Nanostructured thermoelectric materials for transparent and flexible applications

Tomi Koskinen
Nanostructured thermoelectric materials for transparent and flexible applications

Tomi Koskinen

A doctoral thesis completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Electrical Engineering, at a public examination held at the lecture hall T3 of the school (Konemiehentie 2, Espoo) on 4.9.2023 at 12.

Aalto University
School of Electrical Engineering
Department of Electronics and Nanoengineering
Micro and Quantum Systems
Abstract

The global energy use is predicted to grow by up to 50% in the coming decades, placing both pressure on resources and heavy demands on the energy efficiency of technologies around us. The majority of primary energy consumption is wasted as heat, which is ubiquitous in a difficult-to-use low-grade form. At the same time, the number of electronic devices in both everyday life and industry is increasing rapidly.

Thermoelectric materials enable converting heat into electricity, but their large-scale use is hindered by a low power per cost figure. The use of nanostructuring has enabled improving the thermoelectric performance by careful engineering of both electronic and thermal properties of these materials. Concurrently, also other material properties, such as optical transparency or mechanical flexibility, can be improved. The emergence of thermoelectric materials with functional properties could promote the widespread adoption of thermoelectric devices by providing novel uses and application domains.

This thesis presents ways to engineer thermoelectric materials for functional applications using nanostructuring as well as demonstrates a few proof-of-concept devices based on these materials. The thesis first studies the thermal properties of core-shell GaAs-AlAs nanowire arrays, a material system important for a variety of optoelectronic devices. Characterization by the transient thermoreflectance technique indicates that the thickness of the introduced epitaxial AlAs shell can be exploited in controlling the thermal properties of the heterostructure. Second, widely studied transparent thermoelectric material, ZnO, is grown using atomic layer deposition (ALD). Sandwiching of Zr in between ZnO layers grown by ALD is found to improve the room-temperature thermoelectric performance of ZnO at a 2% nominal concentration of Zr. Further, nanoporous grass-like alumina (GLA) surface is used as a template for ALD of Al-doped ZnO (AZO), showing increased carrier concentration and subsequently improved electrical conductivity and thermoelectric power factor. In addition, the transparency of the AZO film grown on GLA is enhanced due to the antireflective behaviour partly inherited from GLA. Finally, nanostructured materials are used in two instances to realize flexible thermoelectric devices. First, a thermoelectric generator based on InAs nanowire networks grown directly on flexible plastic is demonstrated. Second, a thermal distribution sensor based on spray-deposited multilayer graphene is presented.

The results obtained in this thesis demonstrate various ways for engineering the properties of thermoelectric materials for functional applications. Further, approaches enabling the scalable and cost-efficient fabrication of these materials are presented, drafting routes for practical utilization of functional thermoelectric devices.

Keywords thermoelectricity, nanostructures, thin films
Tekijä
Tomi Koskinen

Välitsöskirjan nimi
Nanorakenteiset lämpöäihköiset materiaalit läpinäkyviin ja taipuisiin sovelluksiin

Julkaisija
Sähkötekniikan korkeakoulu

Yksikkö
Elektri- ja nanotekniikan laitos

Sarja
Aalto University publication series DOCTORAL THESES 120/2023

Tutkimusala
Kehittyneet materiaalit ja fotoniikka

Käsikirjoituksen pvm
10.03.2023

Välitöspäivä
04.09.2023

Väittelyluvan myöntämispäivä
19.05.2023

Kieli
Englanti

Monografia
Artikkelivälitsöskirja
Esseevälitsöskirja

Tiivistelmä

Energian kulutuksen arvioidaan kasvavan lähivuosikymmeninä jopa 50%, mikä rasittaa energiantuotantotekijät ja asettaa vaatimuksia käyttämämme teknologian energiatehokkuudelle. Valtaosa kulutetusta primäärienergiasta menetetään hukkalämpöön, jota esiintyy kaikkialla hankalasti hyödynnettävääsä muodossa. Samaan aikaan sähköisten laitteiden määrä niin arkkäyttöissä kuin teollisuudessakin kasvaa nopeasti.


Työn tulokset esittävät tapoja toteuttaa funktionaalisin sovelluksiin sopivia lämpöäihköisiä materiaaleja. Esitellyt lähestymistavat mahdollistavat skaalautumaa ja kustannustehokasta materiaalien valmistusta, viitoittaen siten tietä kohti funktionaalisten lämpöäihköisten laitteiden hyödyntämistä käytännön sovelluksissa.

Avainsanat
lämpöäihköinen ilmiö, nanorakenteet, ohutkalvo

ISBN (painettu) 978-952-64-1374-7
ISBN (pdf) 978-952-64-1375-4
ISSN (painettu) 1799-4934
ISSN (pdf) 1799-4942

Julkaisupäivä
Helsinki
Painopäivä
Helsinki
Vuosi
2023

Sivumäärä
127

urn
The research reported in this doctoral thesis was carried out at the Department of Electronics and Nanoengineering of Aalto University during the years 2019–2023. Funding for this research was provided by the Doctoral School of Aalto University’s School of Electrical Engineering. I also thank the Walter Ahlström foundation and the Waldemar von Frenckell foundation for their additional support.

I am grateful to my supervisor Prof. Ilkka Tittonen for trusting me with the opportunity to conduct this work as a member of his group. I have vastly enjoyed our discussions not only on scientific, but also on gastronomic and aquatic topics. The great freedom given in coming up with the way in which to pursue my research has enabled me to grow to this point. I express my sincere gratitude to Prof. Dario Narducci and Prof. Kari Ullakko for their work in pre-examining the thesis.

I thank all co-authors and past and current MQS members for their contributions to the thermoelectrics research conducted in the group, a small part of which is included in this thesis. I am grateful to Dr. Taneli Juntunen and Dr. Mikko Ruoho for introducing me to the research line of work after hiring me as a research assistant back in 2016 - Taneli is further acknowledged for his guidance and insightful conversations later on. Lassi Hällström is thanked for engaging discussions on any topic conceivable, while Dr. Vladimir Kornienko is thanked for quality company both in the optics lab and in the cafeteria. Dr. Camilla Tossi is thanked for delightful conversations as well as for her contributions towards upkeeping the MQS spirit; Ornella Laouadi is highly appreciated for pleasant roommateship and occasional debates on societal topics. Dr. Matti Raasakka deserves an honorary mention for proving to be a worthy opponent; research assistants Pyry Vaara, Joni Ortela, Ulrika Volin, Weronika Wojnicka and Davide Cassarà are thanked for their help in fabricating samples and running measurements. I express my gratitude also to Dr. Ramesh Raju; not only for providing the invaluable help with XRD related research matters, but also for acting as the Swiss knife of the 4th floor on any problem imaginable.
A large part of the work was conducted in collaboration with researchers from other groups in Micronova and Aalto University. Vladislav Khayrudinov and Dr. Tuomas Haggren as well as group leader Prof. Harri Lipsanen are thanked for supplying nanowires and for engaging in drawn-out discussions on the results, while Dr. Hua Jiang is thanked for providing TEM micrographs on the samples. Dr. Vesa Vuorinen and Fahimeh Emadi are acknowledged for their help with preparing cross-cut samples and with the CMP equipment in general. Dr. Christoffer Kauppinen is thanked for sharing his expertise on ALD as well as for being a cheerful encounter in general.

The presented research took extensive advantage of the Micronova clean-room environment, the well-maintained facilities of which are largely to Dr. Päivikki Repo and her team to thank for. Particularly, Dr. Matti Hokkanen, Dr. Andreas Liapis and Edgar Maiorov are acknowledged for their help and collaboration in maintaining tools and processes critical to our research. Hands-on work on the equipment together with you certainly provided both a valuable learning experience and a healthy balance for the sometimes tedious research work.

I thank my friends for providing opportunities to occasionally forget about the research and for showing plausible interest during monologues on nanowires. This holds especially for Simo and Toni, of which the first one was likely more interested, but the latter showed more plausibility. I also thank Juha-Pekka for valuable peer support and perspective provided over lunch discussions and Petra for her help on vanishing point related issues.

I thank my parents, Jaana and Antti, for their support during my studies as well as in life in general. Finally, I thank Reetta for the love and understanding through these times.

Helsinki, August 2, 2023,

Tomi Koskinen
# Contents

Preface i  
Contents iii  
List of Publications v  
Author’s Contribution vii  
Abbreviations ix  
Symbols xi  

1. Introduction 1  

2. Background 5  
  2.1 Fundamentals of thermoelectrics .......................... 5  
    2.1.1 Electron transport and the thermoelectric effect 5  
    2.1.2 Thermal transport ..................................... 8  
  2.2 Nanostructuring ........................................... 10  
  2.3 Functional thermoelectrics .............................. 12  

3. Materials and Methods 15  
  3.1 Preparation of nanostructured materials .................... 15  
    3.1.1 Growth processes ................................... 15  
    3.1.2 Liquid-phase exfoliated graphene .................... 18  
  3.2 Thermoelectric and thermal characterization ............... 19  
    3.2.1 Measuring the power factor .......................... 19  
    3.2.2 Measuring the thermal conductivity .................. 20  

4. Results 23  
  4.1 Thermal conductivity engineering of core-shell nanowires 23  
  4.2 Transparent thermoelectrics with atomic layer deposited  
    zinc oxide .................................................. 27  
  4.3 Flexible thermoelectric devices .......................... 33
This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


Author’s Contribution

Publication I: “Thermal conductivity suppression in GaAs–AlAs core–shell nanowire arrays”

The author participated in designing the experiments and contributed significantly to sample preparation and characterization. He participated in modelling, data analysis and interpretation of the results as well as the preparation of the manuscript.

Publication II: “Atomic layer deposition of Zr-sandwiched ZnO thin films for transparent thermoelectrics”

The author designed the experiments and contributed significantly to sample fabrication, thermoelectric and thermal characterization. The manuscript was mainly prepared by him.

Publication III: “Grass-like alumina enhances transmittance and electrical conductivity of atomic layer deposited Al-doped ZnO for thermoelectric and TCO applications”

The author designed the experiments and contributed to sample fabrication. He carried out the thermoelectric measurements and part of the structural characterization. He carried out the analysis and wrote the first draft of the manuscript.

Publication IV: “Thermoelectric Characteristics of InAs Nanowire Networks Directly Grown on Flexible Plastic Substrates”

The author contributed to designing the study and carried out parts of the
sample preparation. He carried out the characterization with the exception of transmission electron microscopy measurements and participated in the interpretation of the results. He wrote the first draft of the manuscript.

**Publication V: “Large-area Thermal Distribution Sensor Based on Multilayer Graphene Ink”**

The author participated in designing the study and carried out the sample preparation. He contributed significantly in the interpretation of the results and prepared the first draft of the manuscript.
<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>AZO</td>
<td>Aluminum-doped zinc oxide</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>CMP</td>
<td>Chemical-mechanical polishing</td>
</tr>
<tr>
<td>DEZn</td>
<td>Diethylzinc</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>EMM</td>
<td>Effective medium model</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite-element method</td>
</tr>
<tr>
<td>GIXRD</td>
<td>Grazing incidence X-ray diffraction</td>
</tr>
<tr>
<td>GLA</td>
<td>Grass-like alumina</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td>LPE</td>
<td>Liquid-phase exfoliation</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>MOVPE</td>
<td>Metal-organic vapor phase epitaxy</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>PANI</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PDDAC</td>
<td>Poly(diallyldimethylammonium chloride)</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
</tr>
</tbody>
</table>
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGEC</td>
<td>Phonon-glass electron-crystal</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SOG</td>
<td>Spin-on glass</td>
</tr>
<tr>
<td>TBAs</td>
<td>Tertiarybuthylarsine</td>
</tr>
<tr>
<td>TEMAZ</td>
<td>Tetrakis(ethylmethyamino)zirconium</td>
</tr>
<tr>
<td>TMAl</td>
<td>Trimethylaluminum</td>
</tr>
<tr>
<td>TMGa</td>
<td>Trimethylgallium</td>
</tr>
<tr>
<td>TMIn</td>
<td>Trimethylindium</td>
</tr>
<tr>
<td>TTR</td>
<td>Transient thermoreflectance</td>
</tr>
<tr>
<td>UALPE</td>
<td>Ultrasonic-assisted liquid-phase exfoliation</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapor-liquid-solid</td>
</tr>
</tbody>
</table>
### Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_v$</td>
<td>Isochoric heat capacity</td>
</tr>
<tr>
<td>$d$</td>
<td>Layer thickness</td>
</tr>
<tr>
<td>$e$</td>
<td>Thermal effusivity</td>
</tr>
<tr>
<td>$E$</td>
<td>Energy</td>
</tr>
<tr>
<td>$f$</td>
<td>Fermi-Dirac distribution</td>
</tr>
<tr>
<td>$g$</td>
<td>Density of states</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>Reduced Planck’s constant</td>
</tr>
<tr>
<td>$I$</td>
<td>Electric current</td>
</tr>
<tr>
<td>$J$</td>
<td>Electric current density</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$l$</td>
<td>Mean free path</td>
</tr>
<tr>
<td>$L$</td>
<td>Lorenz coefficient</td>
</tr>
<tr>
<td>$m^*$</td>
<td>Effective mass</td>
</tr>
<tr>
<td>$n$</td>
<td>Charge carrier density</td>
</tr>
<tr>
<td>$q$</td>
<td>Elementary charge</td>
</tr>
<tr>
<td>$Q$</td>
<td>Gaussian pulse shape function</td>
</tr>
<tr>
<td>$R$</td>
<td>Interfacial thermal resistance</td>
</tr>
<tr>
<td>$s$</td>
<td>Laplace variable</td>
</tr>
<tr>
<td>$S$</td>
<td>Seebeck coefficient</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
</tbody>
</table>
Symbols

\( v_g \)  
Group velocity

\( V \)  
Voltage

\( x \)  
Packing density

\( z \)  
Material thermoelectric figure of merit

\( Z \)  
Device thermoelectric figure of merit

\( \eta \)  
Efficiency, temperature resistance

\( \kappa \)  
Thermal conductivity

\( \mu \)  
Mobility

\( \sigma \)  
Electrical conductivity

\( \tau \)  
Relaxation time

\( \omega \)  
Angular frequency
1. Introduction

The progress in the production of integrated circuits has resulted in an unprecedented growth in computing capacity, driven by the availability of ever smaller and cheaper electronic devices enabled by the reduced component size. At the same time, the number of different sensors monitoring inputs of various origins has exploded, and more real-time data is produced than ever before in the history. This trend is complemented by the growing energy consumption, that is predicted to further grow by up to 50% during the nearest three decades [1]. As over two thirds of the primary energy consumption is wasted as heat [2], this development also raises several sustainability issues regarding the production and use of it, energy efficiency of electronic devices being one of them. The power densities of modern processors are reaching a level similar to what is encountered inside a nuclear reactor, which inevitably leads to challenges in efficiency and heat dissipation, therefore requiring advanced thermal management [3]. On the other hand, a major share of the environment-monitoring sensors and wearable devices rely on batteries as their primary power source, which require upkeep and scarce raw materials, supplies of which are currently heavily burdened due to the current trend of electrification.

Due to the nature of thermodynamic processes, heat is ubiquitous but its exploitation is often difficult. Electricity, on the other hand, is versatile and easily controllable, but its production requires extensive resources. Thermoelectric materials can convert heat into electricity without any moving parts, quietly, scalably and without emissions during the use. The thermoelectric phenomenon was found in the beginning of the 1800s and named after Thomas J. Seebeck [4], with the first application in temperature sensing using a thermocouple. The interest towards thermoelectric technology first peaked in the 1960s after Bi$_2$Te$_3$ [5] and other metal chalcogenide alloys were found to be effective thermoelectric materials, which resulted in thermoelectric generators being applied as power sources in space missions accompanied with a radioisotope heat source [6]. The enthusiasm for the technology eventually petered out due to incompetitive cost and efficiency, resulting in the field experiencing a temporary dismissal.
In the 1990s, Hicks and Dresselhaus published seminal papers [7, 8, 9] essentially showing that nanostructures could offer a way for significantly improving the efficiency of thermoelectric materials. Soon after, Mahan and Sofo followed with calculations specifying the optimal electronic structure for a thermoelectric material [10]. Today, the same nanofabrication techniques that are used to produce ever smaller transistors have largely been adopted in realizing nanostructured thermoelectric materials envisaged by Hicks and Dresselhaus in practice [11]. Moreover, it is possible to realize thermoelectric devices also in form factors other than bulk, thus giving way for miniature thermoelectric generators [12] and thin film based devices [13]. Driven by the increasingly abundant nanostructuring methods, the field of thermoelectrics has been living a renaissance since the 1990s [14], which continues to this day with unitless figures of merit as high as 3.1 being reported recently [15]. Despite of the encouraging progress, the power-per-cost ratio of the best-performing materials is still lacking compared to alternative power production technologies, inhibiting the adoption in large-scale use. In the meanwhile, the thermoelectrics community has looked for alternative application domains, with waste-heat harvesting from otherwise unusable low grade sources as one of the promising routes [2]. Many of the sensor devices mentioned above could be powered by thermoelectric generators. On the other hand, thermoelectric materials can be directly used for temperature sensing, thus potentially replacing technologies that are otherwise more complex or power hungry. Unlike many conventional heat engines, thermoelectric devices scale well to low power levels and can therefore be assigned to distributed applications requiring a small amount of power, while larger impact in terms of total energy use can be attained through large numbers of devices [14].

This thesis presents experimental work on certain nanostructured thermoelectric materials and related application examples. First, the thermal properties of III–V semiconductor nanowires are engineered by applying an epitaxial shell structure, resulting in reduced thermal conductivity. Second, atomic layer deposited zinc oxide films are investigated in two instances: first by applying zirconia as a dopant, and second by growing an Al-doped film on a nanoporous grass-like alumina coating. Finally, we look into flexible applications based on nanostructured thermoelectric materials: first by investigating InAs nanowires directly grown on flexible polyimide and then by demonstrating a thermal distribution sensor based on ink-based multilayer graphene films prepared by spray deposition.

The contents of this thesis have been structured as follows. Chapter 2 briefly covers the material properties affecting the performance of functional thermoelectric devices and outlines the key advantages enabled by nanostructuring. Chapter 3 then presents the fabrication and characterization techniques used to prepare and investigate the materials and devices presented in this work. The key results obtained in this work are presented.
in Chapter 4, which is divided into three sections covering the thermal properties of core-shell nanowires, transparent atomic layer deposited thermoelectric films and flexible thermoelectric devices, respectively. The thesis is then concluded in Chapter 5 by offering a brief perspective on the development of the field.
2. Background

2.1 Fundamentals of thermoelectrics

This chapter presents the necessary semiconductor physics for describing thermoelectric transport and understanding the interrelated nature of the parameters that affect the performance of thermoelectric devices, such as a thermoelectric generator presented in Figure 2.1 a. We begin by briefly describing electron transport in semiconductors, after which we discuss the effect of a temperature gradient and thermoelectric efficiency. In the second part we look into thermal transport and phonons.

2.1.1 Electron transport and the thermoelectric effect

In crystalline solids, the electric current is carried by charge carriers, which include negative electrons and positive holes, representing the lack of electrons. A material’s capacity to carry electric current is determined by its electronic conductivity expressed as

$$\sigma = nq\mu.$$  \hspace{1cm} (2.1)

The electrical conductivity depends on the concentration of charge carriers $n$ and electron mobility $\mu$, which describes the ease of their movement in the semiconductor. In the case of elastic charge carrier scattering, mobility can be expressed as

$$\mu = \frac{q\langle\tau\rangle}{m^*_I},$$  \hspace{1cm} (2.2)

where $\langle\tau\rangle$ notes the average relaxation time and $m^*_I$ is the inertial effective mass. The charge carrier concentration is determined by the density of electronic states (DOS) $g(E)$ in the energy bands and the portion of those states that are occupied by electrons. The occupation is determined by the Fermi-Dirac statistics as
\[
f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1},
\]
(2.3)
where \( f(E) = 0.5 \) determines the position of the Fermi level relative to the band gap, where no available states exist.

The development of modern semiconductor technology has relied largely on the possibility of adjusting the position of the Fermi level in relation to the energy band edges either by elemental doping or gating with an external voltage source. The position of the Fermi level is crucial also from the thermoelectrics perspective, as two of the three parameters determining material performance, the electrical conductivity and the Seebeck coefficient, depend on the charge carrier concentration.

The Seebeck coefficient presents the disproportion in the electron and hole distributions driven by thermal excitation near the Fermi level. When a thermal gradient is imposed over a material, the charge carriers diffuse from the hot end towards the cold end. As a result, a net current density is formed:

\[
J = -\sigma(\nabla V + S \nabla T),
\]
(2.4)
in which \( \nabla V \) denotes the voltage gradient, \( \nabla T \) the temperature gradient and \( S \) the Seebeck coefficient. In an open circuit condition this results in the Seebeck coefficient being defined as

\[
S = -\frac{\Delta V}{\Delta T}.
\]
(2.5)
The interrelation of the Seebeck coefficient and other electronic properties can be better understood via the Mott relation for degenerate semiconductors and metals [16], expressed as

\[
S = \frac{2}{3} \frac{k_B^2}{q \hbar^2} m^* T \left( \frac{\pi}{3} \right)^{2/3} n^{1/3},
\]
(2.6)
from which we observe that the Seebeck coefficient is inversely proportional to the charge carrier concentration \( n \), also known as the Pisarenko relation [17]. The thermoelectric power factor determining the power output from a thermoelectric generator is defined as

\[
PF = S^2 \sigma,
\]
(2.7)
which means that the electrical conductivity in Equation 2.1 and the Seebeck coefficient in Equation 2.6 have conflicting dependencies on both the charge carrier concentration and the effective mass. This observation leads us to one of the pivotal difficulties in increasing the thermoelectric performance of a material by doping: an increase in charge carrier concentration leads to an increase in electrical conductivity, but at the same time the Seebeck coefficient decreases - therefore, an optimal value for \( n \) exists. This
Background

is further illustrated in Figure 2.1 b. Fortunately, experimentally verified strategies to circumvent the interdependency exist. Essentially, this means engineering structures that promote asymmetry near the Fermi level by i) allowing the high-energy charge carriers in the hot end to travel to the cold end and ii) preventing the low-energy charge carriers in the cold end from traveling to the hot end.

In addition to the power factor, which determines the obtainable power output from a thermoelectric material, another important factor is the efficiency of a thermoelectric material. Factors affecting the efficiency were first studied by Lord Rayleigh and Altenkirch [18, 19]. Later, Ioffe introduced the unitless figure of merit, which is commonly used in assessing the thermoelectric performance [20]

\[ zT = \frac{S^2 \sigma}{\kappa}, \]  

(2.8)

where in addition to the power factor in the nominator, \( \kappa \) in the denominator denotes the total thermal conductivity. This expression now relates the contribution of the material thermal properties to the thermoelectric performance. In addition to the coupling between the Seebeck coefficient and electrical conductivity, another cumbersome interrelation appears when the total thermal conductivity \( \kappa = \kappa_e + \kappa_l \) is examined; it consists of contributions from the electronic and lattice thermal conductivities, respectively. Maximising \( zT \) requires minimizing the total thermal conductivity, but since electrons also transport heat in addition to charge as epitomized in the Wiedemann-Franz law \( \kappa_e = \sigma LT \), where \( L \) denotes the Lorenz number [21], any approach aiming to regulate the electronic thermal conductivity will also affect the electrical conductivity. The effects of both the electronic and thermal properties on the \( zT \) are illustrated in Figure 2.1 b below.

![Figure 2.1. a Schematic of a thermoelectric generator consisting of n- and p-type semiconductor legs connected electrically in series and thermally in parallel. b The evolution of thermoelectric material parameters as a function of charge carrier concentration.](image-url)
In practice, the pathways for controlling the thermal properties consist mainly of engineering the vibrational properties of the lattice, the principles of which are covered in the following section.

Finally, the thermal efficiency of a thermoelectric generator is given by the Carnot efficiency multiplied by a factor representing the efficiency of the thermoelectric generator as

$$\eta = \frac{T_h - T_c}{T_h} \sqrt{1 + ZT - 1} \frac{1}{T_h}$$

(2.9)

where $T_h$ and $T_c$ denote the temperatures at the hot and cold end of the device, respectively, and capital $Z$ denotes the device figure of merit apart from $z$ for material figure of merit.

The efficiencies achieved with practical thermoelectric generators have this far been limited to levels below 10% in the low-grade heat range below 250 °C [22]. Efficiencies exceeding 8% have been reported for Bi$_2$Te$_3$ generators ($ZT \sim 1$) at hot side temperature of 523 K [23] and for tellurium-free antimonide generators ($ZT \sim 1$) at hot side temperature of 550 K [24].

### 2.1.2 Thermal transport

The thermal properties of a solid material dictate how efficiently heat is conducted through it. In non-metals, the majority of heat is carried by lattice vibrations or phonons, which are quasiparticles with quantized energy $\hbar \omega$. Phonons have analogous properties to other bosons such as photons, and display wave-particle duality.

A first approximation to the lattice contribution to thermal conductivity $\kappa_l$ as given by Debye [25] states that

$$\kappa_l \propto C_v v_g l,$$

(2.10)

which essentially treats the phonons as an ideal gas with an isochoric heat capacity $C_v$, effective group velocity $v_g$ and effective mean free path $l$. A more realistic description that takes the phonon frequency distribution into account was derived by Peierls [26] as

$$\kappa_l = \sum_i C_v(i) v_g(i) l(i),$$

(2.11)

where the sum is over the phonon wavevectors and the phonon branches in the first Brillouin zone.

Each of the three parameters constituting the lattice thermal conductivity $\kappa_l$ are affected by different aspects of the material structure, which, as will be discussed later on, affects the way in which they can be manipulated. The heat capacity $C_v$ depends on the partial derivative of internal energy density with respect to temperature at constant volume [27]. It
Background

is largely determined by the size and structure of the unit cell of the material, therefore leaving limited room for effective engineering outside of modifying the unit cell [28]. The group velocity, instead, is determined by the phonon dispersion relation, which is presented for GaAs in Figure 2.2 a. Finally, the phonon mean free path or alternatively, the relaxation time of momentum, is determined by the rate of scattering events taking place in the material.

One way to categorize the different approaches of structural engineering attempting to tune the thermal conductivity is to assort the way in which they attempt to affect the phonon transport; either by targeting the wave nature or the particle nature of phonons. In practice, this means either constructing elements that cause specular reflections or localization of phonons (and alter the dispersion relation) or ones that cause diffusive scattering of phonons (and alter the mean free path). Often, the latter are easier to come up with in practice, since in order for specular reflection to take place, the roughness of the reflective surface has to be smaller than the wavelength of the reflected (or transmitted) wave. Since the wavelength spectrum of phonons reaches as low as 1 nm [29] (corresponding to a couple of atoms), atomically flat interfaces would be required. Realizing such interfaces in experimental heterostructures is an arduous task even with the significant advances in modern epitaxy equipment.

**Figure 2.2.** a Phonon dispersion relation in the high symmetry directions for GaAs. Adapted from [30]. b Different phonon scattering mechanisms.

Approaches exploiting diffusive phonon scattering have a variety of ways to target phonons with different mean free paths due to the range of available scattering processes. Figure 2.2 b visualizes some of the typical processes. Typically, phonon-phonon scattering processes are divided into normal and Umklapp scattering processes based on whether they conserve momentum (elastic) or not (inelastic). Albeit a rather simple picture, the total phonon scattering rate is commonly expressed as a sum of the independent scattering rates according to the semi-classical Matthiessen’s rule [31]
\[ \tau_j^{-1} = \tau_b^{-1} + \tau_i^{-1} + \tau_N^{-1} + \tau_U^{-1} + ..., \quad (2.12) \]

where \( j \) denotes either transverse or longitudinal phonon polarization and the subindexes correspond to phonon boundary, phonon impurity, normal phonon and Umklapp phonon scattering processes, respectively. While normal phonon processes conserve momentum and do not therefore themselves act as a resistive element affecting the thermal conductivity, it is important to note that they contribute by feeding the resistive Umklapp process.

As discussed earlier in this chapter, a good thermoelectric material should have as low thermal conductivity as possible to maximise the unitless figure of merit \( zT \). A practical lower limit to which the thermal conductivity can be reduced to in a given material is called the minimum thermal conductivity \( \kappa_{\text{min}} \). It is typically considered to take place when thermal transport is purely diffusive and no phonon transport occurs. In nature, \( \kappa_{\text{min}} \) is found in amorphous solids, i.e. glasses, where no phonon transport-facilitating crystal structure exists.

### 2.2 Nanostructuring

Conventional attempts to reduce the thermal conductivity without affecting the electronic properties have revolved around the concept of alloying, with the binary tellurides such as Bi\(_2\)Te\(_3\) and PbTe constituting the most well known examples. [32, 33] As briefly touched upon in the introduction part of this thesis, the possibility of precise control over the material structure at the nanoscale has made it possible to further modify the material properties that affect the thermoelectric performance. Commonly exploited nanostructuring strategies used in achieving this include the use of low-dimensional materials [11, 34, 35], introduction of defects at various size scales [36] and designer structures such as superlattices [13], to name a few. The challenge lies largely in implementing structures that simultaneously improve electrical conductivity and Seebeck coefficient and reduce thermal conductivity, i.e. result in an improved \( zT \). As discussed in the preceding part, the interdependent nature of these properties is what makes such modification challenging.

From the historical perspective, nanostructuring approaches affecting the electronic properties of thermoelectric materials, such as the quantum confinement approach proposed by Hicks and Dresselhaus, were the first to gain widespread attention [7, 8]. However, due to the difficulty of fabricating practical structures in the below-10 nm scale required for the highest predicted performances, the majority of experimental research exploiting nanostructuring has concentrated on attempting to modify \( \kappa \) without disturbing the electronic properties. On the other hand, the modification
of thermal properties through nanostructuring approaches is a feasible strategy due to the differences in typical wavelengths and mean free paths of electrons and heat transporting phonons, therefore allowing the design of structures that only affect the latter. A prominent idea following this route was the phonon-glass electron-crystal (PGEC) concept proposed by Slack [29], which considers structures that suppress the lattice thermal conductivity but at the same time allow crystal-like electron transport. The practical realization of the PGEC approach has been attempted using materials with complex unit cells, including filled skutterudites [37] and clathrates [38]. Congruent to some of the PGEC ideas, a large part of the current nanostructuring techniques aim at affecting the lattice thermal conductivity by, for example, the installation of hierarchical nanostructures such as in polycrystalline materials with nanoscale inclusions at the grain boundaries [39], nanoscale porosity [40] or multiphase composites such as thin film superlattices [41] or core-shell structures [42]. Publication I presents the introduction of epitaxial shells in core-shell GaAs-AlAs nanowires for altering the thermal properties of the ensemble.

While $zT$ can certainly be improved by bringing the thermal conductivity down, increasing it by enhancing the power factor without simultaneous increase in the electronic thermal conductivity has turned out to be challenging. This is largely due to the interrelated nature of electrical conductivity and the Seebeck coefficient due to the inverse dependencies on the charge carrier concentration and the effective mass, as shown in Equations 2.2 and 2.6. Many of the successful approaches are essentially engineering the energy spectrum at which the charge transport is taking place as well as its relative position to the Fermi level [43].

Conventional approaches in improving the power factor of thermoelectric materials deal with decoupling the electrical conductivity and the Seebeck coefficient. This is made possible by the fact that $m^*_f$ and $m^*_S$ appearing in Equations 2.2 and 2.6 are the same only in a simple case of isotropic, parabolic bands resulting in a spherical Fermi surface [44]; if band anisotropy or multiple valleys are present, also the two effective masses are going to be different, which therefore allows engineering each of them independently to a certain degree [45, 46]. In addition to anisotropic structures targeting to differentiate the two effective masses, electronic properties can be modified by introducing low-dimensional nanostructures such as quantum dots, nanowires or two-dimensional flakes, that show altered electron DOS compared to bulk [35]. Resembling the delta-function like features suggested by Mahan and Sofo [10], both quantum dots and nanowires show sharp features in their DOS, which can be utilized to improve $S$ through positioning the Fermi level close to a such feature, resulting in large asymmetry for the product $(E - E_F)g(E)\frac{\partial f(E)}{\partial E}$ around $E_F$. [47]

Finally, periodic structures such as discussed in the case of manipulat-
Background

ing the phonon transport can be also used in modifying the electronic properties. A concept called energy filtering uses heterostructures with energy barriers to filter electrons based on their energy, targeting to allow high energy electrons to travel undisturbed but hindering the transport of low energy ones, therefore improving the Seebeck coefficient. Nevertheless, successful practical implementations of the concept are still largely lacking. [48]

2.3 Functional thermoelectrics

Introducing thermoelectric materials in novel application domains typically requires material properties not found in conventional bulk thermoelectric materials. For instance, optical transparency, mechanical flexibility and stretchability are all characteristics that are not associated with the current state-of-the-art thermoelectrics, but can offer additional value from the applications perspective. The absence of these properties from conventional materials range is not surprising, as each require compromises on the ultimate thermoelectric performance. As discussed above, the ideal thermoelectric material should conduct electricity well along the thermal gradient direction and not conduct heat at all; achieving this typically requires charge transport confined to a very narrow energy distribution close to but not overlapping the Fermi level [10], a narrow band gap, high band degeneracy and preferably a complex crystal lattice structure resulting in low lattice thermal conductivity. [49] On the other hand, nanostructuring, the use of which in improving the thermoelectric properties was covered in the previous section, can be exploited also to introduce and enhance functional properties, such as flexibility or transparency. Some potential application domains for thermoelectric generators that take use of these properties have been illustrated in Figure 2.3 a.

Apart from the requirements for thermoelectric performance, additional criteria arise when evaluating the suitability of a material to functional applications. An optically transparent material is required to transmit radiation at the optical wavelength range of 400–700 nm, which corresponds to having a rather large band gap of ~3 eV. This criterion results in an inescapable restriction to the electronic properties of the class of materials and limits their ultimate thermoelectric performance. This is further illustrated in Figure 2.3 b. On the other hand, the optical properties also depend on the reflectivity and the optical haze of the material, which are affected by surface roughness and, in the case of polycrystalline materials, the crystallite size [50].

To this date, both n- and p-type material candidates for transparent thermoelectric applications have been proposed. Perhaps the most studied n-type material is ZnO with a band gap of ~3.3 eV, although also
doped SnO$_2$ has received attention [52]. In addition to use in thermoelectrics, (doped) ZnO has been adopted as transparent conductive oxide layer for a variety of applications, including photovoltaics [53] and optoelectronics [54]. It has been fabricated using a range of methods, including (reactive) sputtering [55, 56, 57], sol-gel processes [58, 59], and atomic layer deposition [60, 61]. In thermoelectrics use, the power factor of ZnO has been typically enhanced by elemental doping using elements including Al and Ga [62]. In this thesis, the use of ZnO as a transparent thermoelectric material is investigated in two instances; Publication II studies the effect of Zr doping on ALD-grown ZnO films and Publication III presents conformal growth of Al-doped ZnO films on nanoporous grass-like alumina.

Until recently, potential transparent p-type counterparts were largely lacking, partly due to the difficulty of stable p-type doping of ZnO [63]. Nevertheless, Copper iodide (CuI) has been presented as a p-type material with a band gap of $\sim$3.1 eV and high zT values reported in a range 0.2–0.3 [64]. The previously reported pivotal fabrication routes for CuI include the iodization of Cu [65], CuO [66] and Cu$_3$N films [67] either via vapor or solid route, thermal evaporation [65] and reactive sputtering [68, 51].

In addition to the prevalent inorganic transparent thermoelectrics, some conductive organic polymers have shown promising thermoelectric properties. One of the recently discovered transparent organic thermoelectrics is the p-type poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), which has shown respectable performance and zT values above 0.2 achieved after secondary doping or other chemical post-treatments [69, 70, 71]. PEDOT:PSS has also been employed in devices that are simultaneously transparent and flexible [72, 73].

Hindrances similar to the band gap requirement of transparent materials apply also to flexible and stretchable devices, which are desirable especially from the wearable applications perspective. However, highly conductive semiconductors associated with conventional thermoelectrics

---

**Figure 2.3.** a Potential application domains for functional thermoelectric devices. b Room temperature $zT$ for both conventional and transparent materials as a function of band gap. Data from [51].
Background are typically crystalline, which makes them rigid and brittle and therefore rather unsuited for flexible applications. To obtain mechanical flexibility with inorganic substances, the materials typically need to be made very thin and possibly supported either by a flexible substrate or a host matrix in case of a composite structure. Despite of the challenge, a rather large number of flexible thermoelectric materials and devices have been reported recently, with many of the studies investigating alternative thermoelectric materials such as organic polymers or carbon nanomaterials. Commonly explored materials include polymers such as polyaniline (PANI) [74] and PEDOT:PSS, which do not suffer from the brittleness issue, composite films made of carbon nanomaterials such as carbon nanotubes [75] and graphene [76, 77], organic-inorganic hybrids often combining either inorganic nanoparticles, nanowires or flakes and polymers [78], and to some extent, inorganic thin films [79].

Publications IV and V present proof-of-concept thermoelectric devices based on two different nanostructured thin films. Publication IV investigates the thermoelectric properties and mechanical flexibility of InAs nanowire networks, and Publication V demonstrates a temperature distribution sensor based on large-area films consisting of spray-coated graphene flakes.
3. Materials and Methods

This chapter presents the key techniques used in both sample fabrication as well as thermal and thermoelectric characterization. The first section briefly introduces the fabrication techniques used in Publications I–V. The methods used in measuring the thermoelectric properties are presented in the latter subsection along with a description of the transient thermoreflectance thermal conductivity measurement and related analysis methods.

3.1 Preparation of nanostructured materials

A variety of fabrication processes can be exploited to produce materials comprising nanoscale structures. A common way to classify them is a division to bottom up and top down processes depending on if they are based on growing the structures from precursors or on modifying bulk structures, respectively. In this work, both approaches are utilized separately. Materials investigated in Publications I, II, III and IV are prepared using bottom-up growth processes, whereas the thermoelectric layer of the device in Publication V is prepared by a top-down exfoliation method.

3.1.1 Growth processes

During the latest decades, chemical vapor deposition (CVD) processes have become increasingly more important in electronics and photonics industries. In addition to shrinking device size, the couple-of-nm thin gate oxides of modern integrated circuits are often made possible only by a cyclic variant of CVD, atomic layer deposition (ALD), which can be used to grow amorphous or polycrystalline films of arbitrary thickness with excellent conformality and atomic layer level thickness control [80]. On the other hand, the widespread availability of light-emitting diodes and lasers, which typically rely on epitaxially grown III–V and III-N semiconductors, are fabricated either by molecular beam epitaxy (MBE) or metal-organic vapor
Materials and Methods

phase epitaxy (MOVPE) [81]. The overall demand for these techniques in the semiconductor industry have made them readily available for growing nanomaterials also for applications other than integrated circuits and light emitting diodes. The ALD and MOVPE processes have been depicted in Figure 3.1 a and b, respectively.

![Figure 3.1](image)

**Figure 3.1.** a Steps of the ALD cycle: introduction of the first precursor, purging, introduction of the second precursor, purging. b Structure of a typical horizontal-flow MOVPE reactor. The precursors are introduced from the left end of the reactor and the sample is placed on the heated platform presented in red.

The two processes have similarities in the sense that both use gaseous phase precursors, depend on chemical reactions at the substrate surface and require elevated reaction temperatures. A key difference, however, is that the MOVPE process uses continuous gas flows whereas the ALD process is based on half-reactions enabled by cyclic introduction of the precursor gases. As a result, the two processes are sensitive to completely different parameters. Since the precursors are not present in the ALD reaction chamber at the same time, the exact flow rates and their ratios are not critical, and the use of more reactive precursors is possible because particles forming in the gas-phase mixture do not constitute a similar concern [82]. On the downside, the ALD process is a lot slower compared to MOVPE.

In the ALD chamber, the precursor adsorbs on the substrate surface in a self-limiting manner, ideally resulting in a monolayer of deposited atoms. In practice, however, many precursors require more than one cycle to form a complete monolayer due to steric hindrances, i.e. the precursor molecules being a lot larger than the target element to be deposited, therefore blocking a part of the surface from other precursor molecules [83]. Prior to introducing the second precursor gas, the chamber is purged with a carrier gas (typically nitrogen) to clear out the reaction products and any unreacted remains of the first precursor gas. The second precursor then reacts with the substrate surface now covered with atoms from the first precursor until the chamber is purged again. This process constitutes an ALD cycle, the main controllable parameters of which include precursor and purging gas flows and cycle times and chamber pressure and temperature. The
Materials and Methods

Film thickness can be controlled by controlling the number of ALD cycles and the chamber temperature, which to some extent affects the growth rate. In addition, the type of precursors can be changed from cycle to cycle, which allows the growth of multilayer structures consisting of different materials.

In Publications II and III, ALD is used to grow transparent ZnO films. In Publication II, sandwiched ZrO$_2$ acts as a doping agent, while in Publication III aluminum doped ZnO (AZO) is grown on nanoporous template. The films are grown in a Beneq TFS-500 reactor using diethylzinc (DEZn) and H$_2$O, tetrakis(ethylmethylamino)zirconium (TEMAZ) and H$_2$O and trimethylaluminum (TMAl) and H$_2$O as the precursors for ZnO, ZrO$_2$, and Al$_2$O$_3$, respectively. The sandwiching approach in positioning the ZrO$_2$ dopant layers takes advantage of the inherent properties of the technique: the number and relative position of the dopant cycles can be accurately controlled.

MOVPE, on the other hand, is mainly used to grow epitaxial films. Contrary to ALD and cyclic introduction of precursor gases, in MOVPE, they are introduced simultaneously with a very precise control over each precursor flow rate separately. In Publications I and IV, MOVPE is exploited to grow III–V nanowires on both crystalline and plastic substrates. The nanowires are grown via the vapor-liquid-solid (VLS) growth method in a horizontal flow reactor. The VLS process consists of three primary steps: a catalyst particle deposited on the substrate that melts to form a droplet, and which then causes atoms to adsorb from the precursor vapor introduced to the reaction chamber. The vapor then reaches a supersaturation level at the droplet surface, driving the crystal nucleation at the droplet-substrate interface. This results in axial growth finally forming a nanowire [84]. In the context of III–V nanowires and this work, the precursor gases include TMAl, trimethylgallium (TMGa), trimethylindium (TMIn) and tertiarybuthylarsine (TBAs). As a result, GaAs, AlAs and their alloys as well as InAs can be grown.

Publication I presents core-shell nanowires with GaAs core and either AlAs or AlGaAs shell grown with self-assembled Au nanoparticles. The self-assembly is controlled by functionalizing the substrate using poly(diallyldimethylammonium chloride) (PDDAC), resulting in high catalyst nanoparticle areal densities, which again allow high nanowire areal densities up to ~8%. The growth of core-shell nanowires then consists of two consecutive VLS steps at different temperatures and under different precursor flows: the first step at lower temperature forms the GaAs core nanowire while the second step at higher temperature is used to grow either an AlAs or AlGaAs shell around the core.

Publication IV presents InAs nanowires directly grown on polyimide plastic. Contrary to a conventional MOVPE process exploiting the crystalline properties of the substrate in guiding the epitaxial growth, the
amorphous plastic results in nanowires growing in all directions. Instead of conventional Au catalyst particles deposited prior to the MOVPE step, the growth on plastic is combined with in situ deposited In droplets by flowing TMIn precursor into the chamber for an extended period of time prior to starting the growth step.

### 3.1.2 Liquid-phase exfoliated graphene

The rise of the field of two-dimensional (2D) materials has been rapid after the discovery of graphene by A. Geim and K.S. Novoselov in 2004, with entire material families including 2D transition metal dichalcogenides \([85]\) and MXenes \([86]\) established since. From the thermoelectrics perspective, many encouraging results on 2D materials have already been published in both simulation and experimental domains \([87, 88, 76]\), in addition to graphene including \(\text{MoS}_2\) \([89]\) and 2D black phosphorus \([90]\), but rather few practical application examples have been demonstrated so far.

The original Scotch tape method exploited in producing the single-layer graphene flakes was relatively soon complemented by both bottom-up and top-down methods aiming for increased controllability, efficiency and scalability in the fabrication process. Today, the most widely adopted examples of each category are CVD \([91, 92]\) and liquid-phase exfoliation (LPE) \([93]\), respectively. The CVD method can be exploited to produce continuous single-layer films of large area, but it suffers from the high cost of the catalytic substrate and in the case of certain material systems, high cost of starting materials. The LPE methods, on the other hand, are based on exfoliating the bulk forms of 2D materials immersed in a liquid by introducing cavitation and shear forces to the dispersion, which produce cracks in the graphite crystals allowing the peeling-off of graphene flakes \([94]\). Compared to the CVD method, the 2D material quality is lower and less controllable in terms of the lateral flake size and the number of layers, but other benefits arise: the batch size can be scaled, the process equipment and starting materials are relatively inexpensive, and the resulting 2D material dispersions can be processed into an ink form that is suited for deposition using standard industry techniques, such as gravure or silk screen printing. \([95]\)

In the present work, the graphene ink used to fabricate a thermal distribution sensor in Publication V is produced by ultrasonic-assisted liquid-phase exfoliation (UALPE), in which the layered bulk material dispersed in a liquid is exfoliated by the forces stemming from ultrasonic cavitation and the collapsing of thus generated bubbles. In this case, the bulk material is 100 mesh (corresponding to a sieve opening of 149 \(\mu\text{m}\)) graphite flakes, which are dispersed in isopropyl alcohol (IPA). In addition, polyvinylpyrrolidone (PVP) is introduced in the mixture to alter the surface energy of the exfoliated graphene flakes, thus stabilizing the dispersion \([96]\). Compared
to conventionally used solvents such as N-methyl-2-pyrrolidone (NMP), the use of IPA is benefited from its non-toxicity as well as low boiling point and viscosity directly suitable for a range of deposition methods such as spray coating or inkjet printing, therefore eliminating the need for solvent change after the LPE process. UALPE can be operated either using a bath or a probe ultrasonic. In all fabrication routes relying on LPE methods, a crucial step in arriving at stable and uniform 2D material dispersions is the separation of non-exfoliated bulk species after the LPE step. Most commonly, this is achieved by centrifugation of the dispersion. The centrifugation allows controlling the lateral flake size and number of layers by adjusting the centrifugal force and centrifugation time to separate flakes with mass larger than a certain threshold into the sediment, after which the supernatant dispersion is collected for further use. Additionally, sophisticated centrifugation sequences utilizing multiple substeps and collecting either the supernatant or sediment aiming at picking flakes of certain morphology exist [97].

The UALPE process discussed above results in up to $\sim 1 \text{ mg mL}^{-1}$ concentration [98] multilayer graphene dispersions, which have rheological properties suitable for direct spray-coating or inkjet printing. Moreover, as witnessed in a previous study, the films produced this way show promising thermoelectric performance when compared to the low material cost, simplicity and process scalability [98]. The films are further merited by their extreme flexibility, which in conjunction with flexible plastic substrates allows their use in a variety of different applications. The results in Publication V show one possible large-area application exploiting these properties of the solution-processed graphene material.

3.2 Thermoelectric and thermal characterization

3.2.1 Measuring the power factor

As discussed in the first section, the thermoelectric power factor is the product of electrical conductivity and the Seebeck coefficient squared. Both can be obtained via essentially electrical measurements and the measurements can therefore be easily combined in the same setup. We use a commercial setup (Linseis LSR-3) with access to a temperature range from room temperature to 450 °C and the option to use He and forming gas atmospheres instead of air. The system utilizes an off-axis configuration, comprising end electrodes of which the bottom one doubles as a heater to produce a suitable temperature gradient for the Seebeck coefficient measurement, and two perpendicular Pt thermocouples contacting the middle part of the sample, both measuring the imposed temperature gradient as
well as acting as the electrodes for voltage measurement in the four-wire configuration.

A typical measurement in a single temperature point is performed by applying five different temperature gradients in the range 5–30 K over the sample and measuring the corresponding thermovoltages in a four-wire configuration, while subsequently recording the actual temperature gradients using Pt thermocouples. The relative effect of the Pt thermocouples on the thermovoltage is compensated in the resulting data, after which any error in the offset voltage of each measurement is excluded by obtaining the Seebeck coefficient as the slope of a linear regression fit to the recorded thermovoltage data as a function of the temperature gradient. The electrical conductivity is obtained by measuring the current-voltage characteristics using the same configuration when the sample dimensions are known. In a typical measurement, this process is repeated at multiple different temperatures to obtain the temperature-dependent behaviour. A standard atmosphere is He, which as an inert gas inhibits sample oxidation otherwise easily taking place at higher temperatures. A schematic of the measurement configuration is presented in Figure 3.2 a.

![Figure 3.2. Schematic representations of the samples and the measurement methods.](image)

**Figure 3.2.** Schematic representations of the samples and the measurement methods. **a** Seebeck coefficient and electrical conductivity measurement in the off-axis four point geometry. **b** Transient thermoreflectance measurement. The inset shows the transient signal along with a corresponding fit.

### 3.2.2 Measuring the thermal conductivity

Measuring the thermal properties of nanoscale structures is notoriously difficult due to short characteristic lengths, which leads to fast heat dissipation and restricted temperature gradients as well as difficulty of accurately defining the temperature. Three main types of characterization methods exist; microfabricated devices suitable for measuring individual nanoscale objects such as nanowires [99] or 2D material flakes [100], the 3ω method [101] that utilizes heat dissipation from a thin wire and alternat-
ing currents at distinct frequencies, as well as optical methods, which can be further divided into pump-probe thermoreflectance methods [102, 103], transient thermal grating technique [104] and Raman thermometry [105].

The pump-probe thermoreflectance methods have gained rather widespread use in the characterization of thin films despite the instrumentation remaining somewhat complex. Compared to alternative thermal conductivity characterization approaches mentioned above, the apparent benefit of the thermoreflectance methods lies in the straightforward sample fabrication: if the sample surface is reflective, the only preparation step required is the deposition of a transducer layer, which is typically a thin metal film. The transducer film material and thickness are selected so that the thermoreflectance coefficient defined as \((\Delta R/R)K^{-1}\) is as high as possible at the probe wavelength [106]. At the same time, the thickness of the transducer should be great enough to not transmit any of the incoming laser radiation to the films below, as this could result in an additional reflection interfering with the measurement.

In the works included in this thesis, we utilize a commercial nanosecond transient thermoreflectance (ns-TTR) setup (Linseis TF-LFA). The technique uses a Nd:YAG nanosecond pulsed pump laser operating at 1064 nm for heating up the sample surface and a continuous-wave diode laser at 473 nm for probing the temperature-dependent change in sample reflectivity. The samples are prepared for the measurement by evaporating a layer of 20 nm/200 nm Ti/Au which acts as the transducer. Au is selected due to its high thermoreflectance coefficient \((\sim 2.5 \times 10^{-4} K^{-1})\) at the probe laser wavelength. The measurement principle is illustrated in Figure 3.2 b.

The thermal conductivity of the sample is extracted from the measured temperature excursion data by fitting a transmission line model containing the thermal properties of each layer in the sample [108, 109, 110] when the thermal properties of the rest of the layers are known. In the model, the surface temperature of the transducer is expressed in the Laplace domain as

\[
T(s) = \frac{Q(s) C_{11}}{e_1 s C_{21}},
\]

where \(Q(s)\) denotes the Laplace transform of the nanosecond pump laser pulse represented as a Gaussian function, \(e_1\) is the thermal effusivity \(\sqrt{C_v i \kappa_i}\), and \(C_{11}\) and \(C_{21}\) are elements of matrix \(C = M_i R_i \ldots M_1 R_1 \cdot B\), in which the matrices

\[
M_i = \begin{bmatrix}
\sinh(\eta_i \sqrt{s}) & \cosh(\eta_i \sqrt{s}) \\
e_i e_{i-1}^{-1} \cosh(\eta_i \sqrt{s}) & e_i e_{i-1}^{-1} \sinh(\eta_i \sqrt{s})
\end{bmatrix}
\]

and

\[
R_i = \begin{bmatrix}
0 & 1 \\
1 & R_i e_i \sqrt{s}
\end{bmatrix}
\]
Materials and Methods

represent the $i$th layer and the interface between the $i$th and $i+1$th layers with interfacial thermal resistance $R_i$, respectively. $B$ represents the semi-infinite boundary condition at the rear surface of the stack and $\eta_i = d_i e_i \kappa_i^{-1}$ denotes the temperature resistance normal to the layer. Given that values for the thickness $d$, thermal conductivity $\kappa$ and isochoric heat capacity $C_v$ are known, the time domain surface temperature is obtained from Eq. 3.1 by the inverse Laplace transform using the Stehfest numerical method [109]. The thermal conductivity of the sample layer is finally obtained by fitting the above calculated signal to the measured one. The goodness of fit is evaluated from the mean squared error which is minimized using the thermal conductivity values obtained from a genetic algorithm [110]. Typically, we measure 50–100 transients per a single measurement point and conduct the analysis procedure on the resulting average signal.

Depending on the sample layer material and structural properties, the thickness $d$ for samples characterized in this work is obtained either via cross-cut scanning electron microscopy (SEM) imaging (Publication I) or spectroscopic ellipsometry (Publication II). The Ti/Au transducer layer thickness is typically obtained via stylus profilometry. The values for the volumetric heat capacity $C_v$ are obtained from the literature.
4. Results

This chapter covers the main findings of this thesis. Section 4.1 presents the results of the pump-probe thermoreflectance experiments conducted on the core-shell nanowires. Section 4.2 covers the work on atomic layer deposited ZnO thin films including the effects of zirconia doping and the effect of deposition on nanoporous alumina surfaces. Finally, Section 4.3 presents the results on flexible devices on plastic, including the thermoelectric and mechanical characterization of MOVPE nanowires directly grown on polyimide as well as thermal distribution sensing with spray-deposited multilayer graphene thin film sensor.

4.1 Thermal conductivity engineering of core-shell nanowires

As discussed in the previous sections, nanowires provide an interesting platform for studying both electronic and thermal phenomena at the nanoscale; the structural properties can be engineered in both vertical and radial dimensions, and heterostructures such as superlattices or shells can therefore be realized relatively easily. In recent years, core-shell structures have also been exploited in a range of applications including light emitting diodes [111] and photovoltaic devices [112]. The thermal properties of such devices heavily affect the ultimate performance and power consumption, emphasizing the need for understanding the effects brought by the shell structure. Interestingly, the altered thermal properties introduced by the shell might provide a route for improving the figure of merit in thermoelectric applications by decreasing the thermal conductivity without too much disturbance to the electronic transport.

The thermoelectrics society gained interest in nanowires after Hicks and Dresselhaus reported on the effects of quantum confinement altered density of states on the thermoelectric figure of merit [7, 8]. From the purely thermal properties perspective, plain nanowires manifest reduced thermal conductivity due to the reduced number of available phonon modes and increased phonon surface scattering due to the spatial confinement in
two dimensions. Engineering the nanowire into a heterostructure by introducing a shell layer of a different material provides an additional degree of freedom in engineering these properties. Indeed, several simulation works have observed altered thermal properties upon the introduction of a shell structure, which have been attributed to phonon mode localization arising from the mismatch in vibrational properties of the core and the shell [113, 114].

Accessing wave-like phonon transport requires a high interface quality with little interfacial mixing, as briefly discussed in Chapter 2. In experimental systems this can be attained by epitaxial growth techniques such as MOVPE presented in Section 3.1. In VLS growth, an epitaxial interface in the radial direction can be realized rather simply by tuning the growth temperature and precursor flows after the growth of the core nanowire, therefore resulting in excellent control over the structural properties of the heterostructure. In recent years, simulation works have been accompanied by experimental studies investigating the effect of the shell on the thermal properties of the core-shell nanowire, though relatively few works have been published. Amongst them, material combinations including Si/Ge [115, 116] and Bi/Te [117] have been investigated.

In Publication I, III–V semiconductor nanowires with GaAs cores and AlAs and AlGaAs shells were exploited as a platform for investigating the effects of varying the shell thickness and composition. Instead of the rather widely adopted micro bridge devices tailored for individual nanowires, the thermal diffusivity was measured from nanowire arrays using the ns-TTR technique introduced in the previous chapter. The approach is merited by the fact that each measurement provides an ensemble average of the nanowire array underlying the transducer film, reducing the effects of inconsistencies taking place during the VLS growth procedure. As presented in Figure 4.1a, the arrays were prepared for the measurement by embedding them in a spin-coated layer of spin-on glass (SOG), which results in the bulk part of the nanowire height getting covered by SOG. The resulting optically hazy composite surface was planarized via chemical-mechanical polishing (CMP) to increase the reflectivity. After washing the CMP residue from the sample surface, a subsequent Ti/Au (20/200 nm) transducer layer was deposited with a relatively high optical quality enabled by the CMP.

Since the nanowires are embedded in a composite, extracting the thermal conductivity value from the composite values requires the use of an effective medium model (EMM), according to which

\[ \kappa_{\text{composite}} = x\kappa_{\text{NW}} + (1-x)\kappa_{\text{SOG}}, \]  

where \( x \) denotes the packing density of nanowires, which is obtained from SEM micrographs acquired after the nanowire growth. The use of the EMM together with the transmission line model was validated through a finite-element method (FEM) simulation considering a single nanowire embedded.
in SOG, covering parameters including the areal packing density in the range 0.01–0.1, nanowire diameter in the range 50–100 nm and nanowire thermal conductivity in the range 1–10 W m\(^{-1}\) K\(^{-1}\). The results obtained from FEM are compared with the output of the transmission line model fed with the signal produced in FEM in Figure 4.1 b, showing excellent correspondence throughout the studied range. In addition, the effect of interfacial thermal resistance between the transducer and the composite layer as well as between the nanowire and the SOG were investigated without any remarkable effect detected, which is attributed to the very low thermal conductivity of the SOG.

![Figure 4.1. a Nanowire-SOG composite fabrication process flow.](image)

**Figure 4.1.** a Nanowire-SOG composite fabrication process flow. b Comparison of the effective thermal conductivity of the nanowire-SOG composite obtained from the FEM simulation and from the transmission line model fed with FEM results. Reproduced from Publication I. © 2019 the Authors.

The obtained thermal conductivity values for both pure GaAs nanowires and for those decorated with the epitaxial shell are presented in Figure 4.2. The growth of ∼55 nm GaAs nanowires resulted in a low areal density below 2.0 % which prohibited a reliable extraction of the thermal conductivity value from the composite measurement. On the other hand, this result implies that the nanowires possess a low thermal conductivity value of < 5 W m\(^{-1}\) K\(^{-1}\). For the thicker ∼100 nm diameter GaAs nanowires without the shell structure we obtain a thermal conductivity of 6.6 W m\(^{-1}\) K\(^{-1}\) calculated from an effective thermal conductivity of 0.8 W m\(^{-1}\) K\(^{-1}\) for the composite and implying a significant 78 % reduction from bulk GaAs thermal conductivity. While rather few results for the thermal conductivity of GaAs nanowires exist for comparison, those reported for ∼150 nm diameter nanowires by Soini et al. [118] fall rather close to our result in the range 8–36 W m\(^{-1}\) K\(^{-1}\). Further, Ghukasyan et al. [119] measured the thermal conductivity of both twinning superlattice and polytypic GaAs nanowires of ∼130 nm diameter using the 3ω method, finding thermal conductivities of 5.2 ± 1.0 W m\(^{-1}\) K\(^{-1}\) and 8.4 ± 1.6 W m\(^{-1}\) K\(^{-1}\), respectively. Moreover, a comparison to size-dependent thermal conductivity models by Holland [120] and Liang and Li [121] as well as results by Martin et al. [122] and Mingo [123] in Figure 4.2 a shows a relatively good agreement. The best
correspondence is obtained with the results by Martin et al. when the surface roughness parameter $\Delta$ is set to 6 Å. The validity of this choice of value is further supported by the transmission electron microscopy data presented in Figure 2d of Publication I, showing that the nanowire surfaces are smooth to a sub-nanometer level.

The effect of the introduction of an epitaxial AlAs shell at various thicknesses on the thinner 55 nm GaAs nanowires is presented in Figure 4.2b, showing a non-monotonous behaviour as a function of the shell thickness. We note that the thermal conductivity of bulk AlAs is almost twice the value of that for bulk GaAs (91 W m\(^{-1}\) K\(^{-1}\) vs 47 W m\(^{-1}\) K\(^{-1}\), respectively), which suggests that an AlAs shell on GaAs core should increase the thermal conductivity of the heterostructure compared to the value obtained for plain GaAs nanowires. Our findings therefore indicate that the addition of the shell results in heavily altered phonon transport properties. Moreover, the non-monotonous thickness dependence of thermal conductivity implies that there are competing mechanisms in play, but the quantitative determination of each contribution likely requires atomistic simulations complemented with temperature-dependent measurements as a part of future work.

A qualitatively similar minimum as a function of shell thickness has previously been observed in molecular dynamics simulation studies. Although limited to considerably smaller domain sizes due to computational capacity, a non-monotonous thermal conductivity as a function of shell thickness was observed for germanium nanowires with a Si shell [124]. Further, prior experimental studies have shown shell-induced thermal conductivity reductions in core-shell systems comprising Bi nanowires coated with Te shells [117], 10–20 nm Ge nanowires coated with Si shells [115] as well as Si nanowires coated with Ge shell [116].

---

**Figure 4.2.** a Obtained thermal conductivity values for uncoated GaAs nanowires along with diameter-dependent predictions from different size-dependent models [120, 121, 123, 122]. b Thermal conductivity values for GaAs-AlAs nanowires with varying shell thickness. The data point for an uncoated GaAs nanowire is from ref. [122]. Reproduced from Publication I. © 2019 the Authors.
Shell thickness-induced effects on the thermal properties of core-shell nanowires are expected to affect the efficiency, power demand and operational lifetime of various optoelectronic devices as briefly discussed above, therefore rendering the topic important for further investigation. In the future, the exhaustive balancing of the electronic, photonic and thermal properties of such devices is deemed crucial when aiming for the optimal device performance.

4.2 **Transparent thermoelectrics with atomic layer deposited zinc oxide**

Transparent thermoelectric materials have received interest in the recent years as a possible route to broaden the application space available for thermoelectric generators and sensors. High optical transparency allows integrating thermoelectric devices onto surfaces which cannot otherwise be covered by opaque devices, and on the other hand, inexpensive thin film sensor devices open up additional opportunities in applications such as large-area user interfaces and temperature distribution mapping. Typically, the appeal for ZnO as a thermoelectric material has concentrated on high-temperature applications where the maximum performance is obtained. Nevertheless, the recent activity on thin film thermoelectric materials has resulted also in growing attention towards its use in room-temperature applications, largely driven by aspects related to environmental friendliness, high abundance of constituting elements and feasible fabrication routes.

Atomic layer deposition of oxides has become increasingly more prevalent with commercial reactors compatible with industrial-level speed and quality. ALD of binary oxides can be carried out at low temperatures allowing the use of plastic substrates and using simple precursors, including the use of water as the oxidizing agent, therefore making the process inexpensive. [125] The method is also merited by the inherent conformality and uniformity of the resulting films, which enable deposition on varying surface topologies. From the materials research perspective, ALD has also additional benefits: deterministic control over the amount of cycles results in precise thickness control and on the other hand, it is possible to introduce dopant cycles with high level of control in terms of the elemental type, atomic concentration, and the structural composition relative to the host film.

Today, atomic layer deposition of ZnO is an established process with DEZn and water most commonly used as the precursors. As already discussed earlier on in this thesis, the typical dopants include group III elements Al and Ga which both prefer substitution in the Zn site, resulting in n-type doping. While the two offer relatively high improvement in
the thermoelectric performance, they have also been reported to suffer from certain issues, including low dopant solubility [126] and only single donated electron per atom due to the oxidation state $3^+$. To overcome these issues, a number of alternative dopants have been investigated in doping ALD-grown ZnO [62]. An interesting group of elements are the subgroup IV dopants, that could alleviate some of the issues by offering increased electronegativity difference relative to oxygen, therefore improving stability. Moreover, some of these elements come in the oxidation state $4^+$, therefore in theory capable of donating two electrons per atom when located on the Zn site [127]. The effect of Ti and Hf doping on the thermoelectric performance of ALD grown ZnO [128] showed that the introduction of Ti significantly increased the charge carrier concentration compared to the undoped ZnO film, whereas the effect of Hf was more moderate but led to improved thermal stability and overall highest power factor due to a low negative effect on the Seebeck coefficient.

In Publication II we investigate the effects of Zr doping on the thermoelectric performance of ALD grown ZnO. Zr is introduced using a DEMAZ precursor, the cycles of which are applied in a sandwich manner relative to DEZn cycles as illustrated in Figure 4.3 a. The approach has previously been shown to conserve the mobility of ZnO better than an even distribution of dopants in unannealed films [129]. In total three supercycles are applied on glass and silicon substrates, totaling 615 cycles and resulting in films of approximately 120–130 nm in thickness depending on the ratio of DEZn and DEMAZ cycles. The growth process is carried out at 150 °C, therefore positioned roughly in the middle of the ALD temperature window [130].

The resulting films are highly transparent and electrically conductive. Grazing incidence X-ray diffraction (GIXRD) investigation presented in Figure 4.3 b shows the characteristic peaks corresponding to the wurtzite structure of ZnO, which is expected based on previous results using similar growth parameters. Further, the spectra show that the preferred growth orientation shifts from (100) plane parallel to the substrate, typical to glass and silicon, to (002) orientation with increasing Zr content, therefore showing similar behaviour to what has previously been observed with both Al and Hf doping. [131, 129, 128]

The thermoelectric characterization was carried out by starting in the room temperature and then ramping up to 180 °C and back. The room temperature results for thermoelectric characterization presented in Figure 4.4 show that sandwiched insertion of Zr dopes the ZnO film, with the thermoelectric power factor maximised at 2 % nominal doping concentration. Interestingly, the electrical conductivity shows a decline at doping concentrations larger than 2 % as shown in Figure 4.4 b. This is attributed to the changes observed in the crystallinity of the films as characterized by GIXRD measurement shown in Figure 4.4. At 2 % nominal doping,
Results

the (100) peak does no longer dominate but instead the (002) peak shows the largest magnitude. In previous studies, the dopant-induced change in the preferred crystalline direction has been proposed to negatively affect the doping efficiency, therefore implying that the effective dopant concentration is self-limited [132].

As a result of the temperature cycling, the room-temperature Seebeck coefficient increased and electrical conductivity decreased in all films. While this behaviour is typical to atomic layer deposited ZnO films grown using water as the oxidising precursor [133], the magnitude of the change in Zr-sandwiched films seems to be highly dependent of the nominal dopant concentration, with the 2 % sample showing the least stable behaviour. The temperature cycling inflicted change is smaller for samples with larger doping concentration as shown in Figure 4 of Publication II, therefore suggesting that the introduction of a sufficient concentration of Zr improves the thermal stability of ZnO.

A comparison with ZnO films doped in a similar sandwiching manner with other subgroup IV elements Ti and Hf [128] shows that the properties...
of Zr-doped films more closely resemble those of Hf-doped than Ti-doped ones. This is observed both in terms of structural properties (Hf-doped ZnO shows the same shift to (002) orientation while Ti does not) and thermoelectric properties (reported room temperature Seebeck coefficients for Hf and Ti-doped samples were approximately $-100 \mu V K^{-1}$ and $-60 \mu V K^{-1}$, while electrical conductivities were $\sim 120 S cm^{-1}$ and $\sim 300 S cm^{-1}$ before the thermal treatment, respectively). In future studies contemplating for example co-doping approaches, Zr should therefore be evaluated as an alternative to Hf and other similar elements.

In addition to the thermoelectric properties, transparent thermoelectric devices have to show high optical performance to satisfy the criteria set by practical applications. Moreover, application domains such as windows, windscreen and user interfaces are typically constrained by the surface area available for the device, which sets additional limitations to the device performance along with the material properties.

In publication III we investigate the optical and thermoelectric properties of Al-doped ZnO grown on grass-like alumina (GLA) by atomic layer deposition. GLA is a highly transparent nanoporous coating, which shows antireflective properties due to the porous structure acting as a graded refractive index film [134]. In addition to its optical properties, the high effective surface area resulting from the porosity brings further benefits when additional coatings are applied on top of GLA. As discussed previously, ALD allows high conformality, which together with the extreme topography of grass-like alumina enables the growth of films that closely follow the underlying structure. Previously, the concept has been applied in preparing superhydrophobic coatings [135] as well as supercapacitor electrodes [136].

We explore the behaviour of AZO in conjunction with GLA by growing 3, 5 and 10 supercycles of Al:ZnO on both GLA coated and reference glass and Si substrates. Similarly to Publication II, the ALD growth is carried out at $150 ^\circ C$ with each supercycle consisting of 50 ZnO cycles and 1 alumina cycle, therefore resulting in a nominal doping percentage of approximately 2%. The film thicknesses for 3, 5 and 10 supercycles are $32.0 \pm 0.1$ nm, $62.7 \pm 1.8$ nm and $108.6 \pm 4.2$ nm, respectively, as determined by spectroscopic ellipsometry measurements from reference AZO films grown on Si. Figure 4.5 presents SEM micrographs of the resulting structures. The porosity of bare GLA is on the order of 200–300 nm, and the conformally grown AZO film of 109 nm thus fills the most of the pores. The thinner films, however, preserve the topography in higher fidelity. The AZO films grown on GLA show also other structural differences compared to films grown on glass based on GIXRD investigation, as presented in Figure 4.6 a. Whereas for films grown on glass the preferred orientation shifts from (002) orientation to (100) orientation parallel to the horizontal substrate with increasing thickness, the relative peak magnitudes stay almost the
same for all thicknesses for films grown on GLA, indicating that the GLA surface is a more stable growth platform compared to plain glass.

The performance of the films grown on GLA was further examined by thermoelectric and electronic measurements, as shown in Figures 4.6 b–f. A Hall measurement in the van der Pauw geometry showed that the charge carrier concentration and the Hall mobility of the thickest films resulting from 10 supercycles are highly similar, which is expected when complemented with the observation of the topography seen in the SEM micrograph. However, for the films resulting from 5 and 3 supercycles the properties start to deviate from those obtained for films grown on plain glass. The samples grown on GLA show a high carrier concentration of $\sim 2.4 \times 10^{20} \text{cm}^{-3}$ for the thinnest film, followed by a decreasing trend with increasing thickness.

This contrasts with the typical thickness-dependent behaviour observed for the reference samples, where the charge carrier concentration shows an increasing trend with increasing thickness. The large values observed
at low AZO thicknesses in the films grown on GLA are attributed to additional Al doping mediated by the GLA coating, the effect of which is therefore highlighted at lower AZO film thicknesses. In the case of the planar reference samples, the increasing charge carrier concentration as a function of film thickness is attributed to changes in crystallinity, which are observed in the GIXRD results. The thinnest films likely carry different strain compared to the thicker ones [137], which can affect the size of the band gap and therefore also charge carrier concentration.

The high charge carrier concentration emerging in the GLA-AZO films results in a high electrical conductivity in comparison to the reference AZO films, as presented in Figure 4.6 e. While the Seebeck coefficients of the GLA-AZO films are slightly lower than those of the reference films, again attributed to the large increase in charge carrier concentration, the simultaneous increase in electrical conductivity results in an overall positive effect to the power factor of the films with the highest improvement of \( \sim 80\% \) for the thinnest AZO film.

Figure 4.7. a Photograph comparing the optical transparency of borosilicate glass coated with AZO (left) or GLA-AZO (right). b Transmission spectra for all films. Reproduced from Publication III. © 2023 AIP Publishing.

The deposition of a high-refractive index AZO film on the optically nearly ideal GLA coating weakens the ultimate transmittance of the GLA film, but the extent of this change remains small enough so that a substantial improvement compared to the reference AZO films is achieved. The thinnest AZO films preserve the topography of the GLA structure well enough for part of the antireflective behaviour to remain, and as a result, the GLA AZO films appear more transparent compared to the reference AZO films as shown in the photograph of Figure 4.7 a. The difference was quantified via spectral transmittance measurements for all samples, showing that the antireflective behaviour is mitigated with increasing AZO film thickness. In the visible range (400–700 nm), the thinnest AZO-coated GLA sample resulting from three supercycles shows the highest average transmittance of 86.9\% whereas the reference sample of the same thickness remains at
The GLA coating therefore enables AZO films with improved optical properties even if the ultimate performance of GLA (95.8% in the same range) is lost when the AZO film is applied. These results showcase the benefits and potential of grass-like alumina as a template for consecutive films, and in general using ALD in fabricating ZnO films for thermoelectric applications.

### 4.3 Flexible thermoelectric devices

The requirements for flexible thermoelectric devices were briefly visited in Section 2.3. In addition to flexibility, which is here defined as a material’s capacity to bend without its thermoelectric properties deteriorating, also other factors affecting the device fabrication and performance must be taken into account. In the case of thin film devices such as investigated in this work, the substrate plays a considerable role. Most often, flexible thin film devices employ a plastic substrate in a thickness range of 50 to 200 µm with typical material choices including polymers such as polyethylene terephthalate (PET) or polyimide, the first of which is merited by its low cost and the second by its excellent chemical and temperature resistance. These properties of polyimide, often also referred to as by the trade name Kapton®, are also exploited in preparing the thermoelectric films presented in Publications IV and V, both of which use materials requiring elevated processing temperatures at 400 °C and above.

#### 4.3.1 Nanowire network directly grown on plastic

The potential benefits provided by nanowire systems in managing the electronic and thermal properties were briefly discussed in Section 2.2. As shown in several experimental works, nanowires can offer drastic performance improvements over bulk materials in various domains [138, 139], but their prevalence in practical applications is still scarce. While this is affected by a multitude of factors, some of the difficulties explaining the low level of utilization arise already early on in the fabrication process flow; typically, the growth of nanowires requires substrates of matching crystalline properties, and in the case of III–V semiconductors, single-crystal wafers are extremely expensive compared to silicon. From the flexible applications perspective, the use of crystalline substrates in the growth step also requires an additional transfer step onto a flexible support structure, the yield and scalability of which can be low.

Integrating nanowires into device applications would therefore benefit from strategies targeting to simplify the above process steps or remove some of them altogether. III–V semiconductor nanowire growth on a variety of alternative substrates has been investigated previously, including
such materials as silicon [140], black silicon [141] and glass [142]. These substrate materials however provide only a partial alleviation to the problem and will not promote the integration into flexible applications, whereas direct growth onto plastic substrates could provide a straightforward route for industrially compatible processes such as roll-to-roll manufacturing. Most plastics, however, have a low glass-transition temperature and their use is therefore hindered due to the poor resistance against elevated temperatures encountered in a MOVPE reactor. InAs nanowire growth directly on plastics was recently demonstrated using flexible polyimide substrates [143]. The approach is based on exploiting the high maximum temperature withstood by the polyimide plastic and the rather low growth temperature below 500 °C for InAs nanowires enabled by TMIn and TBAs precursors. The resulting nanowires have a well defined crystalline structure despite of the amorphous growth substrate as evidenced by the typical InAs photoluminescence signal obtained in the report.

Publication IV investigates the possibility of building flexible thermoelectric devices based on InAs nanowires directly deposited on polyimide substrate. The growth process on plastic illustrated in Figure 4.8 a allows obtaining interconnected networks of InAs nanowires covering areas of multiple square centimeters, currently limited only by the lateral reactor area. The samples were grown on polyimide tape (Figure 4.8 b) attached onto glass pieces using the VLS method and in situ deposition of In catalyst particles, resulting in dark grey films as presented in Figure 4.8 c. A SEM investigation shows that the films consist of interconnected nanowires with a mean diameter of 543 nm. The height of the network is determined from crosscut SEM micrographs, showing an average height of 1.67 µm.

The films were prepared for the thermoelectric measurements by evaporating contact electrode layers comprising 20 nm Ti and 100 nm Au, respectively. A temperature-dependent thermoelectric measurement shows that the films possess a negative room-temperature Seebeck coefficient of \(-110 \ \mu V \ K^{-1}\), highlighting the n-type character obtained without deterministic introduction of any additional dopants. This behaviour most likely originates from carbon impurities associated with the TMIn precursor and is therefore intrinsic to the process [144]. The room temperature electrical conductivity is in the order of 41 S cm\(^{-1}\), resulting in a thermoelectric power factor of 50.4 \(\mu W \ m^{-1} K^{-2}\).

From the perspective of wearables and related applications, thermoelectric devices are required to show high flexibility in both tensile and compressive directions as well as stability to withstand repetitive bending. Mechanical properties and flexibility of the samples were investigated using a setup consisting of a motorized stage and I-V measurement for monitoring the resistance of the sample as a function of the stage movement. The sample is placed on the stage in a way that allows it to bend freely as illustrated in the inset of Figure 4.9 d, and the bending radius is calculated
I. In catalyst particle deposition
II. InAs nanowire growth

Figure 4.8. a Schematic of the process steps of nanowire growth on plastic. b, c Polyimide plastic before and after the nanowire growth. d SEM micrograph showing nanowires growing in random directions, forming an interconnected, electrically conductive network. Adapted from Publication IV. © 2021 the Authors.

for a circle approximating the curvature of the film as a function of the stage position [145]. The relative change in resistance for a single tensile bending cycle is presented in Figure 4.9 d. Interestingly, the film shows a slight negative change implying improved electrical conductivity likely induced by improved interconnections between neighboring nanowires. The long-term stability is investigated by repeating the same experiment multiple times as presented in Figure 4.9 e. At thousand repetitions, the relative change of resistance reaches 5% implying a slight degradation of the film at the relaxed state. The network-like structure of the InAs nanowire film therefore promotes excellent flexibility, in particular when accounting for the high brittleness of the bulk compound.

The direct growth on plastic technique was further exploited to demonstrate a proof-of-concept thermoelectric generator by applying a polyimide mask, thus defining nanowire-covered areas for the legs of the generator. After the removal of the mask, the empty areas were utilized for connecting the legs by conductive silver epoxy, resulting in a four-leg generator as presented in the photograph of Figure 4.9 f. The generator was tested near room temperature using temperature gradients of 3 K and 5 K corresponding to the typical range available in wearable applications. With a 5 K gradient, the proof-of-concept generator produced a maximum power of \( \sim 0.44 \text{ nW} \) at a voltage of \( \sim 1 \text{ mV} \), corresponding to a power density of 2.2 \( \mu \text{W} \text{ cm}^{-2} \).

The thermoelectric properties of individual InAs nanowires have been characterized rather extensively in the past, therefore providing an in-
Figure 4.9. InAs nanowire characterization results. **a** Seebeck coefficient **b** Resistivity and **c** Power factor as a function of temperature. **d** Relative change of resistance as a function of tensile bending. **e** Relative change of resistance accumulation over a thousand bend cycles. **f** Photograph of the proof-of-concept thermoelectric device. Reproduced from Publication IV. © 2021 the Authors.

The Seebeck coefficients obtained from n-type InAs nanowires fall in the range $-220$ to $-125 \mu V K^{-1}$, while the electrical conductivity values range from $90 \ S \ cm^{-1}$ to $580 \ S \ cm^{-1}$ [146, 147, 148, 149]. The Seebeck coefficient obtained in the present work therefore aligns with the earlier results, but the electrical conductivity is lower compared to individual nanowires with the Seebeck coefficient in a similar range. This is attributed to the multiple interfaces between the adjacent nanowires in the network that presumably act as resistive elements. Despite this, the overall performance is in a comparable range, emphasizing the potential for future development.

Future avenues for the concept include the investigation of other III–V materials attainable using a similar process; InSb nanowires have been recognized as the best performing thermoelectric material amongst the III–V candidates [123]. In a related work, we have explored the growth of InSb on polyimide [150], but the mechanical properties are yet not good enough for truly flexible devices. Nevertheless, the possibility to grow also other III–V semiconductors in addition to InAs on polyimide gives promise for the fabrication of delicate structures, such as superlattice nanowires or core-shell structures.
4.3.2 Large-area graphene thermal distribution sensor

The first known practical application of the Seebeck effect, the thermocouple, has been widely adapted as a temperature sensor. Most thermocouples consist of two metal wires connected together on one end, and the technology has been considered mature without any significant alterations appearing recently. The use of thin films instead of wires provides interesting routes for extending the concept, as demonstrated by Ruoho et al. [151] by connecting multiple metal leads onto specific positions of a ZnO thin film to measure thermovoltages from multiple points simultaneously, therefore creating a so-called distributed thermocouple. The distributed thermocouple concept could be used as an inexpensive alternative for measuring temperatures and temperature distributions from a large surface area, potentially replacing more complex solutions in certain applications, such as food safety [152], environmental monitoring [153] or wearable devices [154].

In Publication V the concept of a distributed thermocouple is exploited by using a spray-deposited multilayer graphene thin film as the thermoelectric layer. The use of graphene as an active material is supported by its high mechanical flexibility and durability [155] as well as low price. Moreover, the ink-based form is merited by a range of additional features: it can be scalably produced from graphite by top-down routes using liquid exfoliation directly in the final solvent together with a polymer stabilizer, and the rheological properties of the ink can be adjusted to suit several deposition methods, ranging from spray coating and inkjet printing to large-scale manufacturing techniques such as gravure printing.

The device is fabricated by spray-depositing 45 mL of graphene-containing ink on 6 cm by 6 cm Kapton polyimide substrate. After the deposition, the resulting thin film is annealed at 375 °C to decompose the dielectric PVP stabilizer, improving the electrical conductivity and establishing the p-type thermoelectric character of the film [98]. After the annealing of the film, the rest of the device is fabricated by depositing two different layers by e-beam evaporation: first, a dielectric spacer layer insulating the thermoelectric layer from the contact leads, and then the contact lead layer. 250 nm thick aluminum oxide and 30/250 nm Ti/Au thin films are used for each layer with separate shadow masks to define the patterns, respectively.

The performance of the thermal distribution sensor is first tested at the single pixel level and then using multiple pixels on the whole sensor area. The first category includes obtaining information on the response time as well as the response linearity to inputs at different temperatures. Figure 4.10 shows the signals resulting from the two experiments: the signal reaches \( \sim 45 \, \mu \text{V} \) after a 2 s long finger tap in 150 ms and decays at approximately 15 s.
Two example applications are demonstrated for showcasing the sensitivity and spatial resolution in thermal distribution sensing. The sensor can be attached onto curved surfaces, as presented in Figure 4.10 b, which allows, for example, monitoring the temperature distributions in pipes and cylindrical containers. On the other hand, simple shape recognition of heated objects is made possible by using natural neighbor interpolation between the analog signals obtained from the electrodes in presenting the temperature distributions, as demonstrated in Figure 4.11 with heated objects placed on top of the sensing area. The absolute temperature seen by each pixel is obtained by calculating the temperature difference between the pixel and the reference ground using the Seebeck coefficient value obtained for a reference film of a similar thickness and summing it to the known temperature of the reference ground as $T_{\text{pixel}} = V_{\text{pixel}}/S_{\text{film}} + T_{\text{ref}}$. As a part of future development, the temperature resolution should be investigated in order to calibrate the sensitivity of the device.

The potential practical applications for the thermoelectric thermal distribution sensing technology are ample especially if the manufacturing cost of such devices could be brought to a reasonably low level. A plethora of applications exist in which a conventional single-point thermal sensor can produce only a fraction of the useful information that could be obtained using an area-monitoring sensor, and at the same time, architectures such as presented here benefit cost-wise from upscaling of size.
Results

Figure 4.11. **a** Sensor response to single 1 s long finger tap on the pixel. **b** Sensor response as a function of increasing heat source temperature. **c** Temperature distribution mapping with heated ceramic pieces (top row) placed on top of the sensor. Information obtained using an infrared camera (middle row) is compared to that obtained using the sensor (bottom row). Reproduced from Publication V. © 2020 the Authors.
5. Summary and Outlook

The recent years have witnessed an increasing amount of published results on thin film thermoelectrics, indicating both the availability of viable fabrication routes as well as use cases for thermoelectric energy harvesting especially taking advantage of low grade heat. At the same time, methods for fabricating nanostructures on large areas are becoming widely available, and the emergence of manufacturing methods such as roll-to-roll printing indicate that the cost of thin film sensors and similar devices will decrease drastically in the near future, further speeding up the practical applications of novel thermoelectric concepts.

In this thesis we presented results on the thermoelectric properties of nanostructured thin films and their application in thermoelectric devices, as well as results on engineering the thermal properties of semiconductor nanowire arrays. The presentation of the results was divided into three parts. The first part focused on the thermal properties of GaAs nanowires decorated with epitaxial shells. The second part presented results on transparent thermoelectric thin films based on atomic layer deposited ZnO on two instances, first by investigating the effect of Zr doping and then by demonstrating Al-doped ZnO films with improved power factor and transmittance based on the use of nanoporous growth platform. Finally, the third part presented proof-of-concept flexible thermoelectric devices utilizing nanostructured thin films.

The first part determined the thermal conductivity of GaAs nanowire arrays. Moreover, a substantial reduction in the thermal conductivity was observed in core-shell nanowire arrays with epitaxial AlAs shells. These nanowire arrays show a non-monotonous thermal conductivity as a function of the shell thickness, which might signal the presence of wave-like phonon transport at the core-shell interface.

In the second part, the properties of atomic layer deposition were exploited in two ways in conjunction of the ZnO growth. First, the effects of zirconia doping on the thermoelectric properties of atomic layer deposited ZnO films were examined with the observation that the power factor at room temperature was maximised at 2% nominal Zr content. Second,
grass-like alumina coatings were used as platforms for the ALD growth of Al-doped ZnO, which was found to grow conformally on the nanoporous template, therefore resulting in a substantial increase in the effective surface area of the ZnO layer. A comparison between the films on grass-like alumina and reference films grown on glass showed a significant increase in electrical conductivity, which was attributed to the increase in charge carrier concentration likely driven by additional Al doping induced by the grass-like alumina template. Additionally, the films partly inherited the antireflective behaviour manifested by the grass-like alumina coating, resulting in an improved transmittance in the visible range compared to the reference films.

The third part demonstrated two different thermoelectric devices based on two different nanostructured materials covering macroscopic areas. First, the thermoelectric properties of InAs nanowires grown directly on flexible plastic were characterized with a finding that the thermoelectric properties of InAs nanowire networks are in a comparable range to those obtained from individual nanowires, emphasizing the quality of the growth process. A proof-of-concept thermoelectric generator grown in a single MOVPE run was presented, demonstrating the first thermoelectric generator based on nanowires grown directly on plastic. In addition, the use of liquid-exfoliated multilayer graphene was demonstrated as an active layer of a large-area distributed thermocouple. The sensor was shown to be capable of detecting thermal inputs of various origins, while the fabrication process remains facile, inexpensive and scalable.

Until the recent world events that have heavily reshaped the global energy markets and demand, energy production based on the thermoelectric effect has been considered incompetent in terms of efficiency and cost. With the growing requirements for green energy and unpredictable energy pricing, the position of thermoelectrics-based solutions in the energy mix has potential to become favorable, when also considering the recent development with novel high-performing materials, such as SnSe. In a broader perspective, the results presented in this thesis facilitate the employment of functional nanostructured materials in practical thermoelectric applications, with the emphasis on sensing technologies and other related applications that have yet to gain foothold in commercial markets.
References


References


