The effects of processing conditions on crystallization of rr-P3HT for use in organic electronic devices.

Niclas Ledin
Abstract

Organic semiconductive polymers show great promise for use in solar cells or field effect transistors. However these polymers characteristics are highly dependent on their polymer chain stacking and ordering. In this thesis samples of conductive silicon have been spin coated with regioregular poly-3-hexylthiophene, P3HT, and nanostructured using nano imprint lithography, NIL.

The processing parameters were varied, using different concentrations, surface treatments and imprint pressures. The structural, optical and electrical properties have been examined using atomic force microscope, AFM, x-ray diffraction, XRD, absorbance spectrometry and a simple conductivity setup.

The samples were processed and their pattern quality differed for different concentrations of P3HT and for different surface treatments. The pattern filling seemed to increase with higher P3HT concentrations. Overall the pillar height ranged from roughly 10% minimum to a maximum of 30% compared to the master mold, while the pillar diameter were consistently of roughly 180% of the master mold.

The XRD shows a clear tendency for the imprinting pressure’s effect on the peak intensity. For untreated sample surfaces the peak intensities increase with pressure and for the HMDS treated sample surfaces the peak intensities decrease with pressure. In general the HMDS samples showed significantly higher peak intensities than the untreated samples.

The films of the 0.75% Si samples showed a significantly lower absorbance and of less characteristic form than the other samples, which may perhaps be attributed to the poor pattern filling. In general the 5bar samples show a slightly higher absorbance peak for the amorphous P3HT at around 450nm, while the shoulder peaks indicating crystalline P3HT were hard to compare due to an interfering peak of unknown origin at about 660nm. As the 5 bar samples had a higher amount of amorphous P3HT there is an indication that increased pressure gives a higher amount of crystalline P3HT.

The conductivity measurements show a tendency of higher conductivity for higher imprint pressures. Especially the 50bar samples on HMDS show a significantly higher conductivity while the samples on HMDS in general gives a slight increase in conductivity over the untreated samples.
Contents

Preface ........................................................................................................................................... 1
Abbreviations .................................................................................................................................. 2

1 Introduction .................................................................................................................................... 3
  1.1 Problem Description ................................................................................................................. 3
  1.2 Aim ........................................................................................................................................ 3
  1.3 Scope of project ..................................................................................................................... 3

2 Theory .......................................................................................................................................... 5
  2.1 Physics of photovoltaics ......................................................................................................... 5
  2.2 Organic solar cells ................................................................................................................... 5
  2.3 Organic field effect transistors ............................................................................................. 6
  2.4 P3HT .................................................................................................................................... 6
  2.5 X-ray diffraction ................................................................................................................... 8
  2.6 Absorbance spectroscopy ..................................................................................................... 9
  2.7 Snow jet cleaning .................................................................................................................. 10
  2.8 Atomic force microscopy ..................................................................................................... 12
  2.9 Spin coating ........................................................................................................................ 13
  2.10 HMDS surface treatment .................................................................................................... 13
  2.11 Nano imprint lithography .................................................................................................. 14
  2.12 Required film thickness calculations ................................................................................ 15
  2.13 Conductivity ....................................................................................................................... 15

3 Method ........................................................................................................................................ 16
  3.1 Preparation .......................................................................................................................... 16
  3.2 Solution .................................................................................................................................. 17
  3.3 Spin coating .......................................................................................................................... 17
  3.4 Mold preparation .................................................................................................................... 18
  3.5 Nano imprint lithography ..................................................................................................... 19
  3.6 Atomic force microscopy ..................................................................................................... 20
  3.7 X-ray diffraction ................................................................................................................... 22
  3.8 Absorbance spectroscopy ................................................................................................... 23
  3.8 Conductivity measurements ............................................................................................... 24

4 Results ......................................................................................................................................... 26
  4.1 Patterning .............................................................................................................................. 27
  4.2 Crystallinity ........................................................................................................................... 30
4.3 Optical properties ............................................................................................................. 34
4.4 Conductivity .......................................................................................................................... 38
5 Discussion .................................................................................................................................. 40
  5.1 Patterning .......................................................................................................................... 40
  5.2 Crystallinity ...................................................................................................................... 40
  5.3 Optical properties .............................................................................................................. 41
  5.4 Conductivity ...................................................................................................................... 42
  5.5 Reliability ........................................................................................................................ 42
6 Conclusions ............................................................................................................................. 43
7 Future research ......................................................................................................................... 44
8 References ................................................................................................................................ 45
9 Appendices ............................................................................................................................. 47
Preface

This is a report submitted in partial fulfillment of a degree in Master of Science in Energy Engineering at Umeå University. This work corresponds to 30hp and was carried out at the Department of Physics at Umeå University.

I want to thank my supervisor Dr. David Barbero for this opportunity and for his invaluable knowledge in the field which helped a lot in my work. Special thanks also go out to:

- Vasyl Skrypnychuk, Nicolas Boulanger and Junchun Yu – for their untiring assistance and guidance throughout the project.
- Robert Eklund – for his quick and clear answers and his desire to help.

“No amount of experimentation can ever prove me right; a single experiment can prove me wrong”

– Albert Einstein
Abbreviations

P3HT – Poly-3-hexylthiophene, throughout the thesis rr-P3HT and P3HT are used interchangeably, but the use of the word in all cases refers to regioregular P3HT

XRD – X-ray diffraction

AFM – Atomic force microscopy

HMDS – Hexamethyldisilazane, ((CH3)3-Si-O-Si-(CH3)3)

PDMS - Polydimethylsiloxane

NIL – Nanoimprint lithography

T_g – Glass transition temperature

OFET – Organic Field Effect Transistor

DCB – Dichlorobenzene

CF – Chloroform

SEM – Scanning electron microscope

SiO_2 – Silicon dioxide

CO_2 – Carbon dioxide
1 Introduction

Organic electronic devices, \textit{id est} organic solar cells and organic field effect transistors, have been an object of wide research for the last decade, owing this to their low cost and promising qualities. However, central to these devices is the active material used and the way it is processed as the properties of these devices vary a good deal accordingly. The reason for this is in the nature of the organic material used - the polymer. The electronic and optical properties of the polymer derive in a high degree from the way the polymer chains are assembled and ordered. Highly ordered semiconducting polymer chains can reach high levels of crystallinity and can challenge the semiconductive materials used in today’s solar cells and field effect transistors.\(^{(1)}\) The polymers can often be solved and thusly applied as films on substrates which have good benefits considering future mass production and cost.

In this project the processing of regioregular poly-3-hexylthiophene, rr-P3HT, will be studied. P3HT has by earlier works been shown to be a promising semiconductive polymer and in this project the focus is of the nano structuring of thin films of P3HT and to study the effects this has on the chain orientation and chain packing of the polymer.\(^{(2)}\) To do this the optical and electrical properties will be studied.

1.1 Problem Description

The properties of P3HT have been shown to be highly dependent on the degree of crystallinity in the thin polymer film. There is however no established “best way” to reach a high crystallinity, due to the complicated mechanism involved on a molecular level in the ordering of the molecules. In addition to this, the method of nanostructuring the films using nano imprint lithography have shown to increase the performance of the film.\(^{(3)}\)

All in all there are many parameters to consider when searching for the most efficient use of P3HT in organic electronic devices. To this end, a study of different process variations have been carried out to try and further explain the phenomenon that is P3HT thin films.

1.2 Aim

The aim of the project was to determine the relationship between different processing conditions of the thin P3HT film’s crystalline structure, optical and electronic properties.

1.3 Scope of project

The general purpose of the project was to make as good samples as possible using the methods and parameters presented within this report. The samples were also to be tested in an as reliable and qualitative way as possible given the time frame of the project. Any found tendencies or
correlations was to serve as a basis for future work where the experiments can be further narrowed down and focused to find even more relevant and clear results.
2 Theory

Within this chapter the basics concepts and underlying theory are explained. This includes general background of the field, theory of the methods used, as well as explaining any formula used in the calculations.

2.1 Physics of photovoltaics

The solar photovoltaic energy conversion is the one-step conversion process which generates electrical energy from the energy of light. Light consists of photons whose energy is dependent on the frequency, or the wavelength, of the light. The energy of the visible light is enough to excite electrons in solids up to higher energy levels for many materials. Normally an excited electron is quickly relaxed back to its original lower energy state, but in photovoltaic devices a built-in asymmetry drives the excited electrons away before they can relax, and feeds them to an external circuit. The asymmetry causing the charge separation is most commonly introduced by creating a junction between two materials of different electronic properties. In normal silicon solar cells this is done by creating a junction between electron-doped and hole-doped silicon, a silicon p-n junction. The extra energy of the excited electrons generates a potential difference which drives the electrons in the circuit and can be exploited to do electrical work. The most important properties of the materials used in solar cells are the band gap, which is the energy difference between the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO.

At normal conditions the sun produces a wavelength distribution that favors a band gap between 0.5eV-3.0eV, with the optimum being around 1.4eV. Silicon, the most commercially used solar cell semiconductor, has a band gap of 1.1eV and is not the optimal material from a band gap perspective, but the well advanced silicon processing technology from the microelectronics industry and the relative abundance makes it a favorable material nonetheless.

2.2 Organic solar cells

In conventional inorganic solar cells excited electrons are more or less free to move in the ordered material, for example a silicon crystal. In organic solar cells the active material is made up from organic molecules such as polymer chains and as such the electron transfer between each molecule is very dependent on the molecule stacking and properties, favoring highly ordered and long polymer chains. This means that in general organic solar cells show a lesser efficiency and the conductivity often is different along different directions in the material. This means that the electrons will travel a shorter distance in the material before relaxing back to a lower energy state which calls for different practical solutions for resolving this.

However, the organic solar cells have several advantages over the inorganic solar cells. Organic materials are in general more easily customizable, meaning that the band gap and other properties can be tailored to a higher extent. In addition, many organic materials is soluble and
flexible which highly reduces the potential production costs, by allowing the material to be drop cast, spin coated, sprayed or even printed on a substrate, in addition to being able to produce flexible and less fragile solar cells. All in all the organic solar cells performance is highly dependent on the material and processing conditions and there is wide research going on in the field. (5)

2.3 Organic field effect transistors

Field-effect transistors, FETs, have since their discovery evolved into an integral part in modern day electronics and can be found in a wide range of circuits. The basic principle of a FET is, through appliance of an electric field, open a thin conducting channel in the transistors semiconductor material, often silicon. This leads to the transistor being able to vary its insulating properties. (6)

Organic field-effect transistors, OFETs, work on the same principle but with an organic semiconductor material instead. (6) Unlike silicon transistors, which require high manufacturing process temperatures (>800°C for single crystalline and >200°C for amorphous), can organic transistors be manufactured near room temperature. (7) Moreover, the organic transistors can even be deposited on flexible polymers or paper. These qualities have caught the interest of the commercial industry and academic field alike and products such as foldable or even rollable color displays have been made.

2.4 P3HT

A common and promising material for use in organic solar cells or OFETs is the organic semi conductive rr-P3HT. (1)(6) The genuine polythiophene is insoluble and thusly difficult to deposit into thin films as required. However, polythiophenes that have been alkyl substituted, such as P3HT - shown in Figure 1, do have go solubility for a wide range of organic solvents. (8) This facilitates thin film preparation through methods such as spin coating, dip coating, drop coating, screen printing and inkjet printing.

![Figure 1 - Schematic representation of the molecular structure of a P3HT monomer](9)
However even generic alkyl substituted polythiophenes often form amorphous films with little to no long range structural ordering and as such poor carrier mobilities, below $10^{-3}\, \text{cm}^2/\text{Vs}$.\(^{(7)}\)

There are several specifically synthesized derivatives of polythiophenes and one is regioregular head to tail P3HT, Figure 2, which were initially synthesized in 1993.\(^{(2)}\) It has been shown that the regularly oriented alkyl chains favor a highly ordered lamellar structure. This leads to a more crystalline microstructure with better intermolecular orbital overlap and charge transfer. Consequently the carrier mobility increases from about $10^{-3}\, \text{cm}^2/\text{Vs}$ to about $10^{-1}\, \text{cm}^2/\text{Vs}$. The resulting mobility in rr-P3HT depends mainly on the average polymer chain length, the degree of regioregularity and the deposition conditions, i.e. the time the film formation takes.\(^{(1)}\)

![Figure 2 - Schematic representation of regioregular P3HT \(^{(10)}\)](image)

This lamella formation leads to the electron being easily able to delocalize to neighboring P3HT molecules perpendicular to the lamella plane and as such the carrier mobility is highly anisotropic, i.e. better in one direction and worse in the others. In OFETs the current is usually in a direction parallel to the surface and by choosing a slow deposition rate the more favorable crystal orientation can be achieved.\(^{(7)}\)

A drawback of rr-P3HT is that it is prone to photo induced oxidation, i.e. it degrades when exposed to light and air. This leads to a number of problems for the use of rr-P3HT in for example polymer solar cells; however these will not be discussed in this article.

P3HT has a band gap of 1.9-2.0eV\(^{(11)}\) leading to the polymer absorbing light of wavelengths corresponding well to those of natural sunlight. This makes the polymer a good candidate for use in photo electrics such as polymer solar cells or OFETs. Through the use of UV-vis P3HT films have been found to absorb light in to peaks for 493nm and 517nm wavelengths as well as having a lesser absorbance peak for a 572nm wavelength.\(^{(11)}\) These peaks comes from the pi-pi* bond transition in the polymer, which represents the higher energy excitation levels in the molecules.
2.5 X-ray diffraction

To determine the degree of crystallinity in the P3HT films it is possible to use x-ray diffractometry, XRD. This method utilizes the effects of diffraction between incident x-rays and the crystal planes in a substance. At certain angles of the incident rays the reflected rays are in superposition due to the extra traveled distance for the deeper penetrating rays being equal to a multiple of the ray wavelength. This is detailed with Bragg’s law and further exemplified in Figure 3:

\[ n\lambda = 2dsin\theta \]

**Formula 1 - Bragg's law**

n = Integer, 0, 1, 2…

\( \lambda \) = Wavelength of incident light [m]

d = Interplanar spacing in the crystal lattice [m]

\( \theta \) = Incident angle of light [°]

By varying the angle of the incident x-rays and measuring the reflected rays a number of conclusions can be made about a substrate – mainly chemical composition and degree of crystallinity, the latter of interest for this thesis. The higher reflected intensity at the P3HT characteristic angle, the more crystal ordering must be present in the film, as unordered P3HT does not show well defined peaks. (12)

![Figure 3 - Schematic of Bragg diffraction in crystals](13)
The most prominent angle, $2\theta$, for P3HT is that of the (100) plane corresponding to roughly 5.4° and is the one being examined in this thesis. For characterization of very thin films a very low incident angle are used. This means that the x-rays don’t penetrate as deeply into the underlying substrate. As such, the signals acquired from the film increase in strength and conversely the signals from the substrate decrease. This makes it easier to detect the weaker peaks for the film without being overshadowed by the signals from the substrate.

In addition only the detector is moved and consequently the sample orientation and illuminated area stays the same throughout the measurement process.\(^{(14)}\)

### 2.6 Absorbance spectroscopy

This method refers to the absorption spectroscopy or transmittance spectroscopy in the ultraviolet visible spectral region. This means that light of wavelengths corresponding to visible, near-UV and near-IR are used. The method has been a common method the last 35 years due to its simplicity, accuracy and cost-effectiveness.

The set-up insuresthat the sample is illuminated by monochromatic and parallel light beams. Normally a tungsten lamp is used as a light source. The basic setup for a reflectance measurement is shown in Figure 4.

![Figure 4 - Measurement of diffuse reflectance using an integrating sphere\(^{(15)}\)](image)

The basic principle of the method is to excite electrons to higher molecular orbitals through the absorbance of light of a particular energy. By illuminating a sample and measuring absorbance or transmittance for a broad range of light wavelengths, the characteristics of different molecules can be found.
Electrons belonging to different functional groups require different levels of energy for exciting them to a higher orbital. This is due to the actual bond strength for the different electrons. In addition to certain functional groups or bonds requiring different excitation energies they also affect the molecule as a whole, giving each molecule a unique absorption spectra. However samples are rarely uniform and there are other molecules present such as contamination or the presence of a solution. The absorption in a sample by a certain molecules is proportional to their relative frequency, meaning that one can determine the relative amount of a molecule present. This makes it possible to identify different functional groups and bonds in a sample in a quick and simple way. (16)

The unit in which the absorbance is measured and represented is defined using Formula 2.

\[ A = \log_{10}\left(\frac{I}{I_0}\right) \]

Formula 2 - The definition of absorbance

\( A \) = Absorbance for a given wavelength of light
\( I \) = Light intensity after interaction with sample
\( I_0 \) = Initial light intensity

2.7 Snow jet cleaning

The process called snow jet cleaning refers to the process of cleaning a heated surface by blowing pressurized high velocity liquid carbon dioxide, \( \text{CO}_2 \), at it. This is the method used in the experiments for removing submicron particles and organic residue.

When the \( \text{CO}_2 \) leaves the nozzle of the spray gun, the pressure drop turns the liquid \( \text{CO}_2 \) into both gas and solid particles and the likeness to ice gives the process the nickname of snow jet. The cleaning process is achieved through interaction between this high velocity snow particles and the contaminated surface. The basic schematic of this process is shown in Figure 5.
The cleaning is achieved through two mechanisms. Firstly, the stream of high velocity gas is enough to remove larger particles through their momentum. The moving gas exerts aerodynamic drag force on the particles. This drag force is proportional to the particle size in the gas-flow. If this exerted drag is greater than the surface adhesion force, the particle is swept away with the moving gas. This means that small enough particles will not be removed through drag. Particles of micron size and larger are usually removed through this mechanism.

Secondly, the dry ice particles in the stream bombard the contaminating particles and through transfer of momentum the adhesive forces can be overcome. The contaminating particles are then easily carried away in the high velocity gas flow. The effect of this mechanism of cleaning is not reduced by smaller particle sizes as the drag is. The only requirement is that an ice particle actually hits the contaminating particle. The likelihood of this of course increases with extended clean time if even more rigorous cleaning is required.

Organic residues, which often can be problematic to remove, are removed through the high velocity stream of particles. The removal of these requires the existence of a liquid phase in the stream as liquid CO$_2$ is a great solvent for hydrocarbons and other non-polar substances. When the ice particles hit the surface with a high enough velocity the impacting part of the particle is exposed to a sufficiently high pressure for liquefying some CO$_2$. This liquid part of the CO$_2$ particle dissolves some of the contaminants and thus removes them from the surface when the ice particle bounces off. As the particle moves away from the surface the pressure is lowered back to before impact level and thusly the liquid CO$_2$ solidifies helping to remove any contaminants.

A short coming of this method is that it is not able to remove substances that are chemically bonded to the surface since those substances won’t be dissolved into the CO$_2$.\textsuperscript{(18)}
2.8 Atomic force microscopy

Atomic force microscopy, AFM, is a method for analysis of surfaces below the resolution of traditional optical microscopy by tapping the surface with a small tip attached to a cantilever. The tip is tapped along the surface and the cantilever is bent doing so. A highly dense laser is directed at the back of the cantilever and reflected to a photodiode detector. Due to the high density of the laser beam a very high spatial resolution can be measured, as small as the detector sensitivity is high. Otherwise the sensitivity of the scanning depends on the tip used, which is chosen according to the performance needed. A sharper tip yields more accurate measurements than a dull one. As a tip is used it can be dulled or break entirely, so scan results must be viewed with this in mind. The basic operating principle of an AFM measurement is shown in Figure 6.

![Figure 6 - Schematic of the AFM measuring principle](image)

The measurement methodology means that the AFM can acquire a 3-dimensional scanning of the surface whereas optical and electron microscopes can only acquire a 2-dimensional picture. This makes AFM a good method for measuring patterns and structures on the sample.

There are different operating modes for AFM but the one referred to and used in this thesis is the “tapping mode”. This mode operates by oscillation the cantilever close to its resonance frequency and letting the tip “tap” along the surface when scanning. This mode is a mix of contact mode and non-contact mode and derives the advantages of both. It yields a lower degree of sample damaging than contact mode but is more accurate than non-contact mode. The measurement itself is then made by analyzing the reduction of oscillation amplitude when the tip passes a rough surface. The method also allows for characterizing the material scanned by
measuring the friction, elasticity and adhesion through the induced phase-lag. In short, this is the degree the cantilever is slowed out of phase due to the tapping, and thusly needs to be corrected by the regulation mechanism. (19)

2.9 Spin coating

Spin coating is a simple and effective way of producing thin films of reasonable uniformity. It is a common technique for depositing thin films onto smaller samples. The technique is advantageous for the experiments in this thesis due to the simplicity and reproducibility of the method.

The theory is to drop an appropriate amount solution onto a small substrate and then spin the substrate. During this process the solution is drawn outwards and off the substrate due to the rotational motion. In addition the volatile solution evaporates and leaves a thin layer of dissolved substance.

The thickness of the deposited film is related to the rotational speed of the substrate, the concentration of P3HT in the solution, the surface energy of the substrate and the volatility of the solvent as well as the ambient conditions. There are several theoretical formulas for different cases of spin coating, but for this thesis an empirical approach is applied to find suiting film thicknesses. (20)

The method has several relevant disadvantages to keep in mind. These include leaving a buildup of solution along the substrate edges and incomplete film coverage in the corners for non-circular substrates. Both of these effects are localized towards the edge of the substrates and as such the imprinted patterns are made as centrally as possible to avoid these non-uniformities. (21)

2.10 HMDS surface treatment

Hexamethyldisilazane ((CH₃)₃-Si-O-Si-(CH₃)₃), HMDS, is commonly used to reduce the surface energy of silicon dioxide, SiO₂, surfaces. This has been shown due to the HMDS forming a self-assembled monolayer and the alkane chains helps to increase the hydrophobicity of the surface.

Decreasing the surface energy influence the P3HT film thickness achieved through spin coating. How much and in which direction is determined largely by the solution used. The implications of this are that thickness calibration needs to be done for both untreated and HMDS treated substrates even when using the same solution and concentration.

In addition to this, previous experiments have hinted that the addition of the HMDS treatment can increase the crystallinity in the deposited P3HT films after annealing. However this can be seen as mere observations and more research need to be carried out to verify this. These hints are the reason that this thesis conducted experiments chooses to include HMDS treatment as a parameter to be varied and evaluated. (22)
2.11 *Nano imprint lithography*

This is a method of imprinting nanostructures based on a mechanical embossing principle. The technique has the ability of imprinting patterns of sizes smaller than other techniques, which uses light etching and as such is limited by the diffraction of light.

Basically the nanoimprint lithography works by applying a patterned mold on the layer to the substrate to be patterned. During this process the film is heated to above the glass transition temperature where the film starts to soften and is able to flow into the pattern, as exemplified in Figure 7.

![Figure 7 - Schematic representation of the NIL principle (23)](image)

The glass transition temperature is the temperature limit when an amorphous material stops behaving like a hard and brittle material and instead becoming more flexible or rubbery. This limit is also dependent on time, as the molecules need time to rearrange. As such, time is also an important factor when imprinting to ensure the material has sufficient time to rearrange into the new pattern.

NIL of spin cast P3HT also performs a second important function – annealing, which gives the molecules the possibility to rearrange into a more ordered structure. And as previously stated the crystal structure of the P3HT is an important factor for the performance of the polymer.\(^\text{(23)}\)

It has been shown that the increase in the donor-acceptor interfacial area in bilayer organic solar cells yields increased cell efficiency. This is due to the fact that excitons are more likely to reach the acceptor rather than being relaxed back to a lower energy state in the donor.\(^\text{(3)}\)
2.12 Required film thickness calculations

The required amount of P3HT to fill the patterning and to create a certain residual layer can easily be calculated using the pattern dimensions. For cylinder arrays:

\[ L = \frac{\pi \times d^2 \times h}{4p^2} \]

*Formula 3 – The thickness required to fill a cylinder array pattern*

\( L \) = Required layer thickness [m]
\( d \) = Pillar diameter [m]
\( h \) = Pillar height [m]
\( p \) = Periodicity [m]

2.13 Conductivity

The conductivity of a given electrical circuit can be calculated by knowing the dimensions of the electrical path and measuring the current for a set voltage:

\[ \sigma = \frac{I \times l}{U \times A} \]

*Formula 4 – Calculating conductivity by measuring current and voltage*

\( \sigma \) = Conductivity [S/m]
\( I \) = Current [A]
\( l \) = Material thickness [m]
\( U \) = Voltage [V]
\( A \) = Measured area \([m^2]\)
3 Method

This chapter explains the methods that were used during preparation and experimental setup. This includes everything between the making of the samples to each experiment set to analyze different aspects of the samples.

3.1 Preparation

The samples were cut into roughly 15x15mm squares from (100) conductive silicon wafers. A scratch was made on the edge of the wafer and then light force was applied to break the wafer along the crystal grains. Each sample were then put on a heater set to 300°C, locked in place with a vacuum holder and snow jet cleaning was carried out for approximately 2 minutes. The setup for the snow jet cleaning is shown in Figure 8.

Figure 8 - The snow jet setup used for sample cleaning (24)
The samples that required HMDS surface treatment were placed on a stage and placed in a beaker with a small amount (couple of centiliters) of HMDS. A lid was placed on the beaker and was sealed using parafilm to prevent leakage. Another beaker were filled with ice and placed in an indent in the lid of the bigger beaker. The whole setup was then placed on a heater set on 70°C for 1h.

3.2 Solution

For the solvent a 50-50%wt of chloroform and dichlorobenzene, DCB, was mixed. An amount of chloroform was added to a small jar and then DCB was carefully added using a disposable 2ml syringe until the weight was double that of the initial value, with an accuracy of about 0.01g.

P3HT with a high regioregularity was then mixed with the 50-50 solution using the same method as above to the appropriate concentrations. Then the solution was heated at 50°C for 10 minutes followed by being filtered through a syringe filter with a pore size of 0.45 micron pore size.

3.3 Spin coating

The P3HT layer was applied to the silicon samples through spin coating. The samples was put in position on the spin coater’s stage and locked in place through a vacuum holder. A light blow of N₂ was applied to remove any dust particles from the sample. A pipette was used to apply 50μl solution onto the sample. The pipette was used to make sure the solution covered the whole sample and then the spin coating was started.
Figure 9 - The spin coater used in the experiments

The program run used a spin speed of 1000rpm for 90s followed by a step with 3000rpm for 5s to remove the build-ups otherwise left in the sample’s corners. The spin coater used in the experiments is shown in Figure 9.

3.4 Mold preparation

The master mold used was a silicon mold with a hexagonal array of round pillars with a diameter of 395.3nm, a height of 365.3nm and a periodicity of 780nm. This was then surface treated with HDMS to reduce the adhesion to the polydimethylsiloxane, PDMS. This was done using the same procedure as the normal silicon samples. A scanning electron microscopy image of the master mold used supplied by the mold producer is shown in Figure 10.
An inverted mold was made using the master mold and PDMS. PDMS was mixed with a 1:10 proportion of curing agent and base in a beaker. The PDMS was a Dow Corning Sylgard® Silicone Elastomer. The mix was stirred thoroughly and placed in an air-tight glass jar attached to a pump. The pump was used to reduce the pressure and extricate all air bubbles in the mix, this was done until no bubbles were visible.

The master mold was placed in a small Petri-dish covered in foil over which the PDMS was poured. The dish was then placed in an oven at 150°C for 25 minutes to cure. After the dish had cooled the foil and master mold were removed and then the superfluous PDMS was removed by using a scalpel.

### 3.5 Nano imprint lithography

The samples were imprinted using an Obducat NIL 2.5 imprinting machine. The imprinter stage was loaded with a PDMS spacer with three square holes marginally wider than the samples. Three silicon samples coated with P3HT was loaded into the holes with the made PDMS mold on top of them. In Figure 11, the imprinter used is shown. Note the stage with the PDMS spacer with three specifically cut out squares for the sample sizes.
Then PDMS spacers were used to create a level surface for the imprinter to work against. The imprint was the run with a 900s imprint time at 170°C where after the stage was air-cooled under kept pressure down to 40°C. The imprint pressure used was 5bar, 20bar and 50bar respectively.

3.6 Atomic force microscopy

The samples were studied in an atomic force microscope. A scanning tip was carefully attached to the tip holder and secured. A sample was then mounted on a 10mm round magnetic disc covered in sticky film. The sample was then put in place in the microscope on a magnetic stage, keeping the sample in place. On top of this the tip holder was mounted and secured. The microscope can be seen in Figure 12.
The tip was calibrated using the software’s auto-tune function. The tip was then engaged and the scans were performed on a 3x3μm area using an amplitude set point of 0.5A and a resolution of 512 samples per line. For determination of P3HT layer thickness, a reference sample was scratched using a scalpel and then the scratch depth was analyzed. For the pattern imaging a neutral imprinted area was analyzed, meaning an area free of possible defects and of estimated normal imprint quality.
3.7 X-ray diffraction

The x-ray diffraction was carried out using a Philips XPERT MPD System machine. A sample was mounted on the stage using adhesive tape being careful to let it cover as small piece of the sample as possible and avoiding the imprinted area. This was done to try and reduce any damage on the sample film. The setup can be seen in Figure 13.

Firstly, as the sample was not perfectly aligned parallel to the surface, the machine was calibrated. For this the (001) silicon peak, which resides at 69.2°, was used. A scan was performed for an interval around 69.2° and then the machine was offset the correct amount to get the peak at 69.2°. Then the sample was calibrated in the other angular direction, the psi angle. The scan was performed at 69.2° with varying the psi angle and then the psi angle was set to the obtained maximum.

The main scan was performed with these offsets and with a fixed incident angle of 0.28° and varying the 2theta angle was varied from 4° to 8° with a sample time of 1s and a step length of 0.01°.

Analysis of the results was made with the free software Fityk (26). The background noise was removed by manually adding points for average background noise and letting the program adjust
the graph accordingly. The peaks were found using auto-find and using a Gaussian fit to create the desired peaks.

3.8 Absorbance spectroscopy

The optical measurements were made using a Perkin Elmer Lambda750 UV-vis machine. The machine was set up in a transmittance measurement mode. The sample was loaded into a metal holder with a circular hole of roughly 10mm in diameter. This caused only imprinted area of the sample to be visible, which was the area interesting for study. Special care was taken not to damage the samples when securing them to the holder. The UV spectrometer detector unit can be seen in Figure 14, where the sample would be mounted on the right side of the box and the UV rays coming from the left.

A transmittance scan was performed from 200nm to 2300nm with a step length of 5nm. The first scan was performed with a reflective pad, instead of the loader and sample, for a 100% reflectance baseline correction. The scans were performed in the same set and as such using the same baseline correction for all samples.
The analysis of the UV-vis spectra was made using the free software Spekwin32 (27). The data was loaded and any sharp peaks (due to lamp change at certain wavelengths) were removed using the function remove peaks. The data was cut off at 1000nm and the y-axis was changed to show the absorbance instead of the reflectance.

### 3.8 Conductivity measurements

The electrical measurements were carried out in the sample’s top to bottom direction through the imprinted area. A metallic stage was coated in conductive silver paint and while the paint was still wet a sample was placed on top and given a slight pressure in the corners to really stick. A metallic top electrode was carefully placed on top of the sample. The top electrode had a square contact area of approximately 3x3mm and was covered with dried conductive silver paint. The stage and top electrode can be seen in Figure 15.

![Figure 15 - Experimental setup for conductivity measurements](24)

Both the stage and the top electrode were connected to an adjustable power source, a voltmeter and an amperemeter. The voltage and current values were noted for approximately 0.5V, 1V and
1.5V for each sample. In addition the same values were checked for an empty stage, i.e. the top electrode was placed directly on top of the stage to measure the circuit resistance.

This experiment was carried out twice and an average was taken, to further minimize any human error.
4 Results

The samples were made, using the specified processing parameters and methods. The results are presented in this chapter. Table 1 shows a table for all processed samples and their unique processing parameters.

<table>
<thead>
<tr>
<th>Concentration [%wt]</th>
<th>Surface treatment</th>
<th>Imprint pressure [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75%</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>0.75%</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>0.75%</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>1%</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>1%</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>1%</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>1%</td>
<td>HMDS</td>
<td>5</td>
</tr>
<tr>
<td>1%</td>
<td>HMDS</td>
<td>20</td>
</tr>
<tr>
<td>1%</td>
<td>HMDS</td>
<td>50</td>
</tr>
<tr>
<td>1.25%</td>
<td>HMDS</td>
<td>5</td>
</tr>
<tr>
<td>1.25%</td>
<td>HMDS</td>
<td>20</td>
</tr>
<tr>
<td>1.25%</td>
<td>HMDS</td>
<td>50</td>
</tr>
</tbody>
</table>

The samples looked almost identical, with different color hues depending on deposited concentrations of P3HT. An example of a representative sample is shown in Figure 16. Note the blue/black gradient square which is the imprinted area.

![An example of an imprinted silicon sample](image)

Minimum layer for complete filling was calculated using Formula 3:
1 = 73.8nm

AFM of spun coated but not yet imprinted samples were carried out to determine the P3HT layer thicknesses. Scratches in the film were made and scanned and the resulting thicknesses is presented in Table 2.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Surface</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75%</td>
<td>Si</td>
<td>85nm</td>
</tr>
<tr>
<td>1%</td>
<td>Si</td>
<td>101nm</td>
</tr>
<tr>
<td>1%</td>
<td>HMDS</td>
<td>93nm</td>
</tr>
<tr>
<td>1.25%</td>
<td>HMDS</td>
<td>119nm</td>
</tr>
</tbody>
</table>

As can be seen in Table 2, the obtained thickness varies between the different surfaces for the same spun concentration, which is to be expected.

4.1 Patterning

As AFM images was for reference and is a time consuming method, AFM imaging was done only for one sample for each concentration/surface treatment set. Hence the four samples with 50bar imprint pressure were chosen to be scanned.
Figure 17 - AFM imaging of film patterns of A) 0.75% Si, B) 1% Si, C) 1% HMDS and D) 1.25% HMDS.

As Figure 17 show there was differing qualities of pattern imprint among the samples. A) was clearly the worst imprinting, with B) and C) of equal quality, while D) showed the best quality. Overall none of the samples showed good filling as they ranged from a maximum pillar height of roughly 50nm to 150nm while the master mold height was 365nm.
Figure 18 shows a cross section of one of the samples. As evident in the figure the pillars differ from the master mold on several points. The pillars are rounded instead of having sharp edges, the pillars are significantly wider than the master mold and the pillars are also of a lower height than the master mold. That said there is still a distinct patterning in the film.

The patterning is further visualized in Figure 19 as a 3-dimensional surface. The difference in the pattern compared to the master mold is clearly visible.
An average of the height of all pillars for each sample in Figure 17 was taken to quantify the pattern filling.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Surface</th>
<th>Average pillar height</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75% 50bar</td>
<td>Si</td>
<td>35nm</td>
</tr>
<tr>
<td>1% 50bar</td>
<td>Si</td>
<td>70nm</td>
</tr>
<tr>
<td>1% 50bar</td>
<td>HMDS</td>
<td>70nm</td>
</tr>
<tr>
<td>1.25% 50bar</td>
<td>HMDS</td>
<td>105nm</td>
</tr>
</tbody>
</table>

The results from AFM, shown in Table 3, indicate that there is much that can be improved regarding the patterning of the films as the pillar height range from about 10% to 30% of pillar height. At the same time, as visualized in Figure 18, the pillar diameter is of about 180% of the master mold, however, the periodicity of the pattern is consistent with the master mold.

4.2 Crystallinity

A XRD measurement was carried out on the samples. The data were analyzed and enhanced using Fityk.

In Figure 20 the peak intensity are increasing with increasing imprint pressure. In addition the weakest of the sample peaks, the 5bar one, is shifted towards lower angles.
In Figure 21 the peak intensity are increasing with increasing imprint pressure. In addition the weakest of the sample peaks, the 5bar one, is shifted towards lower angles in much the same way as in Figure 20 but the peak is not as weak. Both Figure 20 and Figure 21 show clear tendencies for the crystallinity increasing with the imprint pressure. The increase is bigger for the step 5bar-20bar than for 20bar-50bar hinting that increasing the pressure even further will yield a smaller count increase for higher imprint pressures.
Figure 22 – Baseline extracted XRD spectra of 1% HMDS

In Figure 22 the peak intensity are increasing with decreasing imprint pressure – the opposite tendency to that of Figure 20 and Figure 21.
In Figure 23 the peak intensity is increased with decreasing imprint pressure. The weakest peak, in this case the 50bar sample, is also shifted a bit towards lower angles.

Overall for all XRD spectra - Figure 20, Figure 21, Figure 22 and Figure 23 – the peaks was broader than expected for P3HT films of this kind. This could be due to a missing thin film collimator on the XRD receiver, which would have given stronger film peak signals. It can also point to a lower crystallinity and more amorphous impurities.

Each peak was integrated to quantify all peaks and be able to compare the peaks in one graph.

Figure 24 shows the peak areas of all samples for easy comparison. In general the HMDS surface treated samples give higher peak intensities, but the weakest HMDS samples are still considerably weaker than the strongest of the untreated samples. To further emphasize what has already been stated, the graph clearly shows that the intensity increases with pressure for untreated samples and decreases with pressure for HMDS treated samples.
4.3 Optical properties

An UV-vis measurement was carried out on the samples, followed by an analysis using Spekwin32.

![Absorbance spectra for 0.75% Si – black) 20bar, red) 50bar, green) 5bar](image)

It can be seen in Figure 25 that the absorbance is quite similar for each imprint pressure. Peaks can be found at 325nm and 640nm wavelengths. There is a slight increase in the 640nm peak absorbance for higher imprint pressures. The 330nm peak is identical for all three samples. The absorbance is significantly lower than the other sample sets. In general, the 0.75% Si samples show spectra that are not consistent with the other results.
As can be seen in Figure 26, the absorbance lines are close to identical for the imprint pressures. Peaks can roughly be found at 205nm, 450nm and 675nm wavelengths. The 5bar sample registers a slight increase in absorbance for the 450nm peak and the 20bar sample show a slightly higher absorbance for the 675nm peak.
Figure 27 - Absorbance spectra for 1% HMDS – black) 20bar, red) 50bar, green) 5bar

Figure 28 - Absorbance spectra for 1.25% HMDS – black) 20bar, red) 50bar, green) 5bar
As can be seen in Figure 27 and Figure 28, the absorbance lines are close to identical for the imprint pressures. Peaks can roughly be found at 210nm, 450nm and 675nm wavelengths. The 5bar samples register a slight increase in absorbance for the 450nm peak.

Figure 29 - Absorbance spectra of all 5bar samples – black) 0.75% Si 5bar, red) 1% HMDS 5bar, green) 1% Si 5bar, blue) 1.25% HMDS 5bar

Figure 29 show a comparison of all samples imprinted under 5bar of pressure. This clearly shows the difference in absorbance between the different types of samples and the trends seen in this figure holds true for the other performed imprint pressure values as well. Apparent is the degree for which the 0.75% sample differs from the other samples. This can probably be attested to the poor pattern filling.
Table 4 – Obtained peak’s wavelength and absorbance

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_1$</th>
<th>$A_1$</th>
<th>$\lambda_2$</th>
<th>$A_2$</th>
<th>$\lambda_3$</th>
<th>$A_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75% Si 5bar</td>
<td>325</td>
<td>0,4997</td>
<td>420</td>
<td>0,438</td>
<td>640</td>
<td>0,5848</td>
</tr>
<tr>
<td>0.75% Si 20bar</td>
<td>325</td>
<td>0,4973</td>
<td></td>
<td></td>
<td>640</td>
<td>0,6482</td>
</tr>
<tr>
<td>0.75% Si 50bar</td>
<td>335</td>
<td>0,4993</td>
<td></td>
<td></td>
<td>640</td>
<td>0,6623</td>
</tr>
<tr>
<td>1% Si 5bar</td>
<td>210</td>
<td>0,9664</td>
<td>445</td>
<td>1,278</td>
<td>675</td>
<td>1,428</td>
</tr>
<tr>
<td>1% Si 20bar</td>
<td>205</td>
<td>0,9266</td>
<td>450</td>
<td>1,25</td>
<td>675</td>
<td>1,467</td>
</tr>
<tr>
<td>1% Si 50bar</td>
<td>205</td>
<td>0,9028</td>
<td>450</td>
<td>1,241</td>
<td>675</td>
<td>1,398</td>
</tr>
<tr>
<td>1% HMDS 5bar</td>
<td>210</td>
<td>0,9732</td>
<td>450</td>
<td>1,3</td>
<td>670</td>
<td>1,414</td>
</tr>
<tr>
<td>1% HMDS 20bar</td>
<td>210</td>
<td>0,9752</td>
<td>450</td>
<td>1,265</td>
<td>675</td>
<td>1,404</td>
</tr>
<tr>
<td>1% HMDS 50bar</td>
<td>210</td>
<td>0,9516</td>
<td>455</td>
<td>1,273</td>
<td>675</td>
<td>1,395</td>
</tr>
<tr>
<td>1.25% HMDS 5bar</td>
<td>240</td>
<td>1,008</td>
<td>465</td>
<td>1,419</td>
<td>690</td>
<td>1,247</td>
</tr>
<tr>
<td>1.25% HMDS 20bar</td>
<td>230</td>
<td>1,022</td>
<td>460</td>
<td>1,35</td>
<td>680</td>
<td>1,279</td>
</tr>
<tr>
<td>1.25% HMDS 50bar</td>
<td>235</td>
<td>1,018</td>
<td>480</td>
<td>1,372</td>
<td>685</td>
<td>1,278</td>
</tr>
</tbody>
</table>

Table 4 sums up the different obtained peaks from the analyzing program. The expected peak values for P3HT films are, as mentioned in Section 2.4, 493nm, 517nm and 572nm. Of these the 493 is the strongest and the other two show up like slightly weaker shoulders for the peak. The obtained values differ a bit from these. This suggests that the peaks found around 210nm and 660nm probably are some sort of noise. This might come from the sample holder for example.

Though looking at Figure 29 there are bumps around 530nm and 590 which probably represent the expected shoulders of the P3HT peaks. However these are too weak to show up as peaks in the program.

**4.4 Conductivity**

Electrical measurements of the samples were carried out on all the samples, and the values were calculated to show the average conductivity for each sample.
As can be seen in Figure 30, the conductivity seems in general to increase with the imprint pressure for both types of surfaces. In addition the HMDS treated samples show an overall higher conductivity as well. Especially the HMDS treated samples imprinted under 50bar show a significant increase in conductivity.
5 Discussion

The processing of the samples encountered not much problems. It should however be noted that it has been observed that the HMDS treated samples are slightly more difficult to spin coat as they sometimes tend to dewet. In response to this, slightly more solution needs to be added to the sample before spinning to ensure a complete coating. In addition the films of HMDS treated samples seem to be more fragile than untreated, meaning that they more often develop scratches during imprinting. This is consistent with the HMDS treated surfaces being more hydrophobic, but it should be noted.

5.1 Patterning

It is clear that neither of these parameters yield a complete pattern filling under these process parameters as well as the different parameters yields varying degrees of filling. The best individual pillar encountered measured about 160nm in height whereas the master mold pillar height was 395nm. However it cannot be said if this depends on the PDMS mold making conditions, the imprinting conditions or both. An AFM measurement of a PDMS mold was attempted, but with little success. To determine the failing factor, this is would be an important step towards improving the technique. There is always a risk of mechanical destruction of patterning, though these are normally of a larger scale and as such the AFM imaging can be seen as a decent estimate of the average patterning on the imprinted area.

Especially the results of the 0.75% Si samples are probably a bit biased since the bad patterning. This makes it hard to draw any hard conclusions regarding this particular sample set. In general, as the patterning quality differs between the sample sets it is difficult to isolate just the effects of the imprinted nanostructures.

It should be mentioned that the intent of the films were to have a pattern with a thinner residual layer and a pattern with thicker. As it turns out, all of the samples produced shows a residual layer of approximately 40-60nm due to poor pattern filling. All in all, to further investigate the effects of the nanopatterning of thin P3HT films, steps should be taken to try and perfect the actual patterning. However there is obviously easier to pattern HMDS treated surfaces according to the results.

5.2 Crystallinity

The XRD results strongly suggest that increasing the imprint pressure increases the crystallinity for samples with untreated silicon and the other way around for HMDS treated silicon. Both sets of untreated silicon samples showing the same tendency as well as both sets of HMDS treated silicon samples showing the same tendency gives the results further strength. The reasons why this is the case is harder to say for certain. It is hard to prove anything based on these results alone but one can reason that the higher surface energy of the HMDS treated silicon samples facilitates the ordering of P3HT and the pressure in this case works in a destructive way on the
ordering. On the other hand, the untreated silicon samples may have a low degree of P3HT ordering in the film, but higher imprint pressures lets the polymer order in a higher degree.

The polymer chain stacking and ordering are probably slightly different for treated and untreated surfaces after the spin coating step, meaning the different samples enter the imprinter in different starting states.

It needs to be stated that the peaks are much broader than expected as normally the peaks should be narrow and high. This means that the actual peak sizes are not to be blindly trusted, but for comparison purposes one can still draw conclusions. In normal cases one can calculate the crystallite sizes from the peaks half-peak intensities, but the results yielded from these peaks are not realistic. Reasons for the peaks being this broad is thought to be in the experimental setup and is the number one factor to look into when trying to improve the results.

Regardless, if the HMDS surface treatment yield higher crystallinity for lower pressures it provides a strong economic incentive to be the most favored method. Especially if the method where to be scaled up to industrial production, the difference between requiring 5 bars of pressure and 50 bar is enormous.

5.3 Optical properties

The UV-vis of the P3HT films shows that there is not that big difference in absorbance between the sampled. The 0.75% once again stands out as the worst set with the lowest absorbance; this is probably attested to the bad pattern filling compared to the other sets. The two best sets are the 1% Si and 1% HMDS samples with no particular stand out between the different imprint pressures.

The results do not support any particular conclusion other than stating that the 0.75% Si shows significantly lower absorbance values. Again, as the whole set show lower absorbance it is reasonable to believe that the parameters are bad, rather than anyone particular sample being damaged or otherwise badly processed.

It should be mentioned that the absorbance peaks does not coincide with reported values particularly well. It is possible there is some sort of influence from the sample holder. Otherwise it could be that the P3HT absorbance peaks are shifted by effects of nanopatterning. This would require further study.

Normally there would be possible to draw conclusions about the amount of crystalline P3HT compared to the amount of crystalline P3HT from the different signature peaks, but in this case it is hard to draw any definite conclusions since the peak shoulders are overshadowed by the big peak at roughly 660nm. This big peak is not expected from P3HT and the setup should be looked into to try and reduce this particular peak.
5.4 Conductivity

The results indicate more or less that the conductivity increases with the imprint pressure. It is not consistent for all samples, but the 50bar samples clearly support this tendency as they have in most cases a greatly increased conductivity. Increased top to bottom conductivity is a good property for a solar cell and it would be beneficial to pinpoint the correlation. The increased conductivity would mean that the polymer chains have ordered themselves in a more favored orientation from a conductivity viewpoint. However, as the XRD results show that the crystallinity might decrease with higher pressures for HMDS treated samples, hinting that the answer is not that straight forward. As the HMDS treated samples show better performance overall, there might be interesting to find an optimal tradeoff between imprint pressure, conductivity, crystallinity and absorbance.

However, this conductivity measurement method in general is not ideal, since the contact area on top of the area depends on the roughness of both the samples and the top electrode, giving an inherent variance of contact area depending on placement. In addition, the rather free placement of sample and electrode means the conductivity path varies between measurements as well. This might be solved by performing the measurements even more times to obtain a reliable value.

It might also be worth mentioning that the conductivity measured is for the total sample, meaning the conductivity is measured for the silicon and film combined. As such the conductivity values cannot be directly compared with other studies. There is of course the possibility of measuring the resistance of a pure silicon sample and subtracting that from the calculations to obtain a value for just the film. However for comparison purposes the presented values works just fine, as the resistance of the silicon is consistent for all samples.

5.5 Reliability

All of these experiments have been conducted in a more qualitative way, rather than quantitative. Meaning that several samples have been processed using the methods until a finished sample with uniform coating, visibly good imprint and little to no impurities such as dust and scratches. Then the experiments have been carried out on the same, single, supposedly, good sample throughout the report. This means that these experiments would need to be redone many more times to be able to make statistically well founded conclusions. As it stands, this means that the results presented should be considered more as observations and suggestions for further work, rather than conclusive results.
6 Conclusions

The HMDS treated samples yielded slightly thicker layers of P3HT on the silicon for the same concentrations of P3HT, in addition to the films being slightly more difficult to spin coat and more fragile and got scratched easier during imprinting.

The samples were processed and their pattern quality differed for different concentrations of P3HT and for different surface treatments. The pattern filling seemed to increase with higher P3HT concentrations. Overall the pillar height ranged from roughly 10% minimum to a maximum of 30% compared to the master mold, while the pillar diameter were consistently of roughly 180% of the master mold. The patterning is not significantly different for the two different sample surfaces. All samples were imprinted with the same types of PDMS mold, which leads to the conclusion that there is something that needs to be done about the imprinting conditions to improve patterning.

The XRD shows a clear tendency for the imprinting pressure’s effect on the peak intensity. For untreated sample surfaces the peak intensities increase with pressure and for the HMDS treated sample surfaces the peak intensities decrease with pressure. In general the HMDS samples showed significantly higher peak intensities than the untreated samples. For all samples, only the strongest and most signature peak was investigated, for P3HT this is a 2θ angle of 5.4°. Increased peak intensities indicate a higher degree of crystallinity in the films. However found peaks were uncharacteristically broad and weak for films of P3HT, leading to suspect an experimental setup that was not optimal.

The films of the 0.75% Si samples showed a significantly lower absorbance and of less characteristic form than the other samples, which may perhaps be attributed to the poor pattern filling. In general the 5bar samples show a slightly higher absorbance peak for the amorphous P3HT at around 450nm, while the shoulder peaks indicating crystalline P3HT were hard to compare due to an interfering peak of unknown origin at about 660nm. As the 5 bar samples had a higher amount of amorphous P3HT there is an indication that increased pressure gives a higher amount of crystalline P3HT. However, the method clearly needs to be refined to give clearer results.

The conductivity measurements more or less show a tendency of higher conductivity for higher imprint pressures. Especially the 50bar samples on HMDS show a significantly higher conductivity while the samples on HMDS in general gives a slight increase in conductivity over the untreated samples.
7 Future research

In general HMDS treatment seems to increase performance on most investigated areas and is a promising treatment for P3HT films on silicon and it is suggested that further work is focused on such surface treated samples.

The methods used are indeed in need of refinement to increase patterning, reduce unwanted signals and to get values more in line with published values. To achieve this further work is required but should be possible to sort out.
8 References


### Table 5 - Conductivity measurements and calculations

<table>
<thead>
<tr>
<th>Sample A [mm²]</th>
<th>l(film) [nm]</th>
<th>l(Si) [μm]</th>
<th>U1 [mV]</th>
<th>I1 [mA]</th>
<th>U2 [mV]</th>
<th>I2 [mA]</th>
<th>U3 [mV]</th>
<th>I3 [mA]</th>
<th>R(1) [Ω+]</th>
<th>R(2) [Ω+]</th>
<th>R(3) [Ω+]</th>
<th>R(avg) [Ω+]</th>
<th>R(avg) - R(0) [Ω+]</th>
<th>ρ [Ωm]</th>
<th>σ [S/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75% Si 5 bar</td>
<td>9</td>
<td>85</td>
<td>525</td>
<td>505</td>
<td>64.6</td>
<td>995</td>
<td>183</td>
<td>1479</td>
<td>269</td>
<td>7.8</td>
<td>5.4</td>
<td>5.5</td>
<td>6.3</td>
<td>9.6E-02</td>
<td></td>
</tr>
<tr>
<td>0.75% Si 20 bar</td>
<td>9</td>
<td>85</td>
<td>525</td>
<td>510</td>
<td>43</td>
<td>1035</td>
<td>115</td>
<td>1501</td>
<td>183</td>
<td>11.9</td>
<td>9.0</td>
<td>8.2</td>
<td>9.7</td>
<td>9.0</td>
<td>1.5E-01</td>
</tr>
<tr>
<td>0.75% Si 50 bar</td>
<td>9</td>
<td>85</td>
<td>525</td>
<td>503</td>
<td>56.9</td>
<td>1005</td>
<td>237</td>
<td>1498</td>
<td>445</td>
<td>8.8</td>
<td>4.2</td>
<td>3.4</td>
<td>5.5</td>
<td>4.8</td>
<td>8.3E-02</td>
</tr>
<tr>
<td>1% Si 5 bar</td>
<td>9</td>
<td>101</td>
<td>525</td>
<td>503</td>
<td>46</td>
<td>1007</td>
<td>100</td>
<td>1513</td>
<td>208</td>
<td>10.9</td>
<td>10.1</td>
<td>7.3</td>
<td>9.4</td>
<td>8.8</td>
<td>1.5E-01</td>
</tr>
<tr>
<td>1% Si 20 bar</td>
<td>9</td>
<td>101</td>
<td>525</td>
<td>499</td>
<td>63.6</td>
<td>1029</td>
<td>371</td>
<td>1509</td>
<td>658</td>
<td>7.8</td>
<td>2.8</td>
<td>2.3</td>
<td>4.3</td>
<td>3.6</td>
<td>6.2E-02</td>
</tr>
<tr>
<td>1% Si 50 bar</td>
<td>9</td>
<td>101</td>
<td>525</td>
<td>500</td>
<td>47.6</td>
<td>1015</td>
<td>123</td>
<td>1509</td>
<td>200</td>
<td>10.5</td>
<td>8.3</td>
<td>7.5</td>
<td>8.8</td>
<td>8.1</td>
<td>1.4E-01</td>
</tr>
<tr>
<td>1% HMDS 5 bar</td>
<td>9</td>
<td>93</td>
<td>525</td>
<td>502</td>
<td>53.3</td>
<td>1006</td>
<td>158</td>
<td>1497</td>
<td>255</td>
<td>9.4</td>
<td>6.4</td>
<td>5.9</td>
<td>7.2</td>
<td>6.6</td>
<td>1.1E-01</td>
</tr>
<tr>
<td>1% HMDS 20 bar</td>
<td>9</td>
<td>93</td>
<td>525</td>
<td>507</td>
<td>73</td>
<td>1008</td>
<td>289</td>
<td>1503</td>
<td>509</td>
<td>6.9</td>
<td>3.5</td>
<td>3.0</td>
<td>4.5</td>
<td>3.8</td>
<td>6.5E-02</td>
</tr>
<tr>
<td>1% HMDS 50 bar</td>
<td>9</td>
<td>93</td>
<td>525</td>
<td>505</td>
<td>159</td>
<td>1009</td>
<td>358</td>
<td>1513</td>
<td>567</td>
<td>3.2</td>
<td>2.8</td>
<td>2.7</td>
<td>2.9</td>
<td>2.2</td>
<td>3.8E-02</td>
</tr>
<tr>
<td>1.25% HMDS 5 bar</td>
<td>9</td>
<td>119</td>
<td>525</td>
<td>499</td>
<td>51.9</td>
<td>1001</td>
<td>235</td>
<td>1497</td>
<td>444</td>
<td>9.6</td>
<td>4.3</td>
<td>3.4</td>
<td>5.7</td>
<td>5.1</td>
<td>8.7E-02</td>
</tr>
<tr>
<td>1.25% HMDS 20 bar</td>
<td>9</td>
<td>119</td>
<td>525</td>
<td>499</td>
<td>55</td>
<td>1019</td>
<td>193</td>
<td>1496</td>
<td>345</td>
<td>9.1</td>
<td>5.3</td>
<td>4.3</td>
<td>6.2</td>
<td>5.6</td>
<td>9.5E-02</td>
</tr>
<tr>
<td>1.25% HMDS 50 bar</td>
<td>9</td>
<td>119</td>
<td>525</td>
<td>503</td>
<td>136</td>
<td>999</td>
<td>317</td>
<td>1514</td>
<td>540</td>
<td>3.7</td>
<td>3.2</td>
<td>2.8</td>
<td>3.2</td>
<td>2.6</td>
<td>4.4E-02</td>
</tr>
<tr>
<td>no sample</td>
<td>9</td>
<td>506</td>
<td>750</td>
<td>1023</td>
<td>1596</td>
<td>0.7</td>
<td>0.6</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- Processing conditions on rr-P3HT.
Table 6 - Average conductivity results

<table>
<thead>
<tr>
<th>Treatment</th>
<th>( \sigma ) [S/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75% Si 5bar</td>
<td>10.1</td>
</tr>
<tr>
<td>0.75% Si 20bar</td>
<td>8.9</td>
</tr>
<tr>
<td>0.75% Si 50bar</td>
<td>16.4</td>
</tr>
<tr>
<td>1% Si 5bar</td>
<td>9.5</td>
</tr>
<tr>
<td>1% Si 20bar</td>
<td>13.8</td>
</tr>
<tr>
<td>1% Si 50bar</td>
<td>11.7</td>
</tr>
<tr>
<td>1% HMDS 5bar</td>
<td>9.3</td>
</tr>
<tr>
<td>1% HMDS 20bar</td>
<td>16.8</td>
</tr>
<tr>
<td>1% HMDS 50bar</td>
<td>26.3</td>
</tr>
<tr>
<td>1.25% HMDS 5bar</td>
<td>12.7</td>
</tr>
<tr>
<td>1.25% HMDS 20bar</td>
<td>12.7</td>
</tr>
<tr>
<td>1.25% HMDS 50bar</td>
<td>34.0</td>
</tr>
</tbody>
</table>