UNIVERSITY OF LATVIA FACULTY OF PHYSICS, MATHEMATICS AND OPTOMETRY



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STUDY OF ELECTRICAL AND THERMOELECTRICAL PROPERTIES OF ORGANIC THIN FILMS WITH DIFFERENT MORPHOLOGY

SUMMARY OF DOCTORAL THESIS

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Abstract

This work is about the electrical and thermoelectric properties of organic materials. In recent decades, functional organic materials compete with and replace traditional inorganic semiconductors in solar cells and light emitting diodes, where organic materials are in an active part, such as organic light emitting diode displays on various portable devices and not only. Unfortunately, the relatively low electrical conductivity of organic materials hampers their use in the TEG, and therefore intensive studies are ongoing for the exploration and improvement of the charge carrier transport in organic materials.

The purpose of this work was to explore the effects of the morphology of low molecular weight materials on electrical and thermoelectrical properties, to create a thermoelectric device from systems with the best thermoelectric properties.

The impact of the structure of organic materials on electrical and thermoelectric properties was studied in the work. For the first time, the effects of the molecule structure of newly synthesised indandione fragment containing AZO molecules and molecular structure of tetrathiotetracene derivatives on thin film morphology, electrical and thermoelectric properties have been studied. The effects of certain spatial molecular groups on electrical properties and morphology were studied. The scanning electron microscopy was used to characterise the morphology of the organic layers. In order to characterise the charge carrier transport in the organic thin films, local trapping states of charge carriers were studied by space charge limited current methods, the mobility of the charge carriers and the electrical conductivity of the thin films were determined. Within the work, the equipment has been established for measuring and the study of charge carrier mobility by Time of Flight method and charge extraction by linearly increased voltage method. The equipment for Seebeck coefficient measurements was created for determination of thermoelectric properties. The facility for the determination of thermal conductivity by the 3ω method was created. The organic thin film doping with iodine was realised to improve the electrical conductivity of p-type organic semiconductor thin films, which also included the creation of new equipment for material thermal evaporation in the iodine atmosphere. The equipment for the simultaneous thermal evaporation of two substances in a vacuum was built to acquire n-type organic semiconductor thin films. As a part of the work, planar-type organic thin film TEG was made, and the working principle was demonstrated.

Keywords: thermoelectric effect, organic materials, thin films, TEG

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Introduction

Energy crisis and environmental pollution are one of the most pressing challenges of the 21^{st} century. Electric power generation is vital for our society due to the necessity of electric power for modern technologies. Renewable natural resources play an increasingly important role in electricity generation due to reducing fossil fuels. Thermoelectric generators (TEG) are devices that directly convert thermal energy into electricity. The source of thermal energy may be specially generated thermal energy and also heat surpluses in the production and other processes, so-called waste heat. It is estimated that 63% of all global energy consumption is wasted as the heat [2–4] and 20% are discarded as a low-level heat < 200 °C. It is about European energy consumption per year. Thus, the TEG tackles several problems at a time: use wasted thermal energy in producing electricity, reducing global warming and dealing with the energy crisis.

Motivation

Organic functional materials have so far successfully proven themselves in organic light emitting diodes and are widely applied in different displays for television sets, smart-phones and other portable devices. Also in solar panels, they give possibilities to build flexible solar panels with sufficiently high efficiency. Unfortunately, until now, the organic materials have not yet strengthened their positions in thermoelectricity, because high enough efficiency has not been achieved so far that the use of organic materials would be useful. For studied organic materials with a large Seebeck factor, the electric conductivity is small, conversely for polymers with high electrical conductivity, the Seebeck coefficient is small. The successful development of organic materials in other fields and the potential benefits of the TEG stimulate increasing amount of organic material studies in the field of thermoelectricity, focusing mainly on improving charge carrier transport.

Aim of the study

The aim of the work is to explore the effects of the morphology of low molecular weight materials on the electrical and thermoelectrical properties. Also, to create a thermoelectric device from the best systems.

The following working tasks were raised to achieve the objectives of the work:

- Study the effects of the structure of the molecule on the electrical properties of the thin films;
- Determine the effect of the morphology of tetrathiotetracene's thin films on

electrical and thermoelectrical properties. Change the morphology of thin films by changing sublimation parameters;

- Form and optimise tetrathiotetracene-based p- and n-type thin films;
- To build an organic material thermoelectric generator.

Author's contribution

The author of the work made all of the samples studied in work and had carried out all electrical and thermoelectrical measurements except spectroscopy. The author has independently made thin films with thermal evaporation in vacuum method and has improved deposition in the vacuum equipment at the Laboratory of Organic Materials in the Institute of Solid State Physics of the University of Latvia. Author has built new vacuum equipment for the co-deposition of two substances in a vacuum and the evaporation in the atmosphere of iodine vapour. The author has himself created samples with the spin-coating method. The author has taken optical and scanning electron microscope images of thin film samples and measured the thickness of the layers with the surface profiler. The author has independently carried out measurements of the charge carrier trap states, as well as measurements of characterisation of electrical and thermoelectrical properties. The author has established equipment for the determination of charge carrier mobility with Time of Flight method and charge extraction by linearly increased voltage method, the equipment for determination the Seebeck coefficient and together with colleague Janis Busenbergs created equipment for thermal conductivity determination by 3ω method.

The author has carried out the results and data processing and has independently carried out analysis and conclusions of the results obtained. The author has presented the results from work at local and international conferences.

Scientific novelty of the work

The effects of bulk tritiloxyethyl groups on electrical properties and morphology have established at work;

For the first time, electrical and thermal properties have studied for a range of tetrathiotetracene (TTT) derivatives.

Thermoelectric properties of thin films of TTT and its derivatives have studied, as well as the effect of doping with iodine on electrical and thermoelectrical properties and morphology.

Thin films of n-type conductivity of TTT and tetracyanoquinodimethane (TCNQ) have been established using the co-deposition in a vacuum, their thermoelectric properties and their morphology dependence on different TTT and TCNQ concentrations are described.

Literature review

2.1.Thermoelectric generator

Thermoelectric generators (TEG) consist of thermoelectric modules located between two heat exchangers. Each of the thermoelectric modules consists of several tens and even hundreds of thermocouples. They are electrically connected in a series and for thermal gradient parallel, directly transforming the thermal energy flowing through them into electric energy. The TEG has the following advantages:

- direct energy conversion compared with many internal combustion engines that convert heat to mechanical energy first and then turn mechanical energy into electricity via electric generator;
- there are no moving parts, working fluids, and there is no need for maintenance that results in additional costs;
- long lifetime;
- silent, no noise operation;
- there is no limited working position, the TEG may be used in different shape systems;
- there is no size effect: TEG can be used as micro-generators in limited room conditions or in large power plants produce kilowatts.

The size and scale of the thermoelectric generator can be changed within a wide range, and their potential application comes from low-power devices that require microwatts to more powerful devices where a wide transformation of thermal energy into electricity is needed, such as cars or power plants.

Despite the benefits listed previously, the low efficiency and high production costs are hampering the use of TEG in the household. Currently, the efficiency of thermoelectric materials and generators is within the range of 5 to 20%. In order to improve the efficiency of TEG, intensive research on thermoelectric materials has been carried out in recent decades with the aim of improving their efficiency and reducing costs, therefore, not only the properties of thermoelectric material, but also production facilities are actively studied.

2.2. Thermoelectric materials

The figure of merit ZT includes properties that are interdependent, such as thermal conductivity and electric conductivity, thereby limiting its improvement by changing them. All these properties depend on the concentration of the charge carriers in the material, and it is not possible to change one without altering other properties. The image 2.2.1a shows the dependence of the Seebeck coefficient, electrical conductivity, thermal conductivity, power factor, and figure of merit on the concentration of the charge carriers. The approach to improving properties for organic materials and inorganic materials varies dramatically. For inorganic materials, work is mostly carried out on methods of reducing lattice contribution in heat transfer by increasing the distribution of phonons. In turn, for organic materials the main work is related to the increase of the electrical conductivity and thermoelectric power factor PF [5]. Looking at studies for material classes of the last three years published in the scientific database ScienceDirect.com (see image 2.2.1b), the majority of investigations are devoted to thermoelectric studies with silicon (Si), mainly because of the potential for easy integration into Si electronics.



Figure 2.2.1: (a) Figure of merit ZT, power factor PF, electrical conductivity σ , Seebeck coeficient S and thermal conductivity κ dependence on concentration of charge carriers in the material. Image adapted from [6]. (b) The proportion of material studies in the ScienceDirect.com database of scientific articles in the last 3 years.

Organic materials attract more and more attention. Figure of merit ZT has been improved by the several orders of magnitude from 10^{-4} to approx 0.5 since active study of organic thermoelectric materials began.

2.2.1.Organic thermoelectric materials

Organic materials can be divided into low molecular weight compounds and high molecular weight compounds or polymers. The advantage of polymers are better transport of their charge carriers, which can occur in the same chain of molecules as well as between them. Part of benefits of organic materials are: low thermal conductivity [7, 8], availability [9], the possibility of modification of the properties by changing the structure of the molecule or by doping [9], low costs [10, 11], effective at low temperatures <200 °C.

An essential characteristic of organic materials is that their working temperature is relatively low - i.e. below 200 °C. In this temperature region, organic materials have already achieved the figure of merit ZT values of an inorganic material. For example, SnSe at high temperatures has ZT > 2.5, but

at low temperature it has ZT < 0.2, and it is similarly for others inorganic materials. [12] In 2013 published results of PEDOT thin films shows ZT = 0.42 [13].

It should be noted that in the work with organic materials mainly thin films are used. Cho with co-authors have published results on multi-layer structures using electro-conductive polymer polyaniline (PANI), graphene layers, carbon nanotubes and electroconductive polymer PEDOT: PSS. For such multilayer structures, achieving a very significant power factor of $PF = 2710 \,\mu W \, m^{-1} \, K^{-2}$ [14, 15].

The most widely studied organic materials with use in thermoelectric devices are electroconductive polymers [5, 16–21] and their composites with different inorganic nanoparticles, inorganic thermal electric materials and carbon nanotubes, graphene and fullerenes.

One of the polymers actively studied in thermoelectric use is PANI. [22–28]. Power factor achieved in PANI thin films is $31 \,\mu W \,m^{-1} \,K^{-2}$. The highest electrical conductivity and thermoelectric power factor of composite material of PANI and carbon nanotubes have been demonstrated by Erden with co-authors: electrical conductivity of 2730 S cm⁻¹ and power factor of 114.5 $\mu W \,m^{-1} \,K^{-2}$.

The power factor of pure P3HT thin films has reached $3.9 \,\mu W \,m^{-1} \,K^{-2}$ [29]. Much higher power factors of $13.6 \,\mu W \,m^{-1} \,K^{-2}$ [29] have been achieved by doping P3HT films or creating composites with other polymers or nanoparticles, such as Bi_2Te_3 or with carbon nantotubes (95 $\mu W \,m^{-1} \,K^{-2}$) [30].

A large part of the charge transfer complexes studied are made of tetrathiophene (TTF) derivatives. Experimental TTF-TCNQ crystals have achieved electric conductivity of 300 to $500 \, \mathrm{S \, cm^{-1}}$ and Seebeck coefficient around $-28 \, \mu V \, K^{-1}$ [31–34].

Tetrathiotetracene

1D structures have high potential in the field of thermoelectric power because they exhibit significant thermoelectric properties [35–37]. Tetrathiotetracene (TTT) molecules tend to form 1D crystals. Theoretical calculations show that promising thermoelectric materials can be based on TTT derivatives [38–40]. For example, the value of the figure of merit ZT to 4 is predicted for TTT iodides, which significantly exceed the inorganic materials that have been achieved so far [41]. Although TTT and its iodides have p-type conductivity, it is possible to obtain n-type conductivity materials from TTT by doping with tetracyanoquinodimethane (TCNQ). The theoretical calculations for such materials predicts ZT to around 1 [40].

F. Huewe with co-authors has published data for 1D monocrystals. P-type crystals were grown from tetrathiotetracene (TTT) iodide and n-type crystals from DCNQI2Cu achieving electric conductivity accordingly 2.1×10^5 S cm⁻¹ and 10^5 S cm⁻¹ simultaneously showing the Seebeck coefficient $42 \,\mu V \, K^{-1}$ and

 $-34 \,\mu\text{V}\,\text{K}^{-1}$ [42]. Calculated power factors *PF* from obtained results are 387 and 110 $\mu\text{W}\,\text{m}^{-1}\,\text{K}^{-2}$, and figure of merit *ZT* accordingly 0.03 and 0.02.

Needle-shaped crystals are fragile, and their growing and processing are difficult. This complicates their applications in practical thermoelectric devices, therefore studies have been made where compressed tablets are obtained from such 1D materials. However, in such a solution, the conductivity of the material decreases in orders of magnitudes [43], mainly due to the grain or crystalline boundaries, which hampers the transport of charge carriers. Composites with conductive polymers are formed to reduce this effect. At the same time, the little-investigated alternative considered in this paper could be the formation of thin films with as monocrystalline morphology as possible, in which the 1D crystalline fragility could be overcome, and they could be formed on different form surfaces.

Experimental Part

3.1.Equipment and methods for the production and measurement of samples

3.1.1.Spin-coating method and equipment

Laurell 650 spin-coater is used in work. The device has a programmable control unit, which allows programming the required parameters - rotational speed, acceleration, rotational duration, etc.

3.1.2. Vacuum equipment for obtaining doped thin films

A new vacuum device was built to realise the co-deposition of the two substances and doping with iodine during sublimation. The set-up consists of a chamber in which two unrelated evaporation sources are located. A quartz crystal resonator is located above each of the sources on the side of the camera to measure the evaporation rate. Frequency meters *TTi TF960* are used to measure the frequency of a resonator. The supply of evaporation sources is provided using the *TTi QPX600DP* power source. Iodine vapour is fed through



Figure 3.1.1: Schematic representation of a vacuum equipment for obtaining doped thin films

the needle valve to the chamber, thus controlling iodine vapour pressure. The typical vapour pressure of saturated iodine is 4×10^{-5} mbar. Turbomolecular pump system *llmVac CDK280* is used to obtain a vacuum in the chamber. A liquid nitrogen trap is arranged in front of a turbomolecular pump to prevent unwanted iodine from entering the turbomolecular pump system. The apparatus is accompanied by a quadrupole mass spectrometer *AmetekDycor LC-D*.

3.1.3. Study of sample morphology

The profilometer is used for measuring the thickness of thin films and topography of the surface. Its operation is based on a needle that slips on the surface of the sample. Needle position is recorded in time. In this work, the profilometer *Vecco "Dektak 150"* was used to measure the thickness of the sample.

For the study of the morphology of the sample, a *Tescan Lyra SEM-FIB* microscope was used, which is equipped with a Schottky field cathode emission in combination with a gallium-ion beam (FIB) and a gas injection system.

3.1.4. Current-voltage characteristic measurement and determination of charge carrier transport traps

Current-voltage characteristics and activation energies were measured in a vacuum cryogenic system. The device's block diagram is shown in figure 3.1.2. The main components of the device are the cryostat, the electrometer *Keithley 6514*, the voltage source *Keithley 6487*, the temperature regulator *Scientific Instruments 9000*, the helium cryogenic system *APD Cryogenics HC-2*, and the computer. Vacuum in a cryostat is obtained with an *Ilmvac CDK250* turbomolecular pump. Measurements are made when the pressure in the cryostat is lower than 2×10^{-5} mbar, measured with the *Inficon TGC 401* pressure gauge. Sample temperature is controlled using programmable



Figure 3.1.2: Block diagram of equipment for electrical measurements

temperature regulator *Scientific Instruments 9000*. The voltage on the sample is applied with a programmable voltage source *Keithley 6487*. The sample current is measured by a programmable electrometer *Keithley 6514*. The sample for activation energy measurements was cooled in 15 K range between 295 and 280 K at the rate of 0.08 K s^{-1} and simultaneously measured current values. This procedure was repeated at different voltage values. The positive voltage

was applied to both ITO and Al electrode, thus attempting to determine appropriate hole and electron trap levels respectively. The activation energy values were calculated from the obtained data.

3.1.5. Equipment of charge carrier mobility measurements

The system for determining the mobility of the charge carriers by the Time of Flight (ToF) method (see figure 3.1.3) consists of a *Tektronix DPO 2012* oscilloscope, a double-shielded voltage source *Hivolt S series*, sample holder, nanosecond pulse laser *Explore NT340*. The sample holder was built



Figure 3.1.3: Shematic representation of apparatus for measurements of Time of *Flight method*

with a built-in block of resistances and a power amplifier. The power amplifier was built using the high-speed operational amplifier *Analog Devices AD8652*, powered by two AA-type batteries.

3.1.6.Equipment and method for Seebeck coefficient measurements

The Seebeck coefficient measuring system consists of a specially designed sample holder with two Peltier elements, voltmeter *Keithley 2182A* and a temperature controller *Standford Research Systems PTC10*.



Figure 3.1.4: Shematic representation of method for Seebeck coefficient measurements

The temperature controller *Standford Research Systems PTC10* is equipped with two Peltier control cards *PTC440 TEC* and one 4-channel K-type

thermocouple card *PTC330*. The Seebeck coefficient is measured in the plane of a thin film (see figure 3.1.4).

3.1.7. Apparatus for determination of electrical conductivity and 4 probe method

The electrical conductivity in the thin film plane was measured with the 4-probe method. The set-up consists of an electrometer *Keithley 6514*, a voltage source with built-in ammeters *Keithley 6487*. The voltage on the sample electrodes was supplied within the range of 0.1 to 100 V. The electrical conductivity was calculated by measuring the current-voltage curve and determining its slope coefficient.

3.1.8. Apparatus for determination of thermal conductivity

Measuring device for determining the thermal conductivity of a thin film with a 3ω method was created. The main components of the device are the vacuum cryostat, the signal generator *Tektronix AFG3021B*, the synchronous detector *Standford Research Systems SR830*, the multimeter *Keithley 2700*, the multimeter *Keithley SMU 2450*, the temperature controller *LakeShore 332* and Thomson Bridge.

3.1.9. Equipment for characterisation of thermoelectric generator

The same sample holder used to determine the Seebeck coefficient with two Peltier elements was used to characterise the thermoelectric generator. Peltier elements were controlled with the same temperature controller *Standford Research Systems PTC10*. TEG voltage and current values were measured with *Keithley SMU 2450*.

The TEG power curves for each of the elements and the two elements together were measured at different temperature gradients.

3.1.10. Equipment for the lithography work-flow

In this work, direct recording lithography equipment *Heidelberg Instruments* μPG 101 was used for the structuring of electrodes. The device uses a laser diode with 375 nm wavelength. It can hold up to 6×6 inches of substrates and create structures with 0.6 μ m dimensions.

3.2.Samples and their preparation methods

Thin films of organic materials were studied, which were obtained by two fundamentally different methods. The spin-coating method was used for the preparation of films from the solution of glass-forming organic low molecular weight compounds. Thermal evaporation in vacuum was used to prepare thin films from organic compounds which do not form qualitative amorphous films from the solution but form polycrystalline thin films.

3.2.1. Preparing the sample substrate

In this work, the *ISOLAB Laborgeräte GmbH "Economy Quality"* microscope slides that were cut in dimensions 25×25 mm or PGO CEC015S with indium tin oxide (ITO) coated glasses with sheet resistance $15 \Omega/sq$ were used as the substrates of thin films. Etching was used to obtain the necessary shape of the electrodes. The cleanliness of the surface of the substrate has a great influence on the formation of thin film morphology. The substrates were purified by successive purification in the ultrasonic bath for 15 min in chloroform, acetone, deionised water, and isopropanol.

3.2.2. Thin film coating methods

Samples from DMAAzi derivatives were obtained by using a spin-coating method from solutions in chloroform with concentration 80 mg ml^{-1} . The samples were spun with the acceleration of 300 rpm s^{-1} rotated with revolution speed of 300 rpm. After reaching the maximum speed, the sample was rotated for 5 min. During this time, every minute a 0.1 ml of the prepared solution was added to the sample. This technique allowed to obtain thicker layers, maintaining the uniformity of the sample thickness. Subsequently, the samples were dried at $80 \,^{\circ}$ C temperature for 20 min.

In this work, vacuum evaporation was carried out for DMAAzi, Alq₃, TTT and TTT derivatives samples. Electrodes from Al, Ag, Cu or Au were also obtained with a vacuum evaporation method. The rate of electrodes deposition was 5 Å s^{-1} .

3.2.3.Co-deposition



Figure 3.2.1: Schematic representation of co-deposition

To obtain n-type TTT thin films, they were doped with TCNQ. Crucibles with substances of TTT and TCNQ were placed into the evaporation sources 1 and 2. Both substances were simultaneously heated to their sublimation temperature. Two independent quartz crystal micro-balances measured sublimation rates of the substances. TTT: TCNQ layers of various compound mass ratios were obtained by changing the evaporation rates. A schematic representation is shown in the figure 3.2.1.

3.2.4. Doping of thin films with iodine

Two types of doping techniques were used to create p-type tetrathiotetracene and its derivatives: the doping of the film after the formation of a pure TTT layer and the simultaneously doping at the time of the coating, so-called reactive TTT sublimation in the iodine atmosphere. They are schematically depicted in the figure 3.2.2. For both of them a new equipments were built.



(a) Postdeposition doping
 (b) Reactive sublimation in the iodine atmosphere
 Figure 3.2.2: Shematic representation of TTT doping

3.2.5.Samples for determining the ionisation potential

The thin film of the investigated material was formed on the ITO glass substrate to determine the ionisation potential. The thickness of the thin layer of organic materials was in the range of 300 to 500 nm. This thickness is sufficient to avoid the influence of ITO electrode. Details of measuring the ionisation potential are described in the article by R.Grzibovskis [44].

3.2.6.Samples for determination of charge carrier transport trap states and charge carrier mobility

Sandwich-type samples in the configuration of the electrode/organic compound thin film/electrode were used to study the electrical properties. ITO was used as the bottom electrode, but the top electrode was made of Al or Cu. The thickness of the organic thin film was in the range of 0.55 to 1.75 μ m.

3.2.7.Samples for studying the effect of thin layer morphology on electrical properties

The samples for the determination of the electrical properties are designed so that one sample can be used to measure electrical properties in a plane with a 4-probe method, as well as to pick up a current-voltage characteristic curve and apply a space charge limited current method to characterise electrical properties perpendicular to the sample plane (See figure 3.2.3).



Figure 3.2.3: Samples design for studying the effect of thin layer morphology on electrical properties

3.2.8.Sample preparation for 3ω method

The 3ω method for measuring the thermal conductivity requires a specific shape electrode on the top of the thin film with a width of about twenty micrometres and a few millimetres length (see figure 3.2.4a).



Figure 3.2.4: (a) Schematic representation of the electrode for 3ω method, (b) Steps for making the electrode 1 - Glass substrate, 2 - Coating of photoresist AZ1518, 3 - Direct recording laser lithography, 4 - Development of photoresist AZ1518, 5 - Cu sublimation, 6 - Removing the remaining photoresist AZ1518, 7 - Glass substrate, 8 - Al sublimation, 9 - Coating of photoresist SU-8, 10 - Lithography with shadow mask, 11 - Development of the photoresist SU-8, 12-Al etching, removing SU-8 film from substrate 13 - Polycrystalline film sample, 14 - Cu sublimation through the prepared shadow mask, 15 - Sample ready for 3ω measurements

A special shadow mask with lithography process was created for the electrode deposition with thermal evaporation in vacuum method. A two-stage lithography process was used for making masks. In the first step, a luminaire shadow mask was created for the second lithography step. The figure 3.2.4b schematically shows the steps for making an 3ω electrode.

3.2.9.Samples for thermoelectric measurements

The samples were designed in such a way that it would be possible to measure conductivity in the plane by 4-probe technique and Seebeck coefficients in the same plane, as well as measure the thermal conductivity with the 3ω method

using the same sample.



Figure 3.2.5: Samples for thermoelectric measurements

3.2.10.Planar thin film thermoelectric generator, design and preparation

A design for a planar thin film TEG was developed to show the potential of the studied thermoelectric materials. It is made on a glass substrate and consists of p-type and n-type active elements. The p-type element is made of tetrathiotetracene iodide, while the n-type element is made of TCNQ:TTT. Electrodes are made of copper. For such a generator, the temperature gradient is applied to a thin film plane.

Selection of a fabrication sequence that avoids use of corrosive iodine in the presence of reactive electrodes and n-type material is vital. The optimal, four step, thin film TEG fabrication process is shown schematically in figure First, a p-type "leg" was fabricated in two steps-TTT thin film 3.2.6. deposition, followed by TTT doping via exposure to iodine vapour in the second step. The post-deposition doping approach was chosen, because it was more easily controlled in our current setup compared to reactive deposition. The measurement of the electrical conductivity during the doping process on an identical thickness sample placed in the doping chamber, obtained simultaneously with the TEG generator films, allowed to obtain an optimal doping concentration. As a post-deposition doping process was used, special care was taken to avoid/minimize film cracking. Third, TTT and TCNQ were co-deposited by thermal evaporation in vacuum. The TEG was completed by copper electrode deposition by thermal evaporation in vacuum.



Figure 3.2.6: *1* - deposition of TTT film, 2 - TTT doping with iodine, 3 - Co-deposition of TTT:TCNQ, 4 - Cu electrode deposition

Results and discussions

4.1. The influence of the molecular structure on the electrical properties of thin films

4.1.1.DMAAzi and its derivatives



(a) DMAAzi (b) DMAAzi-3Ph (c) DMAAzi-6Ph (d) DMAAzi-Si-6Ph Figure 4.1.1: Chemical structure of DMAAZi and its derivatives.

Compounds with an AZO and an indandione fragment containing group were chosen (see figure 4.1.1) to investigate the effect of the molecular structure on the thin film morphology and electrical properties. All compounds were synthesised at Riga Technical University, and synthesis procedure has been described elsewhere [45]. The molecule was modified by attaching different bulky groups that are not conjugated to chromophores. Absorption spectra in dichloromethane solution is shown in figure 4.1.2a. Data for DMAAzi-3Ph, DMAAzi-6Ph, DMAAzi-Si-6Ph are obtained from [46]. As can be seen from the absorption spectra of the thin films (see Fig. 4.1.2), bulky groups have little influence on the absorption spectra. This result implies that these groups have almost no impact on electronic transitions in the chromophore. Small red-shift (less than 8 nm) could be attributed to the bulky group influence on chromophore-solution interaction. It was not possible to measure the absorption spectrum of DMAAzi thin films due to the polycrystalline structure.



Figure 4.1.2: *a)* Extinction coefficient of DMAAzi derivatives in dichloromethane solution, *b)* Absorption coefficient of thin films of DMAAzi and its derivatives.

Thin-film morphology of DMAAzi and their derivatives

The thin films of the DMAAzi compound are polycrystalline, while the other three compounds form an amorphous structure. This is also confirmed by X-ray diffraction measurements (see Fig. 4.1.3a). It shows that bulk groups help to form an amorphous structure. Unfortunately, this structure is not always preserved for a long time. A thin film of a DMAAzi-Si-6Ph compound, where silicon has replaced carbon in the tritiloxyl group centre, begins to crystallise after time (see Fig. 4.1.3b). This property is due to triphenylsilyl groups, like those in DMAAzi-Si-6Ph, having less defined conformation than trityloxyethyl groups in DMAAzi-3Ph or DMAAzi-6Ph [47]. On one hand, it improves the formation of the amorphous films, but on the other hand, it reduces the glass transition temperature; thus the layer formed is less stable.



Figure 4.1.3: (a) X-ray diffraction pattern for DMAAzi and DMAAzi-6Ph thin films; (b) DMAAzi-Si-6Ph thin film surface image 2 months after sample preparation.

The electrical properties of thin films of DMAAzi and their derivatives

To identify charge carrier trapping states, the activation energy was measured with the temperature modulated space charge limited current (TM-SCLC) method. As can be seen in Fig.4.1.4, the model compound DMAAzi has a very large activation energy distribution for both polarities with deep levels at 0.90 eV. In the case of positive Al another level at 0.80 eV appears. The trapping time for $E_t = 0.90 \text{ eV}$ at a temperature of 300 K is a few minutes, and for $E_t = 0.80 \text{ eV}$ it is several seconds. Charge carrier trap concentration $N_t = 4 \times 10^{15} \text{ cm}^{-3}$ and $N_t = 6.5 \times 10^{15} \text{ cm}^{-3}$ was calculated for trap state levels at 0.90 eV and 0.80 eV, respectively. From the calculations of quantum chemistry, the volume of one molecule is determined to be 467.42 Å³. From this, the molecular density in the solid phase could be estimated - $2.14 \times 10^{21} \text{ cm}^{-3}$. This is much more than a predetermined number of traps, indicating that the state of the trap is made up of grain boundaries, where the grains are agglomerates of DMAAzi molecules.



Figure 4.1.4: Dependences of the activation energy on the applied electric field of (a) DMAAzi-Si-6Ph.

The activation energy measured at the positive polarity of ITO rapidly falls with increasing voltage for the samples that were prepared from solution (DMAAzi-3Ph, DMAAzi-6Ph and DMAAzi-Si-6Ph). It points to a narrower energy level distribution for electrons. An increase in the activation energy was observed at low voltages for positive polarity on the Al electrode, which indicates the interface effects when the contacts are not ohmic.

Charge carrier mobility of DMAAzi and their derivatives

Charge carrier mobility in thin films of DMAAzi-3Ph, DMAAzi-6Ph and DMAAzi-Si-6Ph were determined by the electrical ToF method. It was impossible to determine charge carrier mobility in pure DMAAzi, possibly due to the charge carrier local trapping states. Both types of charge carriers in equal numbers are generated when the sample is irradiated with a laser pulse. If we assume that the rapid decay of photocurrent is related to the charge carriers that are extracted through the electrode at which they are generated, then the integral of the decay roughly presents the number of the generated charge carriers. The integration of the signal obtained a charge of 1.1×10^{-10} C. It means that around 7×10^8 charge carriers were generated in each laser pulse. It is much smaller than the number of estimated charge carrier local trapping states in the DMAAzi sample. It means that almost all generated charge carriers are trapped. and no transient photocurrent can be observed. There were no such problems with the samples of glass forming compounds. It was possible to determine charge carrier mobilities of both types of carriers. Therefore the attached bulky group improved not only optical but also electrical properties. We observed photocurrent signals that were typical and valid for charge carrier mobility determination for all the amorphous samples. Electron and hole mobility values at various electric fields for DMAAzi-3Ph, DMAAzi-6Ph, and DMAAzi-Si-6Ph samples are shown in Fig. 4.1.5.

Hole transfer should occur between donor parts of the molecules, where bulky groups are attached. These groups assist the formation of thin films with





the amorphous structure, but at the same time, they shield the donor parts of the molecule. It becomes difficult to transfer holes between the molecules, leading to dispersed transport. It is clearly shown with DMAAzi-3Ph and DMAAzi-6Ph, where hole mobility in a thin film of the compound with one bulky group is higher than for the case of a compound with two bulky groups. The highest hole mobility was observed in the sample of DMAAzi-Si-6Ph and can be explained by the close packing. Bulky groups attached to the donor part of a molecule affect the electron transfer less. Nevertheless, it should be taken into account that molecules are randomly oriented in the amorphous structure, and bulky groups could be situated between molecule acceptor groups, thus influencing electron mobility as well. Electron transfer should occur between acceptor parts of chromophores. Acceptor parts are not directly shielded with bulky groups, so electron mobility is many times higher than hole mobility and and is similar for all the studied DMAAzi derivatives (see Fig. 4.1.5).

4.1.2. Tetrathiotetracene and its derivatives, procedure for selecting potential TE materials



(e) 2,8-diMeTTT (f) 2,8-iPrMeTTT (g) 2,8-MeOMeTTT (h) 2,8-diMeOTTT Figure 4.1.6: Chemical structure for TTT and its derivatives.

Thin films of tetrathiotetracene (TTT) derivatives were studied to understand how molecular structures can affect the thin-film morphology and electrical properties of thin films obtained by the thermal evaporation in vacuum method. TTT derivatives were synthesised at Nottingham University under Professor Simon Woodward's leadership. Synthesis of these connections is described in [48]. The compounds differ with various groups that are attached in positions 4 and 10 to the TTT molecule (See Fig.4.1.6).

Direct reaction of readily available tetracenes with elemental sulfur in DMF at reflux, in the manner of Perez-Alberne, afforded the tetrathiotetracene derivatives (see Fig. 4.1.6). Reaction yields are from 74 to 99% with purities of ca. 90%. The products were purified by heating them at 413K in reduce pressure of 10 Pa, which ensured their purity from 87 to 99%. Such easily prepared substances are ideal for initial thin film thermoelectric property screening as only tetrathiotetracenes sublimes during film deposition leading to enrichment to near pristine (<99%) material upon sublimation. A significant advantage of this 'direct precipitation' sublimation approach is that many more TTT derivatives can be prepared and screened per unit time compared to traditional approaches (where multiple purifications by either recrystallisation or sublimation are normally required) before measurement of the TTT thermoelectric properties. The post-sublimed dark green micro-crystalline material was confirmed to be >99% pure by H NMR, IR, MS and elemental analysis.

Thin films of TTT and its derivatives

Thin films of TTT and its derivatives were prepared using the thermal evaporation in vacuum method. All TTT derivatives were prepared at the same deposition rate of 45 ng cm⁻² s⁻¹ and substrate temperature of 300 K.



(e) 2,8-diMeTTT (f) 2,8-iPrMeTTT (g) 2,8-MeOMeTTT (h) 2,8-diMeOTTT Figure 4.1.7: Scanning electron microscope images of thin films of TTT and its derivatives.

As it can be seen in figure 4.1.7, all the thin films of TTT derivatives are polycrystalline. Three archetypical film morphologies were observed: blade-like morphologies (2-MeTTT, 2-PhTTT and 2,8-diMeOTTT), mossy-like behaviour (2-MeOTTT) and needle-like habits as exemplified by 2,8-diMeTTT and 2,8-iPrMeTTT. Since all samples were made at the same sublimation conditions, it can be seen that the addition of groups to the TTT molecule affects their growth morphology and the resulting thin film density. It is well characterized by the thickness of the films, since in all cases the amount of substance (20 ± 2) mg was used, while the thickness of the films varied considerably: from 0.53 to 2.89 µm.

Thermoelectric properties of thin films of TTT and derivatives

As could be anticipated from the different thin film morphology, the films also have very different electrical conductivity. It should be noted that, due to the peculiarities of thin layer thickness determination, electrical conductivity is calculated for a thin film rather than a material. The electrical conductivity in the material itself must be higher.

| Compound | Purity before sublimation [%] | Thickness of thin film d [µm] | Electrical conductivity $\sigma_{planar} [\mathrm{S} \mathrm{m}^{-1}]$ | Seebec coefficient $S [\mu V K^{-1}]$ |
|---------------|----------------------------------|--|---|---|
| TTT* | >99 | 1.40 | 2.37×10^{-3} | 1170 |
| TTT | 95 | 1.13 | 4.33×10^{-3} | 855 |
| 2-MeTTT | 96 | 0.56 | 3.76×10^{-2} | 464 |
| 2-MeOTTT | 87 | 2.89 | 1.34×10^{-2} | 374 |
| 2-PhTTT | 96 | 2.02 | 1.55×10^{-4} | - |
| 2,8-diMeTTT | 98 | 1.89 | 1.26×10^{-2} | 732 |
| 2,8-iPrMeTTT | 96 | 0.68 | 1.45×10^{-2} | 900 |
| 2,8-MeOMeTTT | 98 | 1.51 | 1.40×10^{-3} | 501 |
| 2,8-diMeoTTTT | 97 | 0.53 | 2.95×10^{-3} | 870 |

Table 4.1.1: Thermoelectric properties for thin films of TTT derivatives, TTT * - with gradient sublimation method prepurified TTT.

The highest Seebeck coefficient is for films made of pre-purified TTT. For these films, the electrical conductivity is almost twice as small as those obtained from not pre-purified TTT with the same deposition parameters: the deposition rate of 45 ng cm⁻² s⁻¹ and substrate temperature of 300 K. The thin films obtained from 2-PhTTT had the lowest conductivity from all of the studied TTT derivatives. It is likely that the reason for this is the degradation of the substance during thermal evaporation. Evidence for that is also the colour of this film; before the evaporation material was dark green, but the film was brown, although all the other TTT derivatives were dark green. Because of the low conductivity of the 2-PhTTT thin films, it was not possible to measure its Seebeck coefficient; therefore this material was not studied further.

The other thin films of TTT derivatives showed Seebeck coefficients in

wide ranges from 374 to 900 μ V K⁻¹. Although the purity of the raw material for thermal evaporation is not very high, its effect on the Seebeck coefficient and conductivity should be low. An experiment was carried out: 2-MeOTTT (material with the lowest purity) was evaporated under similar conditions as thin layer preparation and its purity increased from 87 to >99%. Also, XPS analysis does not indicate significant signs of aerial oxidation (0.05 to 0.3%) even after handling in air for several hours [48]. Although the remaining low concentration impurities influence the thermoelectric properties (increasing electrical conductivity and decreasing Seebeck coefficients), the dominant influence on the significant differences in Seebeck coefficients is mainly determined by changes in the structure of the molecules by adding the respective groups. Compound 2,8-iPrMeTTT shows the highest value of the Seebeck coefficient, and its electrical conductivity is the second highest of studied films. The 2-MeTTT thin films show higher conductivity, but their Seebeck coefficient values are one of the lowest (see the table 4.1.1).

4.2. The effect of thin film morphology on electrical properties *4.2.1.Different morphological tetrathiotetracene thin films*

Thin films of tetrathiotetracenes are polycrystalline, and their morphology has a great influence on the electrical and thermal properties of the film. Samples with different morphology were created to find out the effects of morphology on electrical properties. This was achieved by changing the deposition parameters of the film: the rate of deposition of the substance and the temperature of the substrate, as well as the substrate material. For these experiments, TTT purified with a gradient sublimation method was used to avoid the effects of impurities on the results. The effect of substrate type was compared using identical deposition conditions. The morphologies of the TTT films deposited on the three substrates types above at three different temperatures (350 K, 300 K and 222 K) are shown in Fig. 4.2.1. A characteristic basal layer of small TTT grains was initially deposited on thin films grown on bare and ITO covered glass. Above this basal layer, larger needle-shaped crystals grew. In the case of ITO, these needle-shape crystals were more pronounced. No base layers of smaller grains were seen for TTT films grown on bottom gold electrodes, needle-shaped crystals formed spontaneously. Fiedler et al. have shown that on gold (111) surfaces TTT lies flat (planar orientation) and forms ordered structures above 270 K [49]. As amorphous (evaporated) gold thin films are used in our experiments the initial orientation of crystals is not expected to be very pronounced.

As expected, temperature influences the size of the crystals on all types of substrates. In thin films deposited at low substrate temperature, the crystallites are smaller and consequently can pack more densely than those deposited at higher temperatures (Fig. 4.2.1). Further evidence for more dense



Figure 4.2.1: Scanning electron microscope images of TTT thin films on different substrates at different temperatures at deposition rate of $45 \text{ ng cm}^{-2} \text{ s}^{-1}$.

packing at a lower temperature is provided by thin film thickness. Films deposited at lower temperature substrates were thinner than those deposited at higher temperatures. On gold substrates using the same amount of TTT (20 mg) and evaporation rate ($45 \text{ ng cm}^{-2} \text{ s}^{-1}$) the thicknesses of obtained films at different temperatures were: $2.50 \,\mu\text{m}$ ($300 \,\text{K}$), $1.40 \,\mu\text{m}$ ($222 \,\text{K}$), $0.88 \,\mu\text{m}$ ($350 \,\text{K}$). At higher substrate temperatures different types of crystal packing occur which are substrate dependent. On gold, the TTT crystals show a wide angular distribution but are more vertically oriented, whereas those crystals on ITO and glass are oriented largely in the thin film plane (Fig. 4.2.1). Due to the different crystallite packaging one could expect different electrical properties of the TTT thin films.

Table 4.2.1: Electrical properties of the TTT thin films obtained at different substrate temperatures during sublimation. TTT deposited with rate of $45 \text{ ng cm}^{-2} \text{ s}^{-1}$ on glass for in plane measurement and on ITO for perpendicular to the plane measurement.

| Substrate temperature T_s during deposition | 350 K | 300 K | 222 K |
|--|----------------------------------|----------------------------------|----------------------------------|
| $\sigma_{planar}~{ m S}{ m m}^{-1}$ | $(2.67 \pm 0.21) \times 10^{-3}$ | $(2.37 \pm 0.21) \times 10^{-3}$ | $(1.75 \pm 0.21) \times 10^{-3}$ |
| $\sigma_{normal}~{ m S}{ m m}^{-1}$ | - | $(1.21 \pm 0.06) \times 10^{-5}$ | $(1.76 \pm 0.07) \times 10^{-5}$ |
| $\mu_{normal} \operatorname{cm}^2 \operatorname{V}^{-1} \operatorname{s}^{-1}$ | - | $(1.19 \pm 0.12) \times 10^{-3}$ | $(1.90 \pm 0.15) \times 10^{-3}$ |

The electrical properties measured under ambient laboratory conditions in the air at room temperature for a representative TTT film sample are summarised in Table 4.2.1. Charge carrier mobility and conductivity perpendicular to the plane for the sample prepared at a substrate temperature of 350 K could not be determined. The TTT crystal spacing was so large that attempted deposition of the top (Al) electrode leads only to short-circuiting through penetration to the basal electrode.

In the case of needle-shaped organic crystals, electrical conductivity measured longitudinally can be several orders of magnitude higher than transversal conductivity [38]. Hilti et al. reported that the anisotropy of conductivity in TTT₂I₃ crystals are between 100 and 1000 [50]. Our highest in-plane conductivity is for thin film, made at substrate temperatures of 350 K on the glass. Only in this case most of the crystals are placed with their long axis strongly orientated in the plane of the thin film, however not in one dominant direction (Fig. 4.2.1). Nevertheless, charge carriers moving laterally in such films could use easy pass along the crystals supported by carrier hopping from one crystal to another. At lower substrate temperatures in-plane conductivity decreases with the crystal size. The highest conductivity and charge carrier mobility perpendicular to the thin film plane is for the sample made at the lowest (222 K) substrate temperature where the crystals are the smallest with mixed orientations. It means that we cannot deconvolute the specific in-plane and perpendicular contributions to the electrical conductivity for the same sample. For anisotropic crystal reasons, an in-plane orientation of crystals is optimal for achieving high lateral conductivity. For the same samples, the conductivity perpendicular to the film plane is two orders of magnitude lower even though the charge carrier pathway through the crystal is short. Unfortunately, in these randomly oriented small crystals, the charge carrier mobility for such polycrystalline films is limited by the grain boundaries. In the case of closer packing, due to the smaller distance between them, the electron hopping and transport routes are smaller, closer and parallel to the surface.



Figure 4.2.2: *SEM images of the TTT thin films obtained at different evaporation rates on glass at* 300 K.

Evaporation rate also has an impact on the morphology of TTT thin films as shown in Fig. 4.2.2. The evaporation rate is determined by quartz crystal

Table 4.2.2: Density and electrical in-plane conductivity of TTT thin film obtained with different evaporation rates at substrate temperature 300 K on bare glass substrates.

| Deposition rate $[ng cm^{-2} s^{-1}]$ | Thin film density $[g cm^{-3}]$ | $\sigma_{planar} [\mathrm{S} \mathrm{m}^{-1}]$ |
|---------------------------------------|---------------------------------|--|
| 45 | 0.93 | $(2.37 \pm 0.21) \times 10^{-3}$ |
| 136 | 1.22 | $(6.04 \pm 0.21) \times 10^{-3}$ |
| 363 | 1.80 | $(7.03 \pm 0.21) \times 10^{-3}$ |

resonator frequency shift in time. As expected, films obtained at the lowest evaporation rate have more pronounced crystalline appearance. By increasing evaporation rate the size of crystallites in thin film decreases resulting in more dense packing. The in-plane conductivity and thin film density are summarized in Table 4.2.2. The highest in-plane conductivity $(7.03 \pm 0.21) \times 10^{-3}$ S m⁻¹ is for the sample with the highest density obtained at the evaporation rate of $363 \text{ ng cm}^{-2} \text{ s}^{-1}$ which is equivalent to 2.5 nm s^{-1} . In this case the obtained thin film is with the smallest crystallites with the closest inter-crystal distances.

The conductivity dependence on crystallite size in Table 4.2.2 is opposite to the temperature dependence studies of Table 4.2.1. Both low temperatures and high initial TTT surface coverage favour molecular nucleation and this leads to the growth of dense films. The packing density has the dominant role in the electrical conductivity over crystallite size and orientation.

4.3.Thin films with p-type conductivity *4.3.1.TTT thin films with p-type conductivity*

To increase the conductivity of the thin films, they were doped with iodine. Doping of TTT and its derivatives with iodine resulted in films with p-type conductivity. Both methods described in the 3.2.4 section were used.



Figure 4.3.1: Conductivity changes during TTT thin film exposure to iodine vapours. The insets show scanning electron microscopy (SEM) images of thin film morphology when the crack formation is observed.

During post-deposition doping processes the electrical conductivity was

monitored by four contact techniques. As seen in Figure 4.3.1, during exposure to saturated iodine vapour (at atmosphere pressure) the TTT electrical conductivity increased by four orders of magnitude reaching a maximum value within 1 h. Further iodine vapour exposure causes a reduction in TTT thin film conductivity for two reasons. First, the thin film performance is adversely affected by iodine overdoping at the surface, leading the conductivity to decrease bu one order of magnitude from 12.3 Sm^{-1} to 1.5 Sm^{-1} . Second, the absorption of excessive iodine initiates the start of crack formation within the film. After 1.6 h, a steep drop in electrical conductivity of more than three orders of magnitude takes place due to thin film disruption through massive crack formation (see Figure 4.3.1 insets and Figure 4.3.2).

Finally, if the overdoped film is exposed to the air, the electrical conductivity recovers almost one order of magnitude due to desorption of excessive iodine, as well as equalising the iodine concentration in the volume of the film, evenly diffusing it in a thin film volume.





Figure 4.3.2: SEM images of TTT iodide thin films. (a) Cracks in TTT thin film after over doped with iodine and (b) morphology of the TTT thin film made by reactive deposition of TTT and iodine.

For optimal electrical conductivity, cracking of TTT thin film during doping should be overcome or at least minimised. Iodine diffusion into the thin film is relatively slow therefore iodine (over) concentration gradient within a film depth easily develops. To avoid this, we applied short cycles of exposure to iodine vapour. The exposure time for each cycle was 1 min followed by 30 min of equilibration and iodine redistribution between the doping cycles. In the equilibration period, the iodine concentration in the thin film depth is evenly distributed, and overdoping is avoided thus reducing crack formation. By such postdeposition doping methods, thin films with conductivities up to $121 \, \mathrm{S \, m^{-1}}$ were obtained.

The iodine concentration gradient and slow diffusion in the sample are also confirmed by an experiment in which, after each doping cycle, Seebeck coefficients were measured in a thin film plane and perpendicular to the film (see Fig. 4.3.3). The Seebeck coefficient in thin film plane for pure TTT films is $1170 \,\mu V K^{-1}$ and by doping with iodine, electrical conductivity increases by several orders of magnitude, but the Seebeck coefficient is rapidly decreasing.

After one doping cycle, it is seen that the Seebeck coefficient is smaller in the thin films plane than perpendicular to the plane. In the next doping cycles, it is even more pronounced, for example, after the second doping cycle, the Seebeck coefficient is $41 \,\mu V \,K^{-1}$, but perpendicular to the plane $432 \,\mu V \,K^{-1}$. Immediately after the fourth doping cycle, the in-plane Seebeck coefficient is $33 \,\mu V \, K^{-1}$, but perpendicular to the plane $89 \,\mu V \, K^{-1}$. Meanwhile, measuring Seebeck coefficients in both directions for the sample 5 days after the 4th doping cycle, the two Seebeck coefficients are equalised: the in-plane Zebeck coefficient is $62 \,\mu V \,K^{-1}$, but perpendicular to the plane is $75 \,\mu V \,K^{-1}$. As can be seen, the electrical conductivity has increased from 53 S m^{-1} to 121 S m^{-1} . It is explained by the fact that by doping thin films in this way, the surface is overdoped, but the film is not doped enough at the base (see Fig. 4.3.3). By measuring Seebeck coefficient and electrical conductivity in the plane of the thin film, the redundant doped part and the undoped part are in parallel circuit, while by measuring Seebeck coefficients perpendicular to the plane, both parts are in a series circuit that produce more electrical potential than in the case of parallel circuit. As a result of slow iodine diffusion, after five days, it is evenly diffused over the entire sample, and the Seebeck coefficient is equalised in different directions.



Figure 4.3.3: Changes in Seebeck coefficients and electrical conductivity depending on the number of doping cycles and schematic representation of the iodine concentration gradient.

Although initial increases of iodine doping increase the electrical conductivity, the same sample's Seebeck coefficient value decreases from $1170 \,\mu V \, K^{-1}$ (at conductivity $0.02 \, S \, m^{-1}$) for pure thin film of TTT to $28 \,\mu V \, K^{-1}$ at a conductivity of $34 \, S \, m^{-1}$ (see Fig. 4.3.4). Further doping results in a massive recrystallization damage of the thin films. To avoid such crack formation by postdeposition doping of pure TTT thin films a new strategy was

attempted to produce a p-type TTT:I thin films by iodine doping during TTT film deposition. Through reactive deposition TTT and iodine ratio could be manipulated by changing iodine pressure in chamber during TTT sublimation. In Figure 4.3.2, the morphology of a TTT:I sample with conductivity of 160 S m^{-1} is shown. The crystallites obtained in reactive deposition of TTT and iodine are smaller compared to pure TTT crystals in thin films attained with the same evaporation speed $45 \text{ ng cm}^{-2} \text{ s}^{-1}$ and substrate temperature 300 K. The increase in iodine concentration gives a minimal improvement in electrical conductivity, which is limited by the grain boundaries. Because of the low



Figure 4.3.4: Dependence of the Seebeck coefficient and power factor on electrical conductivity of TTT iodide doped thin films for reactive deposited (hollow symbols) and postdeposition doped samples (filled symbols).

Seebeck coefficient, such films have a low power factor. The highest power factor for TTT:I was $0.52 \,\mu W \,m^{-1} \,K^{-2}$ at the electrical conductivity of $130 \,\mathrm{S} \,m^{-1}$ and the Seebeck coefficient of $63 \,\mu V \,K^{-1}$. At this point, exact stoichiometry between TTT and iodine is expected to be TTT_2I_3 , which, according to literature, has the best thermoelectric efficiency [41, 51]. The sample was made by reactive deposition but it is similar to samples made by post-deposition iodine TTT doping where $0.46 \,\mu W \,m^{-1} \,K^{-2}$ and $121 \,\mathrm{S} \,m^{-1}$, respectively, were realized. The obtained power factors are one order of magnitude lower than power factors for doped polythiophenes films reported by Glaudell et al. [52] but we need to mention, that our measurements were made in ambient conditions, while Glaudell et al. made measurements in inert conditions (nitrogen environment). Besides the conductivity of TTT:I thin films could be increased by the orientation of polycrystals.

4.3.2. Thin films with p-type conductivity based on TTT derivatives

Similarly, as thin films of the TTT, also thin films of TTT derivatives were doped with iodine by placing them in iodine vapour. Thermoelectric properties of doped films are shown in the table 4.3.1. The electrical

conductivity rises in all cases by factors ranging from 6 to >10³ times. The highest electrical conductivity improvement has the 2,8-MeOMeTTT thin films - 1607 times, reaching 2.25 S m⁻¹, but Seebeck coefficient has dropped 10 times to 48 μ V K⁻¹. The electrical conductivity of the 2,8-iPrMeTTT compound thin films has improved 483 times, reaching 7 S m⁻¹ and Seebeck coefficient 216 μ V K⁻¹. The relatively high Seebeck coefficient also provides the highest power factor 0.33 μ W m⁻¹ K⁻².

For the TTT the following single crystalline phases are known: TTTI (S/I = 4.00), $\text{TTT}_2\text{I}_{3+\delta}$ ($\delta \sim 0.1$ and S/I = 2.58) and $\text{TTTI}_{\sim 2.8}$ (S/I = 1.43). These show the highest reported single crystal electrical conductivities of: $7 \times 10^3 \,\text{Sm}^{-1}$, $10^5 \,\text{Sm}^{-1}$ and $8 \times 10^3 \,\text{Sm}^{-1}$ respectively [53]. X-Ray fluorescence studies of the films of Table 4.3.1 revealed that TTT, 2,8-iPrMeTTT and 2,8-diMeTT provided doping with $S/I = 2.89 \pm 0.04$ while 2-MeTTT, 2-MeOTTT, 2,8-MeOMeTTT and 2,8-diMeOTTT led to $S/I = 2.02 \pm 0.06$. The former corresponds to a stoichiometry of approximately 'TTT₃I_{4+ δ}' ($\delta \sim 0.1$ equivalent to TTT₂I_{3+ δ}, S/I = 2.93) and the latter to 'TTTI2'.

Table 4.3.1:Electrical properties of iodine doped thin films oftetrathiotetracenes.

| Commonwed | C/L motio | - [9 | -11 c [V V - 1] | DE[wWm=1K-2] |
|--------------|-----------|-------------------------|------------------|-----------------------|
| Compound | S/1 ratio | o _{planar} [Sm | Ισμνκ | $PF[\mu w m K -]$ |
| TTT | 2.86 | 0.952 | 25 | 5.95×10^{-4} |
| 2-MeTTT | 2.06 | 7.22 | 20 | 2.89×10^{-3} |
| 2-MeOTTT | 1.95 | 0.0830 | 17 | 2.52×10^{-5} |
| 2,8-diMeTTT | 2.85 | 0.442 | 85 | 3.20×10^{-3} |
| 2,8-iPrMeTTT | 2.92 | 7.00 | 216 | 3.27×10^{-1} |
| 2,8-MeOMeTTT | 2.08 | 2.25 | 48 | 5.27×10^{-3} |
| 2,8-diMeOTTT | 1.95 | 0.644 | 175 | 1.97×10^{-2} |

In the absence of unambiguous relations between Seebeck coefficient and doping concentration or sulfur/iodine ratio, it can be concluded that the large differences in Seebeck coefficients and electrical conductivity values result from the influence of the structure of the molecule rather than the difference in doping concentration.

4.4.Thin films with n-type conductivity *4.4.1.TTT thin films with n-type conductivity*

TTT and TCNQ reactive co-deposition produced thin films of n-type conductivity. Controlled thermal evaporation of TTT and TCNQ from two independent sources was used. Samples with several stoichiometries were prepared by changing the deposition mass ratio of TCNQ/TTT from 0.34 to 10.77 which corresponds to molar ratios of 0.58 to 18.6. The mass ratio was monitored with two quartz crystal microbalances, one for each compound. The TCNQ:TTT molar ratio has a great impact on the thin film morphology, the thin

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film conductivity, and the Seebeck coefficient (see Fig. 4.4.2). Higher TCNQ concentrations engender the formation of flake-like crystal morphologies, while in thin films with higher TTT concentration the crystallites are more needle-shaped (see Fig. 4.4.1).



Figure 4.4.1: Scanning electron microscope images for TCNQ: TTT thin films with different TCNQ: TTT molar ratios (determined from mass ratio): (a) 1.8, (b) 2.6, (c) 3.9 un (d) 18.6.

As was expected from theoretical calculations, the highest power factor is reached at TCNQ and TTT molar ratio ≈ 2 (see Fig. 4.4.2) [40]. In this case, the maximum power factor is $0.33 \,\mu W \,m^{-1} \,K^{-2}$, the electrical conductivity is $57 \,S \,m^{-1}$, and the Seebeck coefficient is $-75 \,\mu V \,K^{-1}$; however, the highest Seebeck coefficient of $-161 \,\mu V \,K^{-1}$ is obtained when the molar ratio is 3.9. Unfortunately, almost a one order drop in conductivity ($6.8 \,S \,m^{-1}$) takes place at this molar ratio, which results in reduced power factor value $0.18 \,\mu W \,m^{-1} \,K^{-2}$.



Figure 4.4.2: (a) Seebeck coefficient, electrical conductivity, and (b) power factor dependence on TCNQ and TTT molar ratio (estimated from mass ratio).

The obtained power factors are comparable with a majority of recently reported power factors for high performing solution processable n-type materials [54, 55]. As an exception, Shi et al. reported electrical conductivity, and thus the power factor of FBDPPV is two orders of magnitude higher [56]. However, those measurements are made in the inert nitrogen atmosphere while measurements in this work were made in ambient atmosphere. TTT:TCNQ films are stable and do not show degradation of thermoelectric performance in devices during several weeks.

4.5.Thermoelectric generator *4.5.1.Planar thin film thermoelectric electrode*

In order to demonstrate the potential of investigated materials in practical applications, a planar thermoelectric generator was created. The dimensions of the "legs" in this "proof of concept" device are 2 mm long (direction of ΔT) by 9 mm in width. The total "footprint" of the TEG module is 5 cm². The thickness of films or height of "legs" is minimal: 1.2 µm and 2.5 µm.



Figure 4.5.1: (a) TEG I–V curves and (b) output power of TEG.

It is necessary to balance both parts of the p and n-types as they are connected in series to realise efficient TEG. Since high electrical conductivity and a large Seebeck coefficient are not compatible, the golden mean with a maximum power factor must be found. The TEG p and n-type parts must have similar electrical conductivity so that the current generated in one part can pass through the second part. Seebeck coefficients by module must also be similar.

The conductivity of p-type leg is 88 S m^{-1} and of n-type leg is 12 S m^{-1} , while the Seebeck coefficients are $62 \,\mu\text{V}\,\text{K}^{-1}$ and $-118 \,\mu\text{V}\,\text{K}^{-1}$, respectively, this results in power factors of $0.33 \,\mu\text{W}\,\text{m}^{-1}\,\text{K}^{-2}$ and $0.16 \,\mu\text{W}\,\text{m}^{-1}\,\text{K}^{-2}$. The current-voltage characteristics of both the p- and n-type "legs" of the TEG are shown in Figure 4.5.1. A modest temperature gradient of $10 \,^{\circ}\text{C}$ was applied by Peltier elements under the TEG under near ambient conditions. The maximum power of our TEG module at a temperature gradient $10 \,^{\circ}\text{C}$ reaches 55 pW at 0.9 mV under near ambient conditions.

The fabricated TEGs are stable: power generation reduction after two weeks is less than 10%. It is estimated that a 10×10 cm array of TTT TEG modules would realise sufficient power for an "internet of things" sensor applications under near ambient conditions. The power of the organic TEG herein is mostly limited by the electrical conductivity of its thin films. Appropriate orientation of crystals could increase the conductivity of such films. The preferable orientation of the crystallites is along the direction of the temperature gradient because the conductivity of needle-shaped TTT crystals is anisotropic and aligned with this axis. Besides, grain boundaries, as well as orientation, are limiting to charge carrier transport. Dense packing and

orientation of crystallites parallel to thin film surface should minimise the electron hopping "barriers" and shorten charge transport routes.

Conclusions and thesis

5.1.Conclusions

Molecular structures have a major impact on the thin film morphology and electrical, thermoelectric properties. The fact that a closer or more compact packing of molecules provides better charge carrier transport in solids implements in crystals or ordered systems that cannot be created with simple thin film preparation methods. Thin films of low molecular weight compounds often are polycrystalline.

In the case of polycrystalline films, grain boundaries are prominent, which act as traps or barriers for charge carriers. They have a great influence on the electrical properties of the thin films, which is why it is critical to reduce or eliminate grain boundaries. Adding non-conjugated bulky groups to molecules helps to form amorphous films that may not display grain boundaries. Thin films of such compounds can be created using solution based methods that are their advantage. However, it should be taken into account that due to the bulky group, the charge carriers must overcome the greater distance from one molecule to another. The distance can be changed with the number of bulky group and their size. That could influence the mobility of the charge carriers.

Tetrathiotetracene (TTT) is known as a good thermoelectric material. Various TTT derivatives were used to improve the morphology of the thin film. In spite of the added groups, the only way to obtain the film was a thermal evaporation in vacuum, resulting in a polycrystalline film structure. It should be taken into account that the addition of large spatial groups made it difficult to obtain thin films of this compound, for example, TTT with added phenyl group decomposed in the sublimation process. Therefore, the main task is not to obtain an amorphous structure, but to reduce the impact of grain boundaries.

Besides, it should be taken into account that the purity of the film-forming substances influences the thin-film thermoelectrical properties. We have succeeded in implementing a procedure for identifying potentially most suitable TTT derivatives for the generation of thermoelectric devices using only a small amount of substances. During the process of forming thin films with a thermal evaporation vacuum method, sufficient thin film purity was obtained to observe the effect of substitution groups on thin film morphology and successive thermoelectric properties.

For the films obtained by the method of thermal evaporation in a vacuum, the morphology can be optimised by changing the preparation parameters for the thin film. As it was expected, thin films with smaller crystals were obtained by increasing the deposition rate of material or reducing the substrate temperature. These films have the highest electrical conductivity because the smaller crystals can pack denser. From this, it can be concluded that the grain boundaries have a greater effect on the electrical conductivity of the thin layer than the crystal size.

Despite the optimisation of morphology, the maximum thermoelectric efficiency is limited by the thermoelectric properties of the material itself. For further improvement, the doping of materials is required with which both p-type and n-type conductivity in thin films could be achieved. By doping TTT films with iodine, it is possible to obtain p-type films with high electrical conductivity. Two methods were used for doping: the thin film of TTT vapours, preparation in iodine so-called reactive deposition, and post-preparation doping of TTT films in iodine vapour. The second method has the advantage of measuring electrical conductivity during the doping process, which makes it possible to stop doping by achieving the desired electrical properties. The biggest disadvantage of the method is the cracking of the films in case of overdoping. The addition of TTT films to TCNQ molecules with the simultaneous thermal evaporation method of two substances makes it possible to obtain films with n-type conductivity.

The thermoelectric generator requires both p-type active and n-type active components that need to be matched so that the total power generated by both active components is greater than the power generated by each component. On the basis of previous experiments, thin films of n and p-type conductivity were prepared. P-type TTT iodide thin films with the thermoelectric power factor $PF = 0.52 \,\mu\text{W}\,\text{m}^{-1}\,\text{K}^{-2}$, the electrical conductivity $\sigma = 130 \,\text{S}\,\text{m}^{-1}$ and the Seebeck coefficient $S = 63 \,\mu\text{V}\,\text{K}^{-1}$ and n-type TCNQ: TTT films with a thermoelectric power factor $PF = 0.33 \,\mu\text{W}\,\text{m}^{-1}\,\text{K}^{-2}$, the electrical conductivity $\sigma = 57 \,\text{S}\,\text{m}^{-1}$ and the Seebeck coefficient $S = -75 \,\mu\text{V}\,\text{K}^{-1}$. TEG consists of 1 active element pair (1 p-type and 1 n-type element) and its power for one pair of active elements is $5.5 \,\text{pW}\,\text{K}^{-1}$ at ambient temperature. Consequently, the action of the planar-type TEG of organic thin films was demonstrated and its concept proved.

5.2.Thesis

- By adding unconjugated tritiloxyethyl or triphenylsilyl bulky groups to the indandione-containing compounds, mutual distance between important electronic parts of the molecules in solid state changes thereby affecting the energy levels of the molecules in solids and the electrical properties of thin films.
- The electrical conductivity of polycrystalline thin film of tetrathiotetracene is mainly determined by the density of the crystal packing, not its size. In thin films of TTT, it is possible to reduce the grain boundary effect on the electrical properties of the film, providing a denser crystal package with a smaller intergranular distance. It can be achieved by lowering the substrate temperature and increasing the rate of deposition of the substance.
- The best thermoelectric properties of doped polycrystalline tetrathiotetracene containing thin films are obtained at the same stoichiometries as for monocrystals.
- It is possible to create simple structures of thermoelectric generators from p-and n-type doped tetrathiotetracene films using thermal evaporation in vacuum technology.

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