. For nanocomposites a high density is crucial for obtaining good electrical properties. Nanocomposite ITO films with a density exceeding 90 \% of the theoretical value have been prepared by post-deposition heat treatments in air at 1300 – 1600 °C.59,62,64

2.3.3 Segregation

Segregation of doping atoms toward grain boundaries is a problem in ITO nanoparticles. Mostly it is due to the low solubility of Sn in indium oxide.65 The Sn segregation toward the grain boundaries decreases the charge carrier concentration within the particles, and neutral Sn-O complexes may be formed on the particle surface. This changes the electrical properties, giving high resistivity. Several studies have been performed on the segregation of Sn in ITO.65-68
2.4 Open Problems and Specific Aims of This Work

2.4.1 Gold Nanoparticle Films

Grain boundaries in nanocrystalline materials have been of interest to researchers for the past 30 years. The main topic has been to elucidate the structure of the grain boundaries and their effect on other macroscopic features, such as mechanical properties and electrical transport properties. Many papers have been published on these topics.\textsuperscript{1,9-12,19,21,69,71} The structure of the grain boundaries in nanocrystalline metals is still an open problem. Results have been published supporting a strongly disordered grain boundary structure\textsuperscript{72,73} and there are results pointing to a structure similar to that of the polycrystalline counterpart.\textsuperscript{74-76} It may be that the structure of the grain boundary region is related to the choice of sample preparation technique.

Grain boundaries are not easily characterized. Transmission electron microscopy has superior resolution compared to other characterization techniques and is therefore an important tool in analyzing grain boundaries.\textsuperscript{77,78} However, preparation of specimens for electron microscopy is a time-consuming process and it may even be that the grain boundary structure is changed upon sample preparation. Thus it is of significant interest to find other characterization techniques to obtain information regarding grain boundaries in nanocrystalline materials. One interesting characterization technique is to use electric current to probe the structure of the grain boundaries.\textsuperscript{69} The electron-grain boundary scattering may to some extent reveal how disordered the structure is around the boundary. Highly disordered grain boundaries give a large contribution due to scattering to the total resistivity.

In this work, resistivity and optical measurements have been the main characterization techniques for obtaining information about the grain boundaries in nanocrystalline gold. The investigation has concentrated on nanocrystalline gold. Gold is a well-characterized material and it is chemically inert. Resistivity has been measured both as a function of time at elevated temperatures during isothermal annealing and as a function of temperature down to liquid helium temperature. The optical properties of nc-Au have been investigated in samples with different grain size.

2.4.2 Tin-Doped Indium Oxide

Tin-doped indium oxide is mainly produced by physical vapor and chemical vapor deposition techniques. These techniques are employed whenever large area deposition is desirable, for example for transparent
electrodes in smart window applications. In many other applications, such as in flat panel displays, a patterned ITO structure is needed. Patterned ITO structures are today produced in a multi-step process: deposition of the ITO film and then etching. A still open problem is to reduce the number of process steps to produce patterned ITO structures. One way would be to print a patterned structure directly on a substrate using ITO nanoparticles in a dispersion.

This work treats the electrical and optical properties of thin films consisting of ITO nanoparticles. Optical measurements have been performed from the ultra-violet to the far infrared wavelength range. Electrical measurements have been performed in the 77 – 300 K temperature range. The effect of grain boundaries and other scattering mechanisms on the electrical transport properties have been analyzed, which is of significant importance for the design of nanoparticle ITO patterned film structures.
3. Electrical Transport

3.1 Background

Electrical transport is a complex property of materials. Ever since the discovery of the electron by J. J. Thomson in 1897, the conductivity in materials has been widely studied. Around 1900 Drude put forward his theory on electrical and thermal conductivity in metals based on the kinetic theory of gases. Later Sommerfeld modified Drude’s theory, mainly by replacing the Maxwell-Boltzmann electron velocity distribution with the Fermi-Dirac distribution. The equilibrium free-electron theory of Sommerfeld was extended by Bloch theory to be valid for a system where the band structure of the metal is known. This theory, referred to as the semiclassical approach to electron dynamics, describes the dynamics of electrons in an applied electric and magnetic field, neglecting the presence of electron scattering.

This chapter describes the concepts for the dc electrical transport properties in nanocrystalline free-electron like materials, starting from the semiclassical approach and introducing the Boltzmann formalism. Focus is put on the effects of grain boundary scattering on the electrical transport properties. Electron scattering by phonons is also briefly described. Materials under consideration are nanocrystalline metals and heavily doped semiconductors.

3.1.1 Electrical Transport in Metals

Metals is a group of materials with a high concentration of free electrons, \( \sim 10^{22} \text{ – } 10^{23} \text{ cm}^{-3} \) and the room temperature conductivity is mainly limited by inelastic scattering by acoustic phonons. Inelastic scattering is defined as a scattering event where the electron experiences a change in kinetic energy due to a collision with, for example, an acoustic phonon. The (inelastic) mean free path, i.e., the distance an electron travels between scattering events, is approximately 42 nm in the case of Au at 300 K. As the temperature is decreased, other scattering mechanisms become significant,
such as elastic scattering by dislocations and by impurity atoms. Elastic scattering describes an event where the energy of the electron is conserved.

Many investigations on temperature dependent resistivity have been performed in order to evaluate the contribution to the resistivity from dislocations, grain boundaries, phonons, etc.

A nanocrystalline metal with a grain size smaller than the mean free path of the conduction electrons is obviously strongly influenced by elastic scattering by the grain boundaries. Grain boundaries are usually represented as potential barriers, and the conduction electrons may with a certain probability tunnel through these barriers. A more detailed theoretical analysis is presented below.

3.1.2 Electrical Transport in Heavily Doped Semiconductors

Heavily doped semiconductors have similarities with metals. The charge carrier concentration may be as high as $10^{21}$ cm$^{-3}$ and the electrical conductivity is large. The mean free path is of the same magnitude as in metals. However, electron scattering mechanisms may be different in heavily doped semiconductors and in metals. Ionized impurities are a source of scattering often present in doped semiconductors. The temperature-dependent resistivity is different from that in a metal in that heavily doped semiconductors have both intrinsic and extrinsic charge carriers. As the temperature is decreased the number of intrinsic charge carriers is decreased, due to a decreased probability for electrons in the valence band being thermally excited into the conduction band, while the number of charge carriers originating from the doping is constant.

3.2 Charge Distribution Function and Boltzmann Equation

A nonequilibrium charge distribution function $F(\vec{r}, \vec{k}, t)$ is introduced for describing the transport properties in a material with a high concentration of charge carriers, subjected to space- and time-dependent perturbing fields and temperature gradients. Consider the charge distribution at time $t$ at the position $\vec{r}$ in real space and at $\vec{k}$ in reciprocal space. The nonequilibrium charge distribution function deviates from the equilibrium charge distribution function $F^0(\vec{k})$ by

$$\xi(\vec{r}, \vec{k}, t) = F(\vec{r}, \vec{k}, t) - F^0(\vec{k}) \quad (3.1)$$
The equilibrium charge distribution function is given by the Fermi-Dirac function

$$F^0(\vec{k}) = \frac{1}{e^{(E(\vec{k}) - E_\mu)/k_B T} + 1}$$  \hspace{1cm} (3.2)$$

where $E$ is the energy, $E_\mu$ the chemical potential, $k_B$ the Boltzmann constant, and $T$ is the temperature. Under the assumption that no collisions occur between $t - dt$ and $t$, the semiclassical approach to motion can be used. The semiclassical equations of motion are given by

$$\dot{r} = v(\vec{k})$$  \hspace{1cm} (3.3)$$ $$\hbar \dot{\vec{k}} = -e(\vec{E} + \vec{v} \times \vec{B})$$  \hspace{1cm} (3.4)$$

where $\vec{v}$ is the speed, $\hbar$ the Planck constant, $e$ the elementary charge, $\vec{E}$ the electric field, and $\vec{B}$ the magnetic field. It is possible to find an explicit solution of the semiclassical equations of motion to linear order in $dt$ since $dt$ is infinitesimal. This means that an electron at $r$ and $\vec{k}$ must have been at $r - \dot{r} dt$ and $\vec{k} - \dot{\vec{k}} dt$ at $t - dt$, i.e., the Liouville theorem applies. Thus an expression for the distribution function in the absence of collisions is obtained, given by

$$F(\vec{r}, \vec{k}, t) = F(\vec{r} - \dot{r} dt, \vec{k} - \dot{\vec{k}} dt, t - dt)$$  \hspace{1cm} (3.5)$$

To account for collisions, a correction term is added to Eq.(3.5) and the left side is expanded to linear order in $dt$. Then in the limit $dt \to 0$, the Boltzmann equation is obtained, i.e.
\[
\frac{\partial F}{\partial t} + \mathbf{\dot{p}} \cdot \text{grad}_p F + \mathbf{\dot{k}} \cdot \text{grad}_k F = \left( \frac{\partial F}{\partial t} \right)_{\text{coll}} \tag{3.6}
\]

The terms on the left hand side are referred to as drift terms and the term on the right hand side is the collision term.

3.2.1 Relaxation-Time Approximation

In the Drude theory of conduction in metals the relaxation time \( \tau \), i.e., the average time between collisions, is independent of the position and wave-vector of the electron. The probability for an electron to be scattered within an infinitesimal time \( dt \) is given by \( \frac{dt}{\tau} \). Collisions of the conduction electrons are considered as restoring the local thermodynamic equilibrium in the electronic system. The speed of the electrons emerging from a collision is only related to the local temperature, not to the speed before the collision. The relaxation time approximation is given by

\[
\left( \frac{\partial F(\mathbf{r}, \mathbf{k}, t)}{\partial t} \right)_{\text{coll}} = -\frac{\left( F(\mathbf{r}, \mathbf{k}, t) - F^0(\mathbf{k}) \right)}{\tau} \tag{3.7}
\]

This expression can be used as the collision term on the right hand side of Eq.(3.6) above.

3.2.2 General Aspects of Collisions: Scattering Probability

In a general approach to scattering a probability per unit time is defined instead of the relaxation-time approximation. We assume that the scattering event is well localized in space and time, \( \mathbf{r}, t \), and that the non-equilibrium distribution function is given by the properties of the solid at \( \mathbf{r}, t \). Since the scattering probability is derived at \( \mathbf{r}, t \), these variables are omitted in this section. A transition probability \( R_{k,k'} \) is introduced to describe the particular scattering mechanism. The scattering probability \( P_{k,k'} \) for an electron in a state \( \mathbf{k} \) and band \( n \) to be scattered into a state \( \mathbf{k}' \) within the same band, is defined as

\[
P_{k,k'} = \frac{R_{k,k'}}{8\pi^2} dtd\mathbf{k} \tag{3.8}
\]
Eq. (3.8) is valid under the assumption that all states in the volume \( d\vec{k} \) around \( \vec{k} \) are unoccupied. In order to account for the fact that all states in \( d\vec{k} \) are not unoccupied, a correction factor must be added to Eq. (3.8), i.e., \( 1 - F(\vec{k}) \). The relaxation-time can now be formulated as follows

\[
\frac{1}{\tau(\vec{k})} = \int \frac{8\pi^3}{3} [1 - F(\vec{k}')] d\vec{k}'
\]  

(3.9)

The rate of change of the distribution function due to scattering out of level \( \vec{k} \) is defined as

\[
\left( \frac{dF(\vec{k})}{dt} \right)_{out} = -\frac{F(\vec{k})}{\tau(\vec{k})}
\]

(3.10)

and by comparing Eq. (3.10) with Eq. (3.9) the following expression is obtained

\[
\left( \frac{dF(\vec{k})}{dt} \right)_{out} = -F(\vec{k}) \int \frac{8\pi^3}{3} [1 - F(\vec{k}')] d\vec{k}'
\]

(3.11)

The rate of change of the distribution function into level \( \vec{k} \) is defined similarly to Eq. (3.11) and is given by

\[
\left( \frac{dF(\vec{k})}{dt} \right)_{in} = [1 - F(\vec{k})] \int \frac{8\pi^3}{3} F(\vec{k}') d\vec{k}'
\]

(3.12)

Eqs. (3.11) and (3.12) give an expression for the collision term in Eq. (3.6), namely

\[
\left( \frac{dF(\vec{k})}{dt} \right)_{coll} = \left( \frac{dF(\vec{k})}{dt} \right)_{out} + \left( \frac{dF(\vec{k})}{dt} \right)_{in}
\]
Provided that the assumption concerning symmetry, given by

\[ \mathcal{R}_{\hat{k},\hat{k}'} = \mathcal{R}_{\hat{k}',\hat{k}} \]  

is valid, i.e., that the potential describing the interaction between the electron and the source of scattering is Hermitian, the following formula for the collision term is obtained:

\[
\left( \frac{dF(\hat{k})}{dt} \right)_{\text{coll}} = -\frac{1}{8\pi^3} \int \mathcal{R}_{\hat{k},\hat{k}'} \left[ F(\hat{k}') - F(\hat{k}) \right] d\hat{k}'
\]

(3.15)

3.3 Grain Boundary Scattering

3.3.1 The Mayadas and Shatzkes Model

This section is devoted to the one-dimensional model by Mayadas and Shatzkes (MS) describing grain boundary scattering in materials with grain size \( d \) smaller than the mean free path \( \ell_\text{\scriptsize f} \) of the electron. Here only thick samples are considered, i.e., the effect of surface scattering is omitted; see the Fuch’s size-effects theory for further reading on surface scattering.

Figure 3.1 shows a schematic model for the grain boundary distribution in the sample. The distance between adjacent grain boundaries follows the Gaussian distribution function with the average distance being \( d \), i.e. equal to mean grain size. The grain boundaries are assumed to be an assembly of \( \delta \)-function potentials perpendicular to film surface. Scattering by the grain boundaries is assumed only to be elastic, i.e., the energy of the electron is preserved. The electric field is applied parallel to the film surface.
Scattering by grain boundaries, i.e., the electron transition rate for an assembly of parallel \( \delta \)–function potentials, is computed by standard perturbation theory. Scattering by defects and phonons is described by a relaxation time \( \tau_s \). Given that a weak dc electric field is applied, i.e. no time dependence is included, and that there is no spatial dependence in \( F(\vec{r}, \vec{k}, t) \), the following Boltzmann equation is considered

\[
e U_x v_x \frac{\partial F^0(\vec{k})}{\partial E} = \int \mathcal{R}_{x,k}^k \left[ \xi(\vec{k}) - \xi(\vec{k}') \right] d\vec{k} + \frac{\xi(\vec{k})}{\tau_s} \tag{3.16}
\]

where \( e \) is the elementary charge, and \( \mathcal{R}_{x,k}^k \) is the transition probability for grain boundary scattering, \( \tau_s \) is the relaxation time due to scattering by phonons and point defects, \( U_x \) and \( v_x \) are the electric field and the speed of the electron in the \( x \)–direction, respectively.

The \( \delta \)–function potentials are given by
where \( s_{\text{MS}} \) is approximately the height of the potential multiplied by its width and \( V \) is the perturbation on the free-electron Hamiltonian. Evaluating the square of the matrix elements from the first-order perturbation theory and averaging over the distribution of grain boundaries, the following expression is obtained

\[
\Re_{\vec{k},\vec{k}'} = \Im(|k_x|) \delta(k_x - k'_x) \delta(k_x + k'_x) \tag{3.18}
\]

\[
\Im(|k_x|) = \frac{\varphi k_F}{2 \tau_s |k_x|} \frac{1 - e^{-4k_x^2s^2}}{1 + e^{-4k_x^2s^2} - 2e^{-k_x^2s^2}\cos2k_xd} \tag{3.19}
\]

\[
\varphi = \frac{\ell_x}{d} \frac{\Phi}{1 - \Phi} \tag{3.20}
\]

where \( k_x \) is the component of \( \vec{k} \) in the \( y, z \) plane, \( s \) is the standard deviation for the grain boundary distribution, \( \ell_s \) is the mean free path of the background scattering, i.e. scattering by phonons and point defects, and \( \Phi \) is the grain boundary reflection coefficient describing the probability of a conduction electron being reflected by the grain boundary.

The solution to the Boltzmann equation may now be written as

\[
\bar{\eta}(\vec{k}) = \tau_{\text{eff}} eU_s v_s \frac{\partial F^0}{\partial E} \tag{3.21}
\]

where

\[
\tau_{\text{eff}} = \frac{1}{\tau_s} + 2\Im(|k_x|)^{-1} \tag{3.22}
\]
Finally an expression for the conductivity including both grain boundary and background scattering is obtained by

$$\sigma_g = \frac{3}{2} \frac{\sigma_{\infty}}{\tau_s k_F^2} \int \tau_{\text{eff}}(k_x) k_x^2 dk_x$$  \hspace{1cm} (3.23)

where $\sigma_{\infty}$ is the conductivity without grain boundaries given by

$$\sigma_{\infty} = \frac{n_e e^2 \tau_s}{m}$$  \hspace{1cm} (3.24)

where $n_e$ is the charge carrier concentration and $m$ is the free-electron mass. In the limit $k_F^{-1} \gg 1$ Eq. (3.19) is reduced to

$$\mathcal{A}(|k_x|) = \frac{\varphi}{M} k_F \frac{\tau_s}{2 |k_x|},$$  \hspace{1cm} (3.25)

and the following expressions are obtained

$$\frac{\sigma_g}{\sigma_{\infty}} \approx 1 + \frac{3}{2} \varphi, \hspace{1cm} \varphi << 1$$ \hspace{1cm} (3.26a)

$$\frac{\sigma_g}{\sigma_{\infty}} \approx \frac{4}{3} \varphi, \hspace{1cm} \varphi >> 1$$ \hspace{1cm} (3.26b)

3.3.2 The Reiss, Vancea, and Hoffmann Model

In the one-dimensional model by Reiss, Vancea, and Hoffmann (RVH) a correction factor to the Drude conductivity expression taking grain boundary scattering into account is introduced. A conduction electron is assumed to travel the distance $\ell_s$ before being scattered into a new $k$ state and if the mean grain size of the material is shorter than the background mean free path the electron will encounter several grain boundaries; see Fig 3.1. The electron transmission through a grain boundary is given by a probability $\varphi$ and is calculated by the Schrödinger equation for the situation illustrated in Fig. 3.1 and solved using a one-dimensional transfer-matrix approach. The Schrödinger equation considered here is given by

$$\mathcal{A}(|k_x|) = \frac{\varphi}{M} k_F \frac{\tau_s}{2 |k_x|},$$  \hspace{1cm} (3.25)

and the following expressions are obtained

$$\frac{\sigma_g}{\sigma_{\infty}} \approx 1 + \frac{3}{2} \varphi, \hspace{1cm} \varphi << 1$$ \hspace{1cm} (3.26a)

$$\frac{\sigma_g}{\sigma_{\infty}} \approx \frac{4}{3} \varphi, \hspace{1cm} \varphi >> 1$$ \hspace{1cm} (3.26b)
\[
\frac{d^2 \psi^i}{dx^2} + \left[ k_F^2 \frac{2m}{\hbar^2} S_{RVH} \sum_{n=1}^{N^i} \delta(x - x^i_n) \right] \psi^i = 0 \quad (3.27)
\]

where \( \psi \) is the electron wave function, \( m \) is the mass of the conduction electron, \( i \) runs over all possible arrays of grain boundaries along one mean free path, and \( S_{RVH} \) is the strength of the potential given by

\[
S_{RVH} = \left( \frac{1 - \Gamma^i}{\Gamma} \right)^{1/2} \left( \frac{k_F h^2}{m} \right) \quad (3.28)
\]

where \( \Gamma^i \) is the grain boundary transmission coefficient. In a specific array of grain boundary potentials the wave function is given by

\[
\psi^i_0 = e^{ik_F x} + Q^i_r e^{-ik_F x}, \quad x < x^i_j \quad (3.29a)
\]

\[
\psi^i_n = A^i_n e^{ik_F x} + B^i_n e^{-ik_F x}, \quad \begin{array}{l}
\quad \quad x^i_n < x^i_{n+1} \quad n = 1, \ldots, N^i - 1 \quad (3.29b)
\end{array}
\]

\[
\psi^i_{N^i} = Q^i_t e^{ik_F x}, \quad x > x^i_{N^i} \quad (3.29c)
\]

where \( Q^i_r \) and \( Q^i_t \) are the amplitudes of the reflected and transmitted waves, respectively, and \( N^i \) is the number of grain boundaries in array \( i \). The transfer-matrix method then gives the following expression for the total transmission coefficient

\[
\Gamma^i(\ell, d, \Gamma) = |Q^i_t|^2 \quad (3.30)
\]

Averaging over a large number of arrays of grain boundaries, i.e., \( i = 1, \ldots, j \), one obtains
resulting in a convergence towards the probability for electron transmission through $\ell_\omega/d$ grain boundaries. Based on experimental results by Hoffmann and coworkers, the following expression for the conductivity, including grain boundary scattering, was obtained:

$$\sigma_g = \sigma_\omega \Gamma_\ell \frac{n_e e^2 \ell_\omega}{mv_F}$$  \hspace{1cm} (3.32)  

3.4 Temperature Dependent Electrical Transport in Metals

3.4.1 Phonons

Thermal vibrations of the lattice dominate the scattering in metals at room temperature. The thermal vibrations, i.e., phonons, cause the atoms to deviate from their equilibrium positions, which destroys the perfect periodicity of the lattice and it is the perturbation of the one-electron levels that act as the scattering mechanism. Phonon scattering is an inelastic scattering process. An electron scattered from state $\vec{k}$ into state $\vec{k}'$ must fulfil the condition

$$E_{\vec{k}} = E_{\vec{k}'} \pm h\omega(q\vec{q})$$  \hspace{1cm} (3.33)  

$$q\vec{q} = 0$$  \hspace{1cm} (3.34)  

where $q\vec{q}$ is the phonon wave vector. The energy of the phonon, $h\omega(q\vec{q})$, is low compared to the electron energy and the allowed phonon wave vectors for scattering an electron must fulfil

$$\Gamma_j(\ell_\omega, d, \Gamma) = \frac{1}{j} \sum_{j=1}^{J} \Gamma_j(\ell_\omega, d, \Gamma)$$  \hspace{1cm} (3.31)
\[ |\vec{k}', \vec{k}| \gg |\vec{q}| \]  

(3.35)

At temperatures well above the Debye temperature \( T_D \), the number of phonons is given by

\[
n_{ph}(\vec{q}) = \frac{1}{e^{\frac{k_B T}{\hbar \omega(\vec{q})}} - 1} \approx \frac{k_B T}{\hbar \omega(\vec{q})}, \quad T >> T_D \quad (3.36)
\]

Eq. (3.36) states that the number of scatterers increases almost linearly with temperature, which results in a linearly increasing resistivity with increasing temperature above \( T_D \) and we have

\[
\rho(T) \sim T, \quad T >> T_D \quad (3.37)
\]

At temperatures well below the Debye temperature, only phonons with energies comparable to or less than \( k_B T \) are allowed in the single-phonon scattering process. In this temperature range we approach the linear phonon dispersion with \( \omega \approx cq \), where \( c \) is the speed of sound. Allowed phonon wave vectors in the electron scattering process are of the order of \( \frac{k_B T}{\hbar c} \). Thus the area of the sphere of wave vectors allowed to participate for a single-phonon scattering event is proportional to \( T^3 \). The square of the electron-phonon coupling constant decreases linearly with \( \vec{q} \approx k_B T / \hbar c \), when \( \vec{q} \) is small. Combining these two features above the following temperature dependence of the resistivity is obtained, i.e.,

\[
\rho(T) \sim \frac{1}{\ell_{el-phon} T^3} \sim T^3, \quad T << T_D \quad (3.38)
\]

where \( \ell_{el-phon} \) is the mean free path of electron-phonon scattering.

The resistivity may decrease even faster than stated above. At low temperature the resistivity is not only dependent on the scattering rate. The electron-phonon system approaches the behavior of elastic scattering, and the change in angle upon scattering decreases. The small angle scattering on the Fermi surface is more concentrated around the forward direction of the
conduction electrons, and it becomes less effective in degrading the current. This leads to a proportional relationship between resistivity and temperature given by

$$\rho(T) \sim T^5, \quad T \ll T_D$$  \hspace{1cm} (3.39)

This temperature dependence of the resistivity is referred to as the Bloch $T^5$ law. However, this temperature dependence of the resistivity is rarely observed due to imperfections in the crystalline structure, such as lattice strains, defects, grain boundaries, etc.

### 3.4.2 Grain Boundaries

This section discusses the effects of grain boundaries on the temperature dependent resistivity. The discussion will focus on the grain boundary scattering model by Reiss, Vancea, and Hoffman.47 For the temperature dependence of the resistivity, a temperature coefficient of resistivity $\beta$ is introduced according to

$$\beta = \frac{1}{\rho(T)} \frac{d\rho(T)}{dT}$$  \hspace{1cm} (3.40)

At high temperatures $\beta$ is positive in metals, i.e., the temperature dependence is dominated by phonon scattering. However, according to the theory by Reiss et al.47 (as is shown below), at low enough temperatures $\beta$ may become negative due to grain boundary scattering.

Combining Eqs. (3.32) and (3.40) the following expression is obtained

$$\beta = -\left[\frac{1}{\ell_{\alpha}(T)} + \frac{1}{d} \ln \Gamma\right] \frac{d\ell_{\alpha}(T)}{dT}$$  \hspace{1cm} (3.41)

where
From Eqs.(3.41) and (3.42), an expression giving the requirement for a negative temperature coefficient is obtained reading

\[
\Gamma < \exp \left( - \frac{d}{\ell_\infty(T)} \right) \quad (3.43)
\]

When the temperature is decreased \( \ell_\infty \) increases, which results in the right side of the inequality in Eq.(3.43) increasing. Thus small grain size, low \( T \), and low grain boundary transmission coefficient increase the probability for a negative temperature coefficient of resistivity.

3.5 Fluctuation-Induced tunneling

Materials characterized by large conducting segments (\( \sim \mu m \)) separated by thin insulating layers (\( \sim \text{nm} \)) display a negative temperature coefficient of resistivity. Sheng \textsuperscript{93} introduced a new conduction mechanism, fluctuation-induced tunneling. The transport properties are dominated by charge transfer between adjacent conducting segments. The total capacitance is large due to the large conducting segments, which means that charging energy, being inversely proportional to the total capacitance, can be neglected and is therefore not considered in the following theory. Electrons tunnel through the thin insulating layer to the next conducting region, which makes the charge transfer process sensitive to thermally activated voltage fluctuations. The temperature dependent resistivity is related to the form of the potential barrier and is given by the following expression: \textsuperscript{94}

\[
\rho(T) = \rho_0 \exp \left( \frac{T_1}{T + T_0} \right) \quad (3.44)
\]

where \( \rho_0 \) has negligible temperature dependence compared to the exponential factor. \( T_0 \) and \( T_1 \) are constants given by
\[ T_0 = \frac{16 \varepsilon_0 \hbar A V_0^{3/2}}{\pi (2m_e)^{1/2} w e^2 k_B} \]  \hspace{1cm} (3.45) \\

and \\

\[ T_1 = \frac{8 \varepsilon_0 A V_0^2}{w e^2 k_B} \]  \hspace{1cm} (3.46) \\

Here \( A \) is the barrier area, \( V_0 \) the barrier height, \( m_e \) is the effective electron mass, \( w \) is the barrier width, and \( \varepsilon_0 \) is the permittivity of free space.
4. Optical Properties

4.1 Introduction

The response of a material to electromagnetic radiation contains important information on highly mobile (conduction) electrons, bound (valence) electrons, and lattice vibrations, i.e., phonons. The different responses may be added, given that the corresponding excitations are well separated on an energy scale, to a total complex dielectric function, which describes a material’s optical properties, according to

\[ \varepsilon(\omega) = 1 + \chi^{ve} + \chi^{fc} + \chi^{ph} + \ldots \]  (4.1)

where \( \varepsilon(\omega) \) is the frequency dependent dielectric function, \( \chi^{ve} \), \( \chi^{fc} \), and \( \chi^{ph} \) are the susceptibilities of the valence electrons, free carriers, and the phonons, respectively.

The contribution from the valence electrons may be described by the Lorentz model, where the electrons are assumed to be bound to the core with an elastic force. The Lorentz oscillator model may be used to represent direct interband transitions, such as those at the band gap between the valence band and the conduction band in semiconductor materials.

In metals and heavily doped semiconductors, where the charge carrier concentration is high, the dielectric function will be dominated by the contribution from the free electron susceptibility. The Drude model is frequently used to model the free electron susceptibility; see section 4.2.1.

Contribution to the total dielectric function due to phonons is omitted in this work. For further reading on phonons, see for example Ref. 40.
4.2 Dielectric Function of Free Electrons

4.2.1 The Drude Model

The Drude theory of the dielectric function is based on the motion of a charged particle, i.e., an electron, accelerated by an electromagnetic wave. Only the electric force is considered here and the force balance is given by

\[-e\vec{U}(t) = m \ddot{\vec{r}} + m \tau^{-1} \dot{\vec{r}}\] \hspace{1cm} (4.2)

where \(\vec{U}\) is the electric field, \(m\) is the free electron mass, \(\tau\) is the relaxation time, and \(\vec{r}\) is the displacement of the charged particle and the dots are an abbreviation for time derivatives. The first term on the right hand side of Eq.(4.2) is the inertia and the second term is the “damping” term.

A full derivation of the Drude formula is not presented here. The Drude formula is given by

\[\varepsilon_{\text{Drude}} = 1 - \frac{\omega_p^2}{\omega \left( \omega + i \frac{1}{\tau} \right)}\] \hspace{1cm} (4.3)

where \(\omega_p\), the plasma frequency, and \(\tau\) are given by the following expressions

\[\omega_p^2 = \frac{n_e e^2}{m \varepsilon_0}\] \hspace{1cm} (4.4)

\[\tau = \frac{m}{\rho n_e e^2}\] \hspace{1cm} (4.5)

Here \(n_e\) is the charge carrier concentration, \(e\) the elementary charge, and \(\varepsilon_0\) the permittivity of free space. The mobility \(\mu_e\) is related to the relaxation time and is given by

\[\mu_e = \frac{e \tau}{m}\] \hspace{1cm} (4.6)
4.2.2 Comments on the Validity of the Drude Model

The Drude model is a phenomenological description of the response of the free-electron gas to an electromagnetic wave. There are a number of approximations included in the model. For example, the electrons travel with a friction mechanism, often presented as the scattering of the electrons. The scattering, introduced by the relaxation time, is an energy independent parameter in the Drude model, which may in many cases be a strongly simplified description of a real material. Many metals and heavily doped semiconductors display an energy dependent relaxation time. Furthermore, the relaxation time states only the average time between scattering events. It contains no information regarding scattering mechanisms.

4.3 Effect of Grain Boundary Scattering

This section discusses the effect of grain boundary scattering on the optical properties of nanocrystalline metals. Effects of grain boundary scattering in nanocrystalline metals are not only observed at very low frequencies of the electric field, i.e., in the dc electrical conductivity. This effect is also present when a frequency dependent electric field is applied to the sample, as in the case of optical measurements. The effect of the grain boundary scattering is observed at energies below the interband transition range. At and above this energy range the effect of scattering is suppressed.

The Boltzmann equation is solved for the frequency dependent non-equilibrium charge distribution function. The model considers a two-dimensional structure, with the grain boundaries modeled as potential barriers parallel to the surface normal (z-axis). The distance between the grain boundaries is assumed to follow a Gaussian distribution. Mayadas and Schatzkes’ results for the effect of grain boundary scattering on the dc conductivity, see section 3.3.1, is expanded to apply to the frequency dependent (optical) case. The incident electromagnetic radiation is assumed to be polarized in the \(u\)-direction (\(u \in x,y\) plane) and propagates along the \(z\)-axis according to

\[
U(z,t) = U_u(z)\exp\{i(\omega t)\} \tag{4.7}
\]

where \(U_u(z)\) is the amplitude in the direction of polarization.

The following Boltzmann equation is considered:
\[
e v(\vec{k}) \frac{\partial F^0(\vec{k}, z, t)}{\partial E} = \int \mathcal{R}_{\vec{k}, \vec{k}'}^\xi \left[ \xi(\vec{k}, z, t) - \xi(\vec{k}', z, t) \right] d\vec{k} + \frac{\xi(\vec{k}, z, t)}{\tau_s} + \\
+ v(\vec{k}) \frac{\partial \xi(\vec{k}, z, t)}{\partial z} + \frac{\partial \xi(\vec{k}, z, t)}{\partial t}
\]  
(4.8)

\( \mathcal{R}_{\vec{k}, \vec{k}'}^\xi \), i.e., the transition probability, is given by Mayadas and Shatzkes\textsuperscript{45}; see Eqs.(3.18)-(3.20). The third and fourth terms on the right hand side of Eq.(4.8) come from the second and first terms on the left hand side in Eq.(3.6), respectively. When the transition probability is known it is possible to find the charge distribution function, which is the solution to the Boltzmann equation in Eq.(4.8). The solution is given by

\[
\xi'(\vec{k}, q, \omega) = \frac{e v(\vec{k}) \frac{\partial F^f(\vec{k})}{\partial E}}{\tau_{\text{eff}}} U^f(q, \omega)
\]  
(4.9)

where \( \xi'(\vec{k}, q, t) \) and \( U^f(q, t) \) are the Fourier transforms of \( \xi(\vec{k}, z, t) \) and \( U(z, t) \). \( \tau_{\text{eff}} \) is given by Eq.(3.22). From Ohm’s law,

\[
J_{\text{eff}}^f(\vec{q}, \omega) = \bar{U}^f(\vec{q}, \omega)\sigma_{\text{eff}}^{\text{fc}}(\vec{q}, \omega) = \\
= -\frac{e}{4\pi^2} \int v(\vec{k}) \xi'(\vec{q}, \omega) d\vec{k}
\]  
(4.10)

where \( J_{\text{eff}}^f(\vec{q}, \omega) \) is the Fourier transform of the current density \( J_{\text{eff}}(z, t) \), the dynamical conductivity \( \sigma_{\text{eff}}^{\text{fc}} \) of the free carriers, including the effect of grain boundary scattering, is obtained. The dynamical conductivity may then be expressed as

\[
\sigma_{\text{eff}}^{\text{fc}} = \sigma_{\text{Drude}} G(\vec{q}, \omega)
\]  
(4.11)
where \( G(\vec{q}, \omega) \) is a correction term for the dynamical conductivity due to grain boundary scattering and \( \sigma^{\text{Drude}} \) is given by

\[
\sigma^{\text{Drude}}(\omega) = \frac{\varepsilon_0 \omega_p^2}{\varepsilon_s^{-1} - i\omega} \tag{4.12}
\]

The non-local dielectric function is a diagonal tensor and can be expressed in terms of \( \varepsilon_t \) and \( \varepsilon_l \), the transverse and longitudinal dielectric function, as

\[
\varepsilon_{1,uu} = 1 + \chi^{ib} + \chi^{\text{fc}}(\vec{q}, \omega) \tag{4.13}
\]

\[
\varepsilon_i = 1 + \chi^{ib} + \chi^{\text{Drude}}(\omega) \tag{4.14}
\]

Here \( \chi^{ib} \) is the susceptibility due to interband transitions. \( \chi^{\infty} \) and \( \chi^{\text{Drude}} \) are given by

\[
\chi^{\text{fc}}(\vec{q}, \omega) = i \frac{\sigma^{\text{fc}}(\vec{q}, \omega)}{\varepsilon_0 \omega} = \chi^{\text{Drude}} G(\vec{q}, \omega) \tag{4.15}
\]

\[
\chi^{\text{Drude}}(\omega) = i \frac{\sigma^{\text{Drude}}}{\varepsilon_0 \omega} \tag{4.16}
\]

Combining Eqs.(4.13)-(4.16) gives the following expression for the dielectric function, including the effect of grain boundary scattering:

\[
\varepsilon_{1,uu}(\vec{q}, \omega) = \varepsilon_i(\omega) + \chi^{\text{Drude}} (G(\vec{q}, \omega) - 1) \tag{4.17}
\]

The reflectance of a film is calculated using the surface impedance concept. The surface impedance is given by
The reflectance is then given by

\[ R_s(\omega) = \left| \frac{Z_s(\omega)-1}{Z_s(\omega)+1} \right|^2 \]  \hspace{1cm} (4.19)

### 4.4 Ionized Impurity Scattering in Doped Semiconductors

In a perfect crystal the atoms are located at their equilibrium positions, thereby creating a perfect periodic potential. However, in a real crystal this is not the case. Several sources of deviations exist in the periodic potential and among those we recognize, for example, lattice vibrations present at any temperature (also at \( T = 0 \)), lattice defects, impurities, etc. In an applied electric field the conduction electrons are scattered by the interactions with the deviations of the periodic potential.

This section treats the effect of ionized impurities on the optical properties. Impurities are used in a semiconductor to increase the charge carrier concentration, i.e., changing the electrical and optical properties of the material. In the case of indium oxide, tin may be used as dopant material. Tin is incorporated in the indium oxide structure on the indium sites and contributes with an extra electron to the conduction band.

We may represent the free-electron part of the total dielectric function by the Drude model; see Eq.(4.3). To model the effect of ionized impurity scattering a frequency dependent relaxation time is introduced according to

\[ \frac{1}{\tau(\omega)} = \frac{1}{\tau_1(\omega)} + i \frac{1}{\tau_2(\omega)} \]  \hspace{1cm} (4.20)

The real part of the relaxation time \( \tau \) can be expressed as a simple power law of frequency, i.e. \( \tau \propto \omega^{-n} \). The power law is only observed at frequencies higher than the plasma frequency. Above the plasma frequency the response of the electrons to the electromagnetic radiation starts to decrease and become lower than the response at frequencies below \( \omega_p \).

The dynamic conductivity is related to the dynamic resistivity as
\[
\sigma_1(\omega) + i\sigma_2(\omega) = \frac{1}{\rho_1(\omega) + i\rho_2(\omega)} 
\] (4.21)

Eq.(4.21) gives the following expression for \( \sigma_1(\omega) \):

\[
\sigma_1(\omega) = \frac{\rho_1(\omega)}{\rho_1^2(\omega) + \rho_2^2(\omega)} 
\] (4.22)

The dynamic resistivity is given by

\[
\rho(\omega) = \frac{1}{\varepsilon_0 \omega_p^2} - i\frac{\omega}{\varepsilon_0 \omega_p^2} 
\] (4.23)

Using Eqs.(4.20), (4.22), and (4.23) we arrive at the following expression for the real part of the dynamic conductivity

\[
\sigma_1(\omega) = \varepsilon_0 \omega_p^2 \frac{\frac{1}{\tau_1}}{\left(\frac{1}{\tau_1}\right)^2 + \left(\frac{1}{\tau_2} + \omega\right)^2} 
\] (4.24)

Since at high frequencies we have

\[
\omega \gg \frac{1}{\tau_1(\omega)}, \frac{1}{\tau_2(\omega)} 
\] (4.25)

we may neglect \( \tau_2 \) and \( (\tau_2)^{-1} \) in Eq.(4.24), which brings us back to a dielectric function similar to that of the Drude model in Eq.(4.3) but with a frequency dependent relaxation time given by the following expression

\[
\frac{1}{\tau_1(\omega)} \propto \omega^s 
\] (4.26)

The exponent \( s \) has been evaluated for several different scattering mechanisms by Gerlach and Grosse. Their model is based on the
equivalence between energy loss and Joule heat and gives useful expressions for the frequency dependent dynamic resistivity. Using a Coulomb potential to describe the scattering potential of an ionized impurity and a random phase approximation representing the screening, the exponent $s$ is found to be $3/2$ for ionized impurity scattering.

4.5 Effective Medium Theory

4.5.1 General

Composite materials are of interest in many applications, for example, metal nanoparticles embedded in an insulator matrix display selective optical absorption, which is an important property in solar energy research. The two-component case is discussed here, i.e., composite materials consisting of two constituents or a porous film structure.

Effective medium theories are widely used in order to model the materials described above. However, they are applicable only under the condition that the size of the inhomogeneities is much smaller than the wavelength of the incoming light, or in the case of small particles more precisely for 97

$$\pi \sqrt{\frac{e_m}{\lambda}} \frac{d}{\lambda} \ll 1$$

(4.27)

where $e_m$ is the largest dielectric constant of the two constituent materials in the system and $\lambda$ is the wavelength of the incoming electromagnetic radiation.

The inequality in Eq.(4.27) denotes the condition for the quasistatic approximation. Within this approximation the electric field component in the electromagnetic radiation is assumed to be constant over the whole particle, and electrostatic arguments are used to obtain the complex dielectric function of the effective medium.

4.5.2 The Bruggeman Model

This section derives the effective medium model by Bruggeman 98 for constituents A and B. Figure 4.1 represents a microstructure for which the
Bruggeman model is applicable. The grain size is much smaller than the wavelength of the incoming electromagnetic radiation.

Fig. 4.1 Microstructure of a two-component system (A and B) for which Bruggeman’s effective medium theory is applicable.

Fig. 4.2 Random unit cell according to the Bruggeman model, with \( \varepsilon_A \) and \( \varepsilon_B \) being the dielectric function of the components A and B. \( \varepsilon_B^{\text{RUC}} \) is the dielectric function of the effective medium.

A random unit cell (RUC) is defined to describe the major features of the microstructure and when, embedded in the in the effective medium, it should not be detected at any wavelength in the optical measurements. Thus, the extinction should be the same whether the RUC is present or replaced by the effective medium. In Fig. 4.2 the RUC according to the Bruggeman model is shown.
Using an optical theorem by Bohren and Gilranga for absorbing media we find that the extinction \( C_{\text{ext}} \) of a spherical RUC relative to a surrounding medium is given by

\[
C_{\text{ext}} = 4\pi \text{Re} \left( \frac{Q(0)}{|k_e|^2} \right)
\]

where \( Q(0) \) is the scattering amplitude in the forward direction, and \( k_e \) the amplitude of the wave vector in the effective medium. By definition, for an effective medium one has \( C_{\text{ext}} = 0 \), which results in \( Q(0) = 0 \). \( Q(0) \) is obtained by Lorentz-Mie theory. In the case of the Bruggeman model, the series expansion for a sphere is used and the following expression for the scattering amplitude is obtained

\[
Q(0) = i \left( \frac{k_e \rho}{2} \right)^3 \frac{\epsilon - \bar{\epsilon}}{\epsilon + 2\bar{\epsilon}} + O \left( \left( \frac{k_e \rho}{2} \right)^5 \right)
\]

where \( \epsilon \) denotes \( \epsilon_A \) or \( \epsilon_B \) with probabilities corresponding to their respective filling factors; see Fig. 4.1. In a two-component system and using the small sphere limit the Bruggeman model finally becomes

\[
f_A \frac{\epsilon_A - \bar{\epsilon}_B}{\epsilon_A + 2\bar{\epsilon}_B} + f_B \frac{\epsilon_B - \bar{\epsilon}_B}{\epsilon_B + 2\bar{\epsilon}_B} = 0
\]

with

\[
f_B = 1 - f_A
\]

where \( f_A \) and \( f_B \) are the filling factors of the constituents A and B, respectively, and \( \bar{\epsilon}_B \) is the complex dielectric function of the Bruggeman effective medium.
5. Thermal Stability

5.1 Grain Growth Kinetics

The rate of grain growth is inversely proportional to grain size\textsuperscript{101-103} and given by

\[
\frac{dd(t)}{dt} \propto c_1 \frac{\mu_{gb}}{d(t)} \tag{5.1}
\]

where \(c_1\) is a constant and \(\mu_{gb}\) is the grain boundary mobility. The solution to Eq.(5.1) is given by

\[
d(t)^2 - d_0^2 = kt \tag{5.2}
\]

where \(k\) is a temperature dependent rate constant and \(d_0\) is the initial grain size. The rate constant is given by an Arrhenius-type equation, reading

\[
k(T) = k_0 \exp\left(-\frac{E_a}{k_B T}\right) \tag{5.3}
\]

where \(E_a\) is the activation energy for a given process. It has been shown empirically that Eq.(5.2) is not applicable\textsuperscript{25,26} for nanocrystalline materials and a generalized parabolic model is usually used,\textsuperscript{25} which has the form

\[
d(\frac{1}{\eta}) - d_0^{1/\eta} = k_1 t \tag{5.4}
\]

Here \(\eta\) is a constant and \(k_1\) is analogous to \(k\).

The models described above consider grain growth in systems exhibiting no pinning mechanisms for grain boundary motion, i.e., the grain growth is limited only by the finite sample. However, in most materials pinning
mechanisms are present and limit the grain growth. This is taken into account by introducing a grain growth limiting term in Eq. (5.1), giving the following expression:

\[
\frac{dd(t)}{dt} \propto c_2 \frac{\mu_{gb}}{d(t)} - c_3
\]  

(5.5)

where \( c_3 \) is the grain growth limiting term. The solution to Eq. (5.5) is given by

\[
k_2 t = \frac{d_0 - d(t)}{d_{\infty}} + \ln\left(\frac{d_{\infty} - d_0}{d_{\infty} - d(t)}\right)
\]  

(5.6)

Here \( k_2 \) is a constant analogous to \( k \) and \( k_1 \), and \( d_{\infty} \) is the grain size at \( t = \infty \).

A grain size dependent grain growth limiting term has also been suggested. Since pores and impurity atoms increase in concentration in the grain boundaries as the total amount of grain boundaries decrease with grain growth, a constant grain growth limiting factor is incorrect in nanocrystalline materials. As a first approximation the grain growth limiting term is proportional to grain size which can be accounted for by

\[
\frac{dd(t)}{dt} \propto c_4 \frac{\mu_{gb}}{d(t)} - c_5 d(t)
\]  

(5.7)

Here \( c_4 \) and \( c_5 \) are constants. The solution to Eq. (5.7) is

\[
d(t) = \sqrt{d_{\infty}^2 - (d_{\infty}^2 - d_0^2)} \exp(-k_4 t)
\]  

(5.8)

where \( k_4 \) is analogous to \( k \).

5.2 Structural Relaxation

The previous section contained a brief discussion of grain growth kinetics. The present section pursues a slightly different approach to grain growth. The isothermal grain growth process, in the presence of pinning of the grain boundary motion, may be described as a relaxation from an excited
state to a metastable state at the specific temperature. A non-linear relaxation process relevant to glasses\textsuperscript{106} can be expressed by

\[
\frac{p(t) - p_\infty}{p_0 - p_\infty} = \exp\left[-\left(\frac{t}{\tau}\right)^z\right]
\]

(5.9)

where \( p \) is a convenient parameter describing the system and \( z \) is a constant. Eq.(5.9) may also describe the grain growth in nanocrystalline materials by using \( p = d \). The relaxation time is given by the following Arrhenius-type equation

\[
\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right)
\]

(5.10)

### 5.3 Electrical Relaxation

Electrical relaxation can be connected to many processes; grain growth, lattice strain relaxation, structural relaxation in the grain boundaries, etc. Eq.(5.9) can be used to describe electrical relaxation during isothermal annealing experiments. The relaxation is then given by

\[
\frac{\rho(t) - \rho_\infty}{\rho_0 - \rho_\infty} = \exp\left[-\left(\frac{t}{\tau}\right)^z\right]
\]

(5.11)

where \( \rho_0 \) is the electrical resistivity at time \( t = 0 \) and \( \rho_\infty \) is the resistivity at \( t = \infty \).
6. Experimental

6.1 Sample Preparation Techniques

Several methods are used to prepare nanocrystalline materials, for example sputtering, ball milling, evaporation, spin-coating a dispersion containing nanoparticles onto a surface, etc. Here we overview two of these methods; evaporation and spin-coating.

6.1.1 Gas Evaporation

Gas evaporation is a process where particles are deposited onto a substrate. The setup used in this work consists of two chambers. Essentially, the material is evaporated in a lower chamber, the evaporation chamber; see Fig 6.1(a,b), in the presence of an inert gas flow introduced from below the crucible containing the starting material. The vapor is thereby cooled so that nucleation and growth of nanoparticles takes place in the gas. Assuming that no coagulation of the particles occurs, the growth rate of a condensed particle depends on the atomic condensation rate from the metal vapor onto the particles, which is a function of the partial pressure of the metal vapor. The size of the nanoparticles is determined by the condensation rate and the time the particles stay in the growth zone (passage time). Supposing constant condensation rate, the size-distribution is given by the distribution of the passage time and it has been shown that this has a lognormal distribution. Consequently, the particles also have a lognormal size-distribution in the no-coagulation limit.

The nanoparticles that are formed in the evaporation chamber are then brought to the deposition chamber by the inert carrier gas (usually He gas). The deposition chamber is kept at a pressure much lower than in the evaporation chamber. In this way a mixture of inert gas and nanoparticles is forced by the pressure difference to impinge on a substrate mounted in the deposition chamber. Due to a jet nozzle, with a diameter of 0.5 mm, the nanoparticles are estimated to reach a velocity of several hundred m/s. Figure 6.1(a,b) shows a photograph and a schematic drawing of the
experimental equipment for the fabrication of nanocrystalline materials. The heating is provided by an induction coil of copper surrounding a carbon crucible containing the starting material. He gas is introduced below the crucible. The transfer pipe is positioned centrally in the vapor zone where particles are formed. Particles that are not collected are removed by an exhaust pipe connected to a vacuum pump. The temperature of the melt \( T_m \) in the crucible is determined to an accuracy of \( \pm 0.5\% \) by optical pyrometry. The gas evaporation technique is applicable to many materials (mainly metals and metal oxides) and can produce particles with a wide range of sizes.

A few properties of the gas evaporation process are as follows:

- the formed nanoparticles are transported to the substrate without contact with the atmosphere,
- the deposited films exhibit high mass density, often close to bulk density,
- any material that can be evaporated can be used for gas evaporation and the particle size distribution can be very narrow,
- nanoparticles with oxide coats can be fabricated under controlled conditions,
- the substrate is mounted on a movable table in the deposition chamber, which makes it possible to produce patterned samples.

The main disadvantage of the gas evaporation method is the limitation of surface area that can be covered, and hence it is time-consuming and expensive to deposit large areas. A large amount of He-gas is consumed (there are possibilities for a recycling process, though) during the film fabrication. A normal He-gas rate is 15 – 25 l/min.

A sample preparation technique similar to gas evaporation is a technique commonly referred to as thermal evaporation. Thermal evaporation takes place in a conventional bell-jar system, i.e., a single chamber system. The pressure in the chamber may be varied from high vacuum, \(~1\times10^{-7}\) mbar, to atmospheric pressure by introducing a gas. The starting material is put in a tungsten boat, which is mounted between two electrodes in the chamber. Resistive heating is then used to evaporate the material. When evaporating in
a presence of high pressure, small particles nucleate in the gas and are transported by convection toward the upper part of the chamber. A substrate is mounted at the top of the bell-jar to collect the particles formed during evaporation. Film thickness can be varied either by controlling evaporation time or by the amount of starting material used in the deposition. At low pressure (vacuum evaporation) in the deposition chamber, the evaporated atoms (or molecules) travel directly to the substrate without collisions or nucleation and can form a continuous film.

Fig. 6.1 Photograph (a) and schematic picture (b) of the experimental equipment for fabrication of nc-materials

6.1.2 Spin Coating

The ITO nanoparticles used in this work were prepared by a wet-chemical method. All samples investigated in this thesis have a Sn to In atomic ratio corresponding to 5 %. The particle size was typically in the range of 14 – 16 nm in the as-deposited state.

Thin porous films consisting of ITO nanoparticles were prepared by a technique referred to as spin-coating. A substrate is mounted on a sample holder that is rotated at a very high speed, typically a few thousand rpm. A dispersion of ITO nanoparticles is put onto the rotating substrate and is distributed as a thin film over the surface due to the centrifugal force. The
film thickness may be varied by changing the spin speed or time. However, thickness gradients may be present.

This is a fast and inexpensive thin film preparation technique. Deposition is at room temperature, which makes this technique of interest when thermally sensitive substrates are used, such as polymer films and organic substrates.

6.2 Heat Treatments

In this work three types of heat treatments were employed. In the case of the nanocrystalline gold films the heat treatments were performed merely to investigate the thermal stability and grain growth. It is possible to observe changes by electrical transport measurements, both at high and low temperatures, which is described later.

When it comes to the ITO nanoparticle films, the heat treatments were of interest in investigating the change in density of the porous films, the charge carrier concentration, and the mobility of the conduction electrons.

6.2.1 Annealing in Vacuum

The sample was put on a large solid copper piece inside a chamber connected to a vacuum pump system. The pressure was monitored by a pressure meter and the pressure was kept at 0.2 mbar. Heating was provided by a 200 W halogen lamp that was positioned in the center of the copper piece. A Low Noise High Power Temperature Stabilizer system was used as a power supply for the halogen lamp and the temperature was controlled within ± 0.5 K during the experiment. Annealing can be carried out in the range 300 < T < 773 K. The heating rate is typically 10 K/min.

6.2.2 Annealing in Air

Annealing in air at atmospheric pressure was performed using a programmable Logotherm oven with a Program Controller S17, which makes it possible to set a sequence including several annealing steps. The heating rate may be varied. The maximum heat treatment temperature that can be achieved with this setup is 1373 K.

6.2.3 Annealing in Nitrogen

ITO is very sensitive to the atmosphere in which the heat treatment is performed. Annealing in an oxidizing atmosphere leads to the removal of
oxygen vacancies, which yields a decreased charge carrier concentration. A nitrogen atmosphere may increase the number of charge carriers if annealing is performed at a high temperature.

A method presented here employs annealing in two steps. First, heat treatment was carried out in air for 1 h; see section 6.2.2, followed by a subsequent nitrogen treatment for 1 h at the same temperature. Samples presented in this work were annealed in the $573 < T < 1073$ K temperature range. The heating rate was set to 10 K/min.

6.3 Physical Characterization Techniques

6.3.1 Thickness Measurements

Two different instruments for thickness measurements were employed in this work. A Tencor Alpha-Step 200 mechanical stylus instrument was used for thickness determination of the nanocrystalline gold films. A diamond tip is scanned over the edge of the thin film and the thickness is recorded. The vertical resolution of the instrument is 0.2 nm at steps smaller than 1 µm.

Thickness measurements performed on thin ITO nanoparticle films were carried out using a Dektak 3030 stylus profilometer, similar to the Tencor Alpha-Step 200 instrument.

6.3.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is often used for surface analysis and imaging. The sample is hit by a beam of electrons, from a field emission or thermionic cathode, accelerated by a voltage of 1 to 30 kV. When the beam of electrons interacts with the surface of the sample, secondary electrons, back scattered electrons, and Auger electrons can be collected using different detectors; see Fig 6.2.

Scanning electron microscopy can provide information on surface morphology. Using additional equipment, for example an energy dispersive spectrometer (EDS-detector), one can obtain elemental information and produce elemental maps of the sample surface.

In this work a LEO 1550 Gemini instrument was used. Figure 6.3(a) shows a scanning electron micrograph, based on secondary electrons, of a surface of a typical as-deposited nanoparticle ITO film produced by the spin-coating technique; see section 6.1.2. The micrograph shows a fairly porous surface with nanometer-sized ITO particles. A narrow size distribution is seen; see Fig 6.3(b), and the grains display a spherical shape.
Fig 6.2 Different types of signals generated from a sample surface by the incident electron beam in scanning electron microscopy.

Specimen

Incident electron beam

X-rays

Backscattered electrons

Auger electrons

Secondary electrons

Fig 6.3(a) Scanning electron micrograph of an ITO nanoparticle film produced by the spin-coating technique. The surface contains a distribution of fine pores. The size distribution of the ITO nanoparticles is narrow with a mean grain size of 16±2 nm. (b) Size distribution of the ITO nanoparticles, shown in (a), obtained using transmission electron microscopy. The particles were scraped off the substrate and put onto a copper grid covered with a carbon film.
6.3.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a technique with superior resolution for imaging and analytical experiments. Electrons extracted from an electron gun, either from a field emission or thermionic cathode, are accelerated by a voltage of several hundred kV. This work employs a JEOL 2000 FX (200 kV) instrument and a Tecnai F30 (a 300 kV instrument with a point resolution of 0.14 nm), mainly for imaging. For further reading on TEM, see Williams and Carter. Fig 6.4 shows the TEM image, using the Tecnai F30 instrument operating at 300 keV, of a nanocrystalline gold film produced by the gas evaporation method.

![TEM Image](image)

*Fig. 6.4 Transmission electron micrograph of a gold nanoparticle film produced by the gas evaporation technique. At the center of the image one can see a particle of approximately 10 nm.*

6.3.4 X-Ray Diffraction

X-ray diffractometry (XRD) is a powerful technique for the investigation of crystalline matter. Information concerning phase composition, grain size, internal lattice strain, preferred crystal orientation, etc. can be obtained. In this work, x-ray diffraction has been used as a method for grain size determination. As the sample is exposed to a beam of x-rays each atom is the source of a coherently scattered wave that will interfere in a constructive or destructive way with other surrounding atoms. The Bragg law describes the path difference, see Fig. 6.5, between two rays according to

\[
2d_{hkl}^* \sin \theta = n \lambda
\]  

(6.1)
where \( d_{\text{hkl}} \) is the distance between atom planes, \( \theta \) is the angle of incidence, \( \lambda \) is the wavelength of the x-ray, and \( n \) is the order of the reflection.

Further, Scherrer’s formula\(^{110}\) is commonly used for determining the mean grain size, \( d \), in a crystalline material. This quantity is given by

\[
d = \frac{B\lambda}{W \cos \theta} \tag{6.2}
\]

where \( B \) is a dimensionless constant and \( W \) is the width of a diffraction peak at half maximum. The Scherrer method may be used when the effect of internal strain can be neglected. The investigations presented here were performed on a Siemens D5000 diffractometer using CuK\(_{\alpha}\) radiation.

**Fig. 6.5** Features of x-ray diffractometry. The path length difference for the two rays is \( 2d_{\text{hkl}} \sin \theta \). If Bragg’s law is to be fulfilled, this path length has to be equal to an integer times the wavelength of the probe; see Eq.(6.1).

Figure 6.6 presents x-ray diffractograms for three different n-Au films deposited by the gas evaporation method onto glass substrates. The difference between these samples is that different magnitudes of \( T_m \) were used during deposition.

For a low temperature of the melt a clear <111> texture is observed, with the (111) peak much enhanced compared to the (200) and the (220) peak. For the sample prepared with the highest temperature of the melt, a <100> texture is present, with the intensity of the (200) peak being similar to the intensity of the (111) peak. In this work the samples were prepared at low
temperature of the melt, and hence the <111> texture is present in almost all samples.

Fig. 6.6 X-ray diffractograms for three n-Au films prepared by the gas deposition method. The diffractograms correspond to films produced with different temperatures of the melt, $T_m$, as given.

6.3.5 Rutherford Back Scattering

Rutherford back scattering (RBS) is a technique of significant importance for composition analysis and depth profiling. It is a non-destructive method based on collisions between incident $\alpha$ particles and atomic nuclei. An $\alpha$ particle with a certain energy hits the sample and is scattered at some point. Some of the $\alpha$ particles are back scattered and recorded by a detector. At this point the particle has lost some of its incident energy, which is specific for the different elements, and at the distance from the surface the specific atom is situated. The scattering probability is dependent upon the atomic number and mass of the incoming particle and of the sample atoms. In this work, RBS measurements were employed to evaluate the presence of impurities in the samples.

6.3.6 Elastic Recoil Detection Analysis

The basic idea of Elastic Recoil Detection Analysis (ERDA) is that incident particles, with energy the MeV range, hit the sample surface at an off-normal angle. The sample composition is analyzed by collecting the sample atom nucleis, which are elastically recoiled from the sample surface.
This technique is used as a complement to the RBS measurements, since ERDA has the advantage of detecting both light and heavy elements.

6.4 Electrical Measurements

6.4.1 Low Temperature Resistivity

Temperature-dependent electrical transport measurements were performed in a Maglab 2000 cryostat system from Oxford Instruments, which makes it possible to measure at temperatures down to 4 K. Resistance $R$ was measured on samples which were at most $10 \times 10$ mm in size. A four-probe method was used in the investigations presented below. The voltage was recorded, with an accuracy of $10^{-7}$ V, upon the application of a constant current. Data were taken as a function of temperature in the desired range, at an interval of choice, after thorough temperature stabilization ($\pm 0.05$ K at $T < 200$ K and $\pm 0.10$ K at $T > 200$ K) at each temperature. The resistance was determined for the current running in either direction, and the results were taken as the arithmetic mean of these readings. The lowest stable temperature that can be reached is 4.2 K (liquid He temperature). Sample geometry used in the experiments is shown in Fig. 6.7.

![Fig. 6.7 Schematic view of sample geometry used in resistivity measurements. $D$, $w$, and $u$ are the thickness, width, and length of the n-Au film, respectively.](image)

Data were collected in the temperature range 4.2 – 300 K. Figure 6.8 shows typical results on the temperature dependent resistivity for n-Au films with different grain size, along with data for bulk polycrystalline Au.$^{111}$

It is observed that the resistivity at any constant temperature increases with decreasing grain size. All curves exhibit metallic behavior with a linear
temperature-dependence down to approximately 90 K. The residual resistivity increases with decreasing grain size due to the increased number of grain boundaries causing additional scattering in the sample.

Fig. 6.8 Temperature-dependent resistivity for nanoparticle gold films with grain size $d$ as shown. Data are also given for polycrystalline Au (pc-Au).\textsuperscript{111}

6.4.2 High Temperature Resistivity

In-situ electrical transport measurements during isothermal annealing experiments were carried out using a four-probe technique with wires connected to the sample, as in a standard bridge measurement setup. Resistance data were recorded with a Hewlett Packard 3457A Multimeter instrument in an interval of 10 s.

Figure 6.9 shows resistivity as a function of time for n-Au films during isothermal annealing in vacuum at 473, 573, and 673 K. It is observed that the resistivity increases with increasing annealing temperature, which is due to the increased number of phonons.

It is observed in Fig. 6.9 that the resistivity decreases with time, which is a result of aging of the film. Grain growth is the main contribution to the decreased resistivity.
6.5 Optical Measurements

6.5.1 Ultraviolet through Near Infrared Wavelength Range.

Spectrophotometry was employed to measure reflectance and transmittance in order to obtain information regarding optical properties of the material. Two different spectrophotometers have been used in this investigation for measurements in the $0.3 < \lambda < 2.5 \mu m$ wavelength range: a Perkin Elmer Lambda 9 instrument and a Beckman UV 5240 spectrophotometer.

In the Perkin Elmer Lambda 9 instrument, the beam is split into two rays using a rotating mirror device. One beam is used as reference signal and the other is used as the sample beam. The spectrophotometer is equipped with a 60-mm-diameter integrating sphere coated with BaSO$_4$. The detectors are located within the integrating sphere. In the $0.30 < \lambda < 0.86 \mu m$ wavelength range a photomultiplier is used, and from 0.86 to 2.5 $\mu m$ a PbS detector is
A tungsten lamp is used as a light source except in the $0.30 < \lambda < 0.32 \ \mu m$ range where a deuterium lamp is used.

No corrections for port losses in the integrating sphere were performed in this work. The sample reflectance is multiplied by the reflectance for BaSO$_4$. Figure 6.10 presents near normal spectral reflectance $R_r$ and normal spectral transmittance $T_t$ in the $0.3 - 2.5 \ \mu m$ wavelength range for a thin nanoparticle ITO film with a grain size equal to 16 nm.

![Reflectance and Transmittance](image)

*Fig. 6.10 Reflectance $R_r$ and transmittance $T_t$ for a thin n-ITO film with grain size equal to 16 nm.*

The Beckman UV 5240 instrument is a double beam spectrophotometer equipped with a 150-mm-diameter integrating sphere coated with BaSO$_4$. Light sources and detectors are similar to the ones used in the Perkin Elmer Lambda 9. Diffuse and total spectral reflectance and transmittance were measured using a BaSO$_4$-plate as reference.

6.5.2 Infrared Wavelength Range

Near normal spectral reflectance measurements were performed in the $2 - 50 \ \mu m$ wavelength range using a Perkin Elmer 983 double beam infrared spectrophotometer. Due to the strong absorption in the glass substrates used
in this work the normal spectral transmittance was measured in the 2 – 5 µm range. Above 5 µm the glass substrate is opaque.

A ceramic tube heated to 1200 °C is used as light source and a thermocouple, positioned in an evacuated chamber, is used as detector. The water vapor content in the sample chamber was reduced by using an air dryer. Gold mirrors were used as a reference for the reflectance measurements. All measurements were performed using unpolarized light. Figure 6.11 shows infrared near normal reflectance data on a thin ITO nanoparticles film in the 2 – 30 µm range.

Fig. 6.11 Reflectance data for a thin n-ITO film with grain size of 16 nm.
7. Results on Gold Nanoparticle Films

7.1 Electrical Transport Data

7.1.1 Structural Characterization

Thin gold nanoparticle films were prepared by the gas evaporation technique described in chapter 6.1.1. Figure 7.1 presents an x-ray diffractogram of a sample produced at the given gas evaporation parameters. The diffractogram shows a strong <111> texture. Average grain size is estimated to be approximately 10 nm using the Scherrer method.\textsuperscript{110}

Fig 7.1 X-ray diffractogram of a thin nanoparticle gold film, with grain size 10 nm, produced at the given parameters: temperature of the melt $T_M$ and pressure in the evaporation chamber $p$. 
The grain size was verified employing TEM, and Fig. 7.2 presents a micrograph of a sample in the as-deposited state. The particles were evaporated directly onto a TEM copper grid covered with a thin carbon film. Fairly uniform particle size can be observed. The bright areas in the micrograph represent the carbon film without any gold. From several such micrographs, the average grain size was evaluated and found to be 11 nm, which is in close agreement with that found by XRD.

![Transmission electron micrograph of a nanoparticle gold film.](image)

Fig 7.2 Transmission electron micrograph of a nanoparticle gold film.

Annealing was carried out in air at temperatures in the $473 < T < 773$ K range for 0.5 h at each temperature. Figure 7.3 shows grain size as a function of annealing temperature. It is observed that the grain size grows with increasing annealing temperature.

### 7.1.2 Low Temperature Resistivity Data

Temperature-dependent resistivity measurements were performed in the 4 – 300 K temperature range. Figure 7.4 presents typical resistivity data on a nanocrystalline gold sample with average grain size of approximately 10 nm together with bulk data. The nanocrystalline sample exhibits a much higher resistivity than in bulk gold.
Fig 7.3 Grain size versus annealing temperature for a nanoparticle gold film.

Fig 7.4 Resistivity versus temperature for a nanoparticle gold film with grain size $d \approx 10$ nm, and for a polycrystalline (pc) gold film.111
Figure 7.5 presents log-log plots of resistivity versus temperature, in the 4 – 20 K range, for four different grain sizes (the different grain sizes are obtained by annealing; see above). A change in the temperature-dependent resistivity is observed and the temperature at which the change occurs, the cross-over temperature $T_c$, is shifted toward lower temperature with increasing grain size. The cross-over temperature and grain size are listed in Table 7.1. The $T_c$ may be interpreted as a cross-over from an inelastic scattering regime at $T > T_c$, dominated by electron-phonon scattering, ($\rho(T) \propto T^\nu$ with $\nu$s, given in Table 7.1, obtained from the slope at $T > T_c$ in Fig. 7.5) to a regime at $T < T_c$ dominated by electron-grain boundary scattering ($\rho(T) \propto T^\kappa$ with $\kappa$s, given in Table 7.1, obtained from the slope at $T < T_c$ in Fig. 7.5). An extended analysis of these results is given below.

![Fig. 7.5 Log-log plot of resistivity vs. temperature for a n-Au film. Dots represent measured data, and lines were drawn to fit the behavior above and below a cross-over temperature $T_c$. (Note that only the curve for $d = 39$ nm is given with correct magnitude of resistivity. The rest of the curves have been multiplied by a factor of 10, 100, and 1000 for a more clear presentation.)](image)
Table 7.1 Cross-over temperature $T_{cr}$ for a n-Au films with grain size $d$ together with data on temperature exponents $\nu$ and $\kappa$ for the resistivity at high and low temperature, respectively.

<table>
<thead>
<tr>
<th>$d$ [nm]</th>
<th>$T_{cr}$ [K]</th>
<th>$\nu$</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10.0</td>
<td>1.3</td>
<td>3.3</td>
</tr>
<tr>
<td>11</td>
<td>9.3</td>
<td>1.4</td>
<td>3.2</td>
</tr>
<tr>
<td>15</td>
<td>8.9</td>
<td>1.2</td>
<td>3.5</td>
</tr>
<tr>
<td>39</td>
<td>7.2</td>
<td>1.2</td>
<td>3.7</td>
</tr>
</tbody>
</table>

7.1.3 Analysis of Low Temperature Data

The effect of electron-grain boundary scattering on the temperature-dependent resistivity in metals is a complicated problem and the full picture is far from clear.

The resistivity of metals can be represented as a sum of different contributions under the assumption that the different scattering mechanisms are independent of each other. Eq.(7.1) presents the different contributions to the total resistivity in a nanocrystalline metal. A three-dimensional sample will be considered, thus finite size effects are omitted from the treatment.

$$\rho(d,T) = \rho_{s} + \rho^{el-ph}(T) + \rho^{el-ph}(d,T) + \rho^{el-dis}(T) + \rho^{el-dis}(T) + \rho^{el-ap}(T)$$  \hspace{1cm} (7.1)

The first resistivity term represents the temperature-independent resistivity, i.e., the residual resistivity. It includes elastic scattering effects from grain boundaries, lattice defects, impurities, etc.

The second term is the contribution from inelastic electron-phonon scattering.

The third and the fourth terms are the temperature-dependent resistivity due to electron-grain boundary and dislocation scattering, respectively. Karolik and Luhvich\textsuperscript{112} have shown that low-angle misoriented grain boundaries may be described as a set of scattering dislocations. Dislocations are known to exhibit two separate contributions to the resistivity: the long range elastic strain field, which adds a temperature-dependent contribution to the total resistivity, and a short range inelastic distortion of the lattice in the dislocation core, which adds an temperature-independent contribution to the total resistivity.\textsuperscript{81} Karolik\textsuperscript{81} made a calculation on the contribution from the dislocations and grain boundaries to the temperature-independent resistivity, i.e., the residual resistivity, using a model taking the inelastic distortion of the lattice in the dislocation core into account. Localized quasi-stationary electron states within $k_{B}T$ from the Fermi energy are created in
the dislocation core due to the inelastic distortion of the lattice, thereby contributing to the elastic scattering of the conduction electrons. However, experimental investigations by Gantmakher and Kulesko\textsuperscript{113} on the temperature-dependent resistivity due to dislocations in potassium showed that it was possible to fit experimental data to a model describing a temperature-dependent elastic scattering cross-section due to the probability of quasi-stationary electron states being occupied close to the Fermi level.

The fifth term is due to electron-electron interactions. Such effects are observable only at very low temperatures, typically below 4 K.\textsuperscript{114}

The sixth term concerns the temperature-dependence due to electrons scattered by impurities.\textsuperscript{114}

The following section is an extended motivation for the analysis of the cross-over temperature published in paper I. This analysis leads to an approximate prediction of how the cross-over temperature changes with grain size. The following assumptions are made:

I A temperature-dependent resistivity component of the electron-grain boundary scattering exists, also dependent on grain size, $\rho^{\text{el}}(d,T)$ as already shown in Eq.(7.1). It is also assumed that $\rho^{\text{el}}(d,T) \rightarrow 0$ as $d \rightarrow \infty$.

II The grain boundary reflection coefficient, i.e. the probability of a conduction electron being reflected at a grain boundary, is independent of grain size and remains unchanged upon annealing.

III The concentration of impurities is assumed to be negligible compared to the concentration of grain boundaries in a nanocrystalline metal with grain size in the range 10 – 50 nm. RBS and ERDA measurements on gold films prepared by the gas evaporation method did not reveal any trace of impurities.

IV Electron-electron interactions are neglected above 4 K.\textsuperscript{114}

V The concentration of dislocations is neglected since only a limited number of dislocations were observed within the particles in the as-deposited state and annealed films at $T_i \leq 673$ K in the TEM investigation. (However, at $T_i = 773$ K the number of dislocations increased within the particles.)

From the assumptions made above, Eq.(7.1) is now reduced to
\[ \rho(d,T) = \rho_0 + \rho^{el-ph}(T) + \rho^{el-gh}(d,T) \]  
(7.2)

Well above the Debye temperature the resistivity is dominated by inelastic electron-phonon scattering. As the temperature is lowered below the Debye temperature, the resistivity is proportional to \( T^3 \) due to freezing out of phonon modes; see section 3.4.1. The mean free path is given by

\[ \ell^{el-ph}(T) \propto T^{-3} \]  
(7.3)

Below the cross-over point the temperature-dependent resistivity is dominated by grain boundary scattering. It gives a different temperature-dependence of the mean free path, which can be expressed by

\[ \ell^{el-ph}(T) \propto d \cdot G(T) \]  
(7.4)

where \( G(T) \) is a function dependent on temperature.

Considering the list of assumptions made above we may state that at \( T_c \), the temperature-dependent inelastic mean free path due to electron-phonon scattering \( \ell^{el-ph} \) is equal to the temperature-dependent mean free path due to electron-grain boundary scattering \( \ell^{el-ph} \), i.e.

\[ \ell^{el-ph}(T_c) = \ell^{el-ph}(T) \]  
(7.5)

Combining Eqs. (7.3-7.5) gives the following expression at \( T = T_c \):

\[ T_c^{-3} \propto d \cdot G(T) \]  
(7.6)

From Fig. 7.5 and Table 7.1 it is observed that there is a small temperature dependence of the resistivity below the cross-over temperature, i.e. \( \rho(T) \approx T \) and since the mean free path is inversely proportional to the resistivity we have that \( G(T) \propto T^{-1} \). This brings us to the following expression for the cross-over temperature, namely

\[ T_c(d) \propto d^{-1/2} \]  
(7.7)

Figure 7.6 presents the cross-over temperature as a function of average grain size. Two models are fitted to the experimental data. They are normalized so that a grain size equal to 10 nm gives a cross-over at 10 K when adjusted to the experimental data. Eq.(7.7) is represented by the solid curve in Fig. 7.6.
If instead the model in Paper I is used, the corresponding exponent is $-1/3$, which leads to the dashed curve in Fig. 7.6. This earlier model neglected the temperature dependence of the resistivity at temperatures below $T_c$. The fits show good agreement for the small grain sizes but less good agreement with the final value corresponding to $d = 39$ nm. The disagreement between theory and experiment may be due to the large number of dislocations introduced into the grains upon annealing as observed in the TEM investigation. Additional scattering by dislocations should shift the $T_c$ to a higher temperature, according to the observation in Fig. 7.6.

![Figure 7.6](image)

*Fig. 7.6 Cross-over temperature versus grain size for a n-Au film subjected to annealing. Dots with error bars signify experimental data. The solid curve represents a fit to Eq.(7.7), and the dashed curve represents a fit to the theory in Paper I.*

### 7.1.4 Room Temperature Resistivity Data

This section presents grain boundary transmission coefficients for four different samples, prepared by the gas evaporation method. Sample preparation parameters are given in Table 7.2. Figure 7.7 shows grain boundary transmission coefficient data, obtained from Eq.(3.32) in section 3.3.2, as a function of annealing temperature. The annealing was performed in vacuum for 2 h at each temperature. Grain boundary transmission coefficient calculations were performed by setting $\ell_m = 42$ nm, $14\nu_r = 1.4\times10^{-6}$ m/s, $14m = 9.10939\times10^{-31}$ kg. The resistivity and grain size of the samples are presented in Table 7.3.
Table 7.2 Data for n-Au films prepared by the gas evaporation technique at the shown values of the He gas pressure \( p \) in the deposition chamber and temperature of the melt \( T_\text{M} \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( p ) [mbar]</th>
<th>( T_\text{M} ) [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>250</td>
<td>1550</td>
</tr>
<tr>
<td>II</td>
<td>500</td>
<td>1550</td>
</tr>
<tr>
<td>III</td>
<td>750</td>
<td>1550</td>
</tr>
<tr>
<td>IV</td>
<td>1000</td>
<td>1550</td>
</tr>
</tbody>
</table>

Table 7.3 Data on resistivity \( \rho \) and grain size \( d \) (using XRD) at each annealing temperature \( T_\text{A} \) for four samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_\text{A} ) [K]</th>
<th>( \rho ) ([10^{-8} \Omega\text{m}])</th>
<th>( d ) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>as-deposited</td>
<td>9.42±0.05</td>
<td>18.1±0.5</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>7.39±0.05</td>
<td>20.1±0.5</td>
</tr>
<tr>
<td></td>
<td>573</td>
<td>6.15±0.05</td>
<td>20.2±0.5</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>5.52±0.05</td>
<td>20.4±0.5</td>
</tr>
<tr>
<td>II</td>
<td>as-deposited</td>
<td>6.81±0.05</td>
<td>23.3±0.5</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>5.78±0.05</td>
<td>23.5±0.5</td>
</tr>
<tr>
<td></td>
<td>573</td>
<td>5.26±0.05</td>
<td>24.1±0.5</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>4.75±0.05</td>
<td>25.4±0.5</td>
</tr>
<tr>
<td>III</td>
<td>as-deposited</td>
<td>5.26±0.05</td>
<td>25.5±0.5</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>4.28±0.05</td>
<td>27.9±0.5</td>
</tr>
<tr>
<td></td>
<td>573</td>
<td>3.15±0.05</td>
<td>33.3±0.5</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>2.67±0.05</td>
<td>36.1±0.5</td>
</tr>
<tr>
<td>IV</td>
<td>as-deposited</td>
<td>7.55±0.05</td>
<td>20.3±0.5</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>5.94±0.05</td>
<td>22.8±0.5</td>
</tr>
<tr>
<td></td>
<td>573</td>
<td>4.45±0.05</td>
<td>27.6±0.5</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>3.99±0.05</td>
<td>29.3±0.5</td>
</tr>
</tbody>
</table>
Fig. 7.7 Grain boundary transmission coefficient as a function of annealing temperature for four n-Au samples prepared by the gas evaporation method using the production parameters given in Table 7.2. The transmission coefficient data was calculated from Eq. (3.32) using the data given in Table 7.3.

It is observed in Fig. 7.7 that the grain boundary transmission coefficient is slightly increased upon annealing for all four samples. Sample III shows a higher \( \Gamma \) than for the other samples.

### 7.2 Optical Properties

Figure 7.8 presents reflectance data for four nanoparticle gold samples with different grain size, as a function of wavelength in the \( 0.4 < \lambda < 2.0 \) \( \mu \text{m} \) range. The samples are specified in Table 7.4. Sample 1 – 3 were produced by thermal evaporation and sample 4 was produced by the gas evaporation method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( d ) (XRD) [nm]</th>
<th>( d ) (SEM) [nm]</th>
<th>Rms surface roughness [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15±2</td>
<td>---</td>
<td>7.3</td>
</tr>
<tr>
<td>2</td>
<td>20±3</td>
<td>21±3</td>
<td>6.0</td>
</tr>
<tr>
<td>3</td>
<td>30±3</td>
<td>29±3</td>
<td>6.2</td>
</tr>
<tr>
<td>4</td>
<td>45±3</td>
<td>---</td>
<td>8.5</td>
</tr>
</tbody>
</table>
It is clearly shown that the near infrared reflectance is high for all samples. The film with $d = 45$ nm displays the highest reflectance in the whole wavelength range, and it is observed that the near infrared reflectance decreases slightly with decreasing grain size, see the inset in Fig. 7.8. Absorption is prominent at $\lambda < 800$ nm, and for samples 2, 3, and 4 the reflectance displays a sharp step-like decrease at $\lambda \sim 500$ to 600 nm. This is due to interband transitions, where electrons from the d-bands are excited to the Fermi level. Sample 1, however, exhibits different behavior, with an extra absorption in the $550 < \lambda < 800$ nm range, which is discussed in Paper II.

Figure 7.8 also presents theoretical data fitted to the experimental reflectance using the grain boundary scattering model described in section 4.3. The grain boundary reflection coefficient $\Phi$ is used as the only fitting
parameter. The reflectance is calculated for the non-local case, i.e. including the spatial dispersion of the charge distribution function, in order to take the anomalous skin effect into account, see section 4.3 (see also Paper II). Theoretical reflectance data provide an excellent fit to the experimental results in the near infrared range. The agreement between theory and experiment in the interband transition region is less good, since grain size effects on the interband transitions were not included in the model.

Measured spectral infrared reflectance for samples 1 - 3 is presented in Fig. 7.9(a-c), using sample 4 as reference, together with calculated optical data obtained from the same theory as above.

Figure 7.9(a-c) clearly shows that the gold nanoparticle films exhibit high infrared reflectance. The magnitude of the reflectance decreases with decreasing grain size, which is in agreement with the notion of increased grain boundary scattering as the grain boundary concentration is increased. Table 7.5 presents $\Phi$ obtained from the fitting. The reflection coefficient seems to be independent of grain size.

Table 7.5 Data on grain boundary reflection coefficient $\Phi$ obtained from fitting the model described in section 4.3 to measured reflectance of n-Au films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>~ 0.63</td>
</tr>
<tr>
<td>2</td>
<td>~ 0.64</td>
</tr>
<tr>
<td>3</td>
<td>~ 0.68</td>
</tr>
<tr>
<td>4</td>
<td>~ 0.64</td>
</tr>
</tbody>
</table>
Fig 7.9(a-c) Spectral near-normal reflectance for three gold nanoparticle films (samples 1, 2, and 3) as specified in Table 7.4. Dotted lines represent fitted data obtained from the model described in section 4.3.
7.3 Thermal Stability

7.3.2 Grain Growth

Some results on the thermal stability of nanoparticle gold films prepared by the gas evaporation method are presented in this section. Figure 7.10 shows grain size, obtained by XRD, as a function of annealing temperature for four different types of n-Au films. The samples were produced at different He gas pressures in the deposition chamber, as specified in Table 7.2. The samples were annealed in vacuum for 2 h at each annealing temperature.

![Grain size as a function of annealing temperature for four different types of samples as specified in Table 7.2.](image)

It is observed in Fig. 7.10 that samples I and II display a much smaller grain growth after the final annealing experiment than samples III and IV. Further, the grain size of samples I, II, and IV seem to level off at the two final annealing experiments with $T_a$ being 673 and 773 K. A possible explanation for this feature is that samples I and II contain more pores acting as pinning sites to the grain boundary motion, and that the effect of pinning appears at higher annealing temperatures. Concerning sample IV, it is
reasonable to believe that this specimen contains more defects introduced in
the film due to the high speed of the nanoparticles during deposition. The
defects acts as pinning sites and inhibit further grain growth.

It should be observed that the initial grain size increases with increasing
deposition rate, except for sample IV, which instead shows a decrease in
grain size. The particle size is sensitive to a number of parameters during
deposition, for example the residence time in the vapor zone [26], the height
of the vapor zone and the rate of the particle growth in the gas. It is presently
not known how these parameters are affected by the He gas pressure in the
lower chamber.

Figure 7.11 shows grain size as a function of annealing time at three
different annealing temperatures for a sample prepared at the same
parameters as sample III specified in Table 7.2. The annealing was carried
out at a pressure of 0.2 mbar; see section 6.2.1. The two models represented
by Eqs.(5.8) (pinning model; PM) and (5.9) (relaxation model; RM) in
section 5.1 and 5.2, respectively, were fitted to the experimental data. In
Eq.(5.9) the exponent \( z \) was put equal to 0.5. Both models take pinning of
the grain boundary motion into account. Fitting parameters for the pinning
model and the relaxation model are given in Tables 7.6 and 7.7, respectively.
As seen in Fig. 7.11, both models give good fits to the experimental data.
Grain size was measured by XRD using the Scherrer method applied to the
(111) peak in the diffractograms. The activation energies, for the model
given by Eq.(5.9) were calculated using Eq.(5.10) and putting \( \tau_0 \) equal to 10^{-13} s; data are given in Table 7.7. It is observed that the activation energy for
grain growth increases with increasing temperature. This gives a strong
indication of pinning forces being present in the samples produced by the
gas evaporation method. The pinning of the grain boundary motion may be
due to pores in the grain boundary region.

7.3.3 Electrical Relaxation

Figure 7.12 presents data on in-situ electrical resistivity measurements
during isothermal annealing of a nanoparticle gold film at successively
higher annealing temperatures. Grain size before and after each annealing is
shown in Table 7.8. The experimental data were fitted to the relaxation
model (RM) represented by Eq.(5.11); see section 5.3. The exponent \( z \) was
put equal to 0.5.

The activation energy was calculated from the relaxation times obtained
from the fits using Eq.(5.10) and putting \( \tau_0 \) equal to 10^{-13} s. Data on
activation energies are given in Fig. 7.12. It is evident that the activation
energy increases with increased annealing temperature, which is to be
expected in a system where pinning mechanisms are present.
Table 7.6 Data on fitting parameters for the pinning model, see Eq.(5.8), used in Fig. 7.11(a-c).

<table>
<thead>
<tr>
<th>$T_A$ [K]</th>
<th>$d_0$ [nm]</th>
<th>$d_o$ [nm]</th>
<th>$k_4$ [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td>26.9</td>
<td>29.1</td>
<td>2.56</td>
</tr>
<tr>
<td>673</td>
<td>29.1</td>
<td>50.7</td>
<td>1.04</td>
</tr>
<tr>
<td>773</td>
<td>50.7</td>
<td>52.6</td>
<td>2.25</td>
</tr>
</tbody>
</table>

Table 7.7 Data on fitting parameters for the relaxation model, see Eq.(5.9), used in Fig. 7.11(a-c).

<table>
<thead>
<tr>
<th>$T_A$ [K]</th>
<th>$d_0$ [nm]</th>
<th>$d_o$ [nm]</th>
<th>$\tau$ [s]</th>
<th>$E_A$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td>26.9</td>
<td>29.4</td>
<td>319.5</td>
<td>1.45</td>
</tr>
<tr>
<td>673</td>
<td>29.1</td>
<td>50.7</td>
<td>1707.2</td>
<td>2.17</td>
</tr>
<tr>
<td>773</td>
<td>50.7</td>
<td>52.6</td>
<td>388.0</td>
<td>2.38</td>
</tr>
</tbody>
</table>
Fig. 7.11(a-c) Grain size versus annealing time for three n-Au films, together with fitted data according to Eqs. (5.8) (pinning model: PM) and (5.9) (relaxation model: RM). Part (a) corresponds to $T_A = 473$ K, part (b) to $T_A = 673$ K, and part (c) to $T_A = 773$ K. Activation energies $E_A$ were calculated from Eq. (5.10), putting $\tau_0$ equal to $10^{-13}$ s.
Fig. 7.12 Resistivity versus annealing time for n-Au films treated at the shown temperatures, together with theoretical data obtained from the relaxation model, Eq.(5.14), with $z = 0.5$.

<table>
<thead>
<tr>
<th>$T_A$ [K]</th>
<th>$d_{\text{before}}$</th>
<th>$d_{\text{after}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td>23.3</td>
<td>23.5</td>
</tr>
<tr>
<td>673</td>
<td>23.5</td>
<td>24.1</td>
</tr>
<tr>
<td>773</td>
<td>24.1</td>
<td>25.4</td>
</tr>
</tbody>
</table>

Grain size was obtained by XRD.
8. Results on ITO nanoparticle films

8.1 Electrical Transport Properties

Figure 8.1 presents temperature-dependent resistivity data on four ITO nanoparticle samples: as-deposited (A), annealed at 773 K for 2 h at $p = 0.2$ mbar (referred to as vacuum) (B), annealed at 773 K for 2 h at $p = 0.2$ mbar followed by 2 h in air at 773 K (C), and annealed in air at 773 K for 2 h (D). The grain size is 16 nm irrespective of annealing atmosphere and temperature. The data are normalized so that the resistivity at 300 K is set to unity. It is clearly observed that all samples display a negative temperature coefficient of resistivity, TCR. The vacuum annealed sample (B) displays the largest TCR, while the vacuum and air annealed sample (C) appears to exhibit the lowest TCR. The fluctuation induced tunneling model, see section 3.5, was successfully fitted to the experimental results, which indicates that the sample morphology is dominated by large clusters of closely connected ITO nanoparticles and that the clusters are separated by insulating barriers. The fitting parameters, $T_0$ and $T_1$, are given in Table 8.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho_{RT}$ [Ωcm]</th>
<th>$T_0$ [K]</th>
<th>$T_1$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.2</td>
<td>149</td>
<td>224</td>
</tr>
<tr>
<td>B</td>
<td>0.012</td>
<td>240</td>
<td>316</td>
</tr>
<tr>
<td>C</td>
<td>0.008</td>
<td>155</td>
<td>147</td>
</tr>
<tr>
<td>D</td>
<td>0.032</td>
<td>172</td>
<td>178</td>
</tr>
</tbody>
</table>

The parameters $T_b$ and $T_c$ are related to the insulating barrier height, width, and area; see Eqs.(3.44) and (3.45). From Table 8.1 it is obvious that vacuum annealing, sample (B), significantly increases the parameters $T_b$ and $T_c$. The amount of increase in $T_b$ and $T_c$ is of the same order, a factor 1.6 to 1.8, indicating that the main change is an increased barrier area; see Eqs.(3.45) and (3.46). This notion is supported by the fact that $\rho_{RT}$ is decreased after annealing in vacuum, as shown in Table 8.8, which means that the
Fig. 8.1 Experimental data on resistivity versus temperature for four ITO films with grain size 16 nm, together with theoretical data calculated from Eq. (3.43) with parameters given in Table 8.1
number of conducting paths – or the internal area of the existing conduction paths – must have increased. However, it is likely that also the barrier width is slightly decreased since the large decrease in $\rho_{RT}$ can not only be assigned to an increased barrier area by 1.6 to 1.8. The tunneling probability is exponentially dependent on the barrier width, which means that the sample resistivity is very sensitive to changes in this width.

The following annealing in air – to obtain sample C – gives decreased $T_e$ and $T_i$ together with a decreased $\rho_{RT}$. Annealing in air without the preceding vacuum annealing, i.e., sample D, gives a higher $\rho_{RT}$ than in sample C, and $T_e$ and $T_i$ are also slightly larger. Thus annealing in vacuum before a final annealing in air gives better film properties – i.e. lower electrical resistivity – than in films annealed in air only.

### 8.2 Optical Properties

Figure 8.2 shows spectral near-normal reflectance in the $0.3 < \lambda < 30.0$ µm wavelength range and normal transmittance in the $0.3 < \lambda < 2.5$ µm range for two porous ITO nanoparticle samples. The measurements were performed using a Perkin Elmer Lambda 9 instrument. The samples were annealed in air for 1 h followed by annealing in N$_2$ for 1 h at 573 K (ITO-A) and at 1073 K (ITO-B). The grain size, as determined both by SEM and XRD, was found to be $\sim 16$ nm for ITO-A and $\sim 34$ nm for ITO-B; see Table 8.2.

Both samples exhibit high luminous transmittance. At $\lambda < 0.4$ µm, $T_i$ decreases abruptly, partly due to absorption in the glass substrate and the bandgap in ITO, which is $\sim 3.75$ eV. In the near infrared wavelength range, at 1.0 – 2.5 µm, $T_i$ is decreased and $R_e$ is slightly increased. This is due to the collective excitations of the conduction electrons, i.e., the plasma wavelength; see Eq.(4.4). The plasma wavelength is related to the charge carrier concentration. From Fig. 8.2 it is observed that the decrease in $T_i$ in the near infrared occurs at different wavelengths, thus indicating lower $n_e$ for sample ITO-A than for ITO-B.

In the infrared range, the reflectance is higher than in the visible and near infrared wavelength range due to free charge carriers reflecting the incoming electromagnetic radiation.

Theoretical data according to an effective medium model by Bruggeman, see section 4.5.2, were fitted to experimental optical results. The samples were modeled as ITO nanoparticles in air connected in a percolating network. The dielectric function of the ITO nanoparticles was described using Drude theory with a constant relaxation time (Drude); see section 4.2.1. The effect of ionized impurity scattering was incorporated in
the model by the introduction of a frequency dependent relaxation time (IIS); see section 4.4 (see also Paper IV). As seen in Figs. 8.2 and 8.3, the agreement between experiment and theory in the visible and near infrared range is very good in the case of the IIS model. Less good agreement is achieved with the Drude model, thus giving strong indication that the electrical transport mechanism within the ITO nanoparticles is dominated by ionized impurity scattering, with the impurities being preferably ionized Sn dopant atoms.

In the infrared wavelength range, the agreement between experiment and theory is less good, at least for ITO-A. A possible explanation can be grain boundary scattering, since the grain size is only 16 nm, resulting in a decreased reflectance. Another explanation may be that the optical constants for the glass substrate used in the calculation were not taken for the specific glass used in the experiments. However, ITO-B displays an improved agreement with theory. In this sample the average grain size has increased to ~ 34 nm, which should decrease the influence of the grain boundaries on the reflectance. Table 8.2 also presents data on fitting parameters.

Table 8.2 ITO nanoparticle data showing annealing temperature $T_A$, for treatment at 1 h in air and 1 h in $N_2$, and grain size $d$. Fits between theory and experiment were made with the shown values of filling factor $f$, and electron density $n_e$. Data are given also on the derived mobility $\mu_e$ and resistivity of the particles $\rho$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_A$ [°C]</th>
<th>$d$ [nm]</th>
<th>$f$</th>
<th>$n_e$ [$10^{20}$ cm$^{-3}$]</th>
<th>$\mu_e$ [cm$^2$/V·s]</th>
<th>$\rho$ [$10^{-4}$ Ω·cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO-A</td>
<td>300</td>
<td>16</td>
<td>0.334</td>
<td>4.0</td>
<td>22.3</td>
<td>7.0</td>
</tr>
<tr>
<td>ITO-B</td>
<td>800</td>
<td>34</td>
<td>0.349</td>
<td>8.0</td>
<td>39.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

From Table 8.2 it is clear that both $n_e$ and $\mu_e$ increased upon annealing. The filling factor is low in both samples. Thus annealing in air followed by annealing in $N_2$ improves the electrical properties of the ITO nanoparticles.
Fig. 8.2 Experimental reflectance and transmittance data for sample ITO-A as specified in Table 8.1, together with theoretical data calculated according to the Bruggeman effective medium model (section 4.5.2).

Fig. 8.3 Experimental reflectance and transmittance data for sample ITO-B as specified in Table 8.1, together with theoretical data calculated according to the Bruggeman effective medium model (section 4.5.2).
9. Summary and Conclusions

This thesis is devoted to thin metallic and heavily doped semiconductor nanoparticle films. The aim of the work was to investigate the effect of the small crystallite size, i.e., the high concentration of grain boundaries, on physical parameters, such as, electrical resistivity, optical properties, and thermal stability. Specifically two materials have been studied: Au and Sn-doped In$_2$O$_3$.

9.1 Nanoparticle Gold Films

In the case of Au nanoparticle films, the investigation has focused on the effect of grain size on the electrical and optical properties. The grain boundaries were modeled as potential barriers through which an electron can tunnel with a certain probability, the grain boundary transmission coefficient. It was shown that the grain boundary transmission coefficient increases slightly upon annealing in n-Au films prepared by the gas evaporation method.

It was also shown that the activation energy for grain growth was increased with successively increased annealing temperature, which points to pinning mechanisms being present in the samples.

Low temperature resistivity measurements reveal a cross-over temperature. The resistivity above the cross-over temperature is dominated by electron-phonon scattering, and below the cross-over temperature the resistivity is dominated by grain boundary scattering. A model of the cross-over temperature versus grain size was presented and relatively good agreement with experiment was found.

The scattering of the conduction electrons by grain boundaries also influences the optical properties in nanoparticle gold films. Experimental results show that infrared reflectance drops with decreasing grain size, due to increased grain boundary scattering, as obtained from calculations including the effects of grain size. The grain boundary reflection coefficient was found to be independent of grain size in samples prepared by thermal evaporation in vacuum.
9.2 Nanoparticle ITO Films

Theoretical data calculated from effective medium theory, specifically using the Bruggeman model including the effect of ionized impurity scattering, were fitted to the experimental spectral transmittance and reflectance. The good agreement between theory and experiment presented in this thesis strongly indicates that the electrical transport within the ITO nanoparticles is limited by ionized impurity scattering. Furthermore, the fitting gives information on the filling factor of the ITO nanoparticles in the sample as well as the charge carrier concentration and mobility within the nanoparticles. These parameters give valuable information for analyzing the effect of annealing on electrical and optical properties of ITO nanoparticle films. It was shown that an initial annealing in vacuum, before annealing in air, yielded samples with lower resistivity than in samples annealed in air only.

The dc electrical transport in the ITO samples was described by fluctuation induced tunneling, i.e., the samples consist of clusters of many sintered ITO nanoparticles separated by insulating barriers. It should be noted that the temperature-dependent resistivity data could not be represented by the variable range hopping model, the nearest neighbor hopping, or the temperature-dependent model due to ionized impurity scattering.
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