Carbon nanotubes and graphene polymer composites for opto-electronic applications

Nicolas Boulanger

Department of Physics
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“Les chiffres, c’est pas une science exacte figurez-vous!”
– Jean-Christophe Hembert as Karadoc, *Kaamelott*
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>BSE</td>
<td>back-scattered electrons</td>
</tr>
<tr>
<td>CCD</td>
<td>charge-coupled device</td>
</tr>
<tr>
<td>CF</td>
<td>chloroform</td>
</tr>
<tr>
<td>ETFE</td>
<td>ethylene tetrafluoroethylene</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width half maximum</td>
</tr>
<tr>
<td>GIXD</td>
<td>grazing incidence X-ray diffraction</td>
</tr>
<tr>
<td>HMDS</td>
<td>hexamethyldisilazane</td>
</tr>
<tr>
<td>LaB$_6$</td>
<td>Lanthanum hexaboride</td>
</tr>
<tr>
<td>MWNT</td>
<td>multi-wall carbon nanotube</td>
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<tr>
<td>NIL</td>
<td>nanoimprint lithography</td>
</tr>
<tr>
<td>ODCB</td>
<td>orthodichlorobenzene</td>
</tr>
<tr>
<td>P3HT</td>
<td>poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PDMS</td>
<td>polydimethylsiloxane</td>
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<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
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<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>RBM</td>
<td>radial breathing mode</td>
</tr>
<tr>
<td>SE</td>
<td>secondary electrons</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SSRL</td>
<td>Stanford Synchrotron Radiation Lightsource</td>
</tr>
<tr>
<td>SWNT</td>
<td>single-wall carbon nanotube</td>
</tr>
<tr>
<td>T$_g$</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>UV-vis</td>
<td>UV-visible spectroscopy</td>
</tr>
<tr>
<td>wt.%</td>
<td>weight percent</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
List of Publications

Included in this thesis


Other Works


Abstract

Carbon nanotubes are carbon based structures with outstanding electronical and mechanical properties. They are used in a wide range of applications, usually embedded in polymer in the form of composites, in order to affect the electronic behavior of the matrix material. However, as the nanotubes properties are directly dependent on their intrinsic structure, it is necessary to select specific nanotubes depending on the application, which can be a complicated and inefficient process. This makes it attractive to be able to reduce the amount of material used in the composites.

In this thesis, focus is placed on the electrical properties of the composites. A simple patterning method is presented which allows the use of extremely low amounts of nanotubes in order to increase the electrical conductivity of diverse polymers such as polystyrene (PS) or poly(3-hexylthiophene) (P3HT). This method is called nanoimprint lithography and uses a flexible mold in order to pattern composite films, leading to the creation of conducting nanotube networks, resulting in vertically conducting samples (from the bottom of the film to the top of the imprinted patterns).

In parallel, X-ray diffraction measurements have been conducted on thin P3HT polymer films. These were prepared on either silicon substrate or on graphene, and the influence of the processing conditions as well as of the substrate on the crystallinity of the polymer have been investigated. The knowledge of the crystalline structure of P3HT is of great importance as it influences its electronic properties. Establishing a link between the processing conditions and the resulting crystallinity is therefore vital in order to be able to make opto-electronic devices such as transistor or photovoltaic cells.
Chapter 1

Introduction

Polymer composites are used in many applications, ranging from photovoltaics to electrodes, as well as sensors and actuators.\textsuperscript{1,2} They are constituted of a polymer matrix and a filler material, affecting the properties of the resulting mix. Here, focus is placed on the electrical conductivity aspect of the material.

1.1 Percolation in carbon nanotube composites

When a conducting material is mixed in a non conducting matrix above a specific concentration, the whole composite becomes electrically conducting due to the creation of an interconnected network formed by the filler. This phenomenon is called \textit{percolation} and the minimal amount of material needed to be added to the matrix in order to obtain conductivity is called the \textit{percolation threshold} $\phi_c$.\textsuperscript{3} For filler quantities close to the percolation threshold, the electrical conductivity $\sigma$ and the percolation threshold are linked following:

$$\sigma \propto (\phi - \phi_c)^t$$  \hspace{1cm} (1.1)

where $\phi$ is the weight ratio of conducting material in the matrix and $t$ is called the critical exponent. According to percolation theory, $t$ determines the dimensionality of the percolating system, with values around 1.3 for 2D systems and around 1.9–2 for 3D systems.\textsuperscript{3,4}

$\phi_c$ will depend on the type of filler material, its geometry, and the processing conditions used to incorporate it in the polymer matrix.\textsuperscript{5} A percolation process can be identified by varying the amount of filler material in the composite and determine the resulting conductivity. For amounts below the percolation threshold, the composite conductivity will be the one of the matrix. The conductivity will then abruptly increase for amounts starting from the threshold, and will slowly reach a value closer to the conductivity of a network made from the filler material. This maximal conductivity might be lower than the conductivity of the filler itself, depending on the network as the contact resistance between the conducting elements is usually a limiting factor.\textsuperscript{6–8} As an example, the electrical resistivity of single wall carbon nanotubes has been reported to
be \( 5.1 \cdot 10^{-6} \, \Omega \cdot \text{cm} \), which is \( \approx 1.96 \cdot 10^7 \, \text{S} \cdot \text{m}^{-1} \) (as single nanotubes show ballistic charge transport), while maximal conductivity values of composites using nanotubes are much lower, with reported values as high as \( 10^4 \, \text{S} \cdot \text{m}^{-1} \)).

In this work, the main filler component which was used is single-wall carbon nanotube (SWNT) which are tubes made of carbon, and are presented in more details in 2.1.3. They have outstanding electrical and mechanical properties, making them interesting to use in a wide range of applications, such as in organic photovoltaic cells, probes for four-probe measurement techniques, chemical sensors, batteries, electrodes... Here, they were used for their electrical properties, as well as their high aspect ratio, which means that it is possible to increase the conductivity of a composite by a great amount using only a tiny amount of material, resulting in low percolation thresholds. This also means that adding nanotubes into a transparent matrix can result in transparent electrodes with high light transmittance, as the additional light absorption by the nanotubes is expected to be limited due to their low amount. Previously reported values varies widely depending on the type of nanotube as well as the matrix material and the processing conditions. The lowest one reported to date in the case of single wall carbon nanotubes in a polystyrene matrix is 0.17 wt.%. This is of importance as this project is using polystyrene as a matrix material in order to demonstrate the techniques used to create the nanotube network. Indeed, as polystyrene is a non conducting material, it is then simpler to attribute the electrical conductivity of the composite after processing to the nanotubes present in the material.

Poly(3-hexylthiophene) (P3HT) is also used and is a semiconducting polymer with a wide array of applications, including photovoltaic devices, chemical sensors, transistors... This polymer can be used in association with SWNT, resulting in improved stability of photovoltaic devices as well as increased light absorption properties and reduced charge recombination in the devices, which has the potential to result in more stable and efficient cells. It is therefore desirable to better control the nanotube distribution in the polymer, so that lower amounts of material are required to still benefit from the presence of the SWNT. The effects of engineering the nanotube network within the polymer are shown in papers I to IV, where it can be seen that patterned composites showed higher conductivities and lower percolation thresholds than random, non controlled networks.

### 1.2 Synchrotron X-ray diffraction of polymers

In parallel to this work, X-ray diffraction (XRD) measurements were conducted in association with my colleague Vasyl Skrypnychuk in order to determine the crystalline structure of specific polymers and its effect on their electrical conductivity, focusing mostly on P3HT based samples. The crystallinity of a polymer is an important feature as it influences its opto-electronic properties. Indeed, it has been previously demonstrated that by controlling the orientation of crystallites in a polymer, it is possible to greatly affect its charge transport properties along specific directions. It is therefore needed to be able to link
the processing conditions of a composite to its crystalline structure and resulting electronic features in order to optimize the fabrication process of organic electronic devices, whether it be transistors or photovoltaic devices. In particular, the effect of graphene as a substrate on P3HT has been investigated. Graphene is a form of carbon, presented in more detail in section 2.1.2. It has been used in multiple applications, including as electrode material in photovoltaic devices.\textsuperscript{30–33} Here, it was used as a substrate on which P3HT was spun and processed, whether by annealing at different temperatures or by patterning using different pattern dimensions and imprinting conditions. The resulting crystalline structure was then measured by XRD, as well as the electrical conductivity and charge mobilities, as presented in papers V and VI.

XRD gives information about the crystalline structure of a material, which can be used to determine the effects of processing conditions, or interaction between components, on the material. This is achieved by hitting a sample with X-rays of a chosen wavelength at a specific angle, and by recording the diffraction patterns resulting from this exposure. Two main configurations have been used in this work, presented in figure 1.1. The first one is the Bragg configuration, which consists in measuring specular diffraction, where the angle of the incoming beam on the sample is the same as the angle between the detector and the sample. This angle is scanned and the resulting diffraction spectrum is extracted. Such a spectrum can be seen in figure 3.9 section 3.2. The second setup is a grazing incidence X-ray diffraction (GIXD) setup, where the X-ray is incoming at a fixed, small angle (in this work, either 0.08° or 0.13°) and the diffraction patterns are recorded on an area detector.

From the diffraction spectra, it is possible to extract information such as the interplanar distance of the material by taking advantage of the Bragg law:

\[ n\lambda = 2d\sin \theta \quad (1.2) \]

where \( n \) is an integer representing the order of reflection, \( \lambda \) is the wavelength of
the incoming rays, $\theta$ is the angle of incidence and $d$ is the interplanar distance. It is also possible to estimate the coherence length $t$ based on the full width half maximum (FWHM) $B$ of the diffracted peak using the Scherrer formula:

$$t = \frac{0.9 \lambda}{B \cos \theta_B}$$  \hspace{1cm} (1.3)

where $\theta_B$ is the diffraction angle. More about XRD in general can be found in the book by Cullity.\textsuperscript{34}

1.3 Outline

First, some of the materials used in this work as well as a general review of the different techniques used to both create and characterize the different samples are presented in chapter 2. Then, a more detailed description of the preparation process as well as the resulting measurements is available in chapter 3. Finally, a conclusion is available in chapter 4 and a short presentation of the different papers included in this thesis is in chapter 5.
Chapter 2

Materials and methods

2.1 Materials

2.1.1 Polymers

Polystyrene (PS) was mostly used as it is a well known polymer, easy to process and electrically insulating. This last property is of importance when studying the electrical conductivity dependence on the filler content in composites. Indeed, by using an insulating matrix, it is much easier to attribute the differences in conductivities to the filler, in this case carbon nanotubes. Furthermore, the fact that is is easy to dissolve using most available solvents and its relatively low glass transition temperature ($T_g$) makes it ideal to test different patterning methods such as thermal and room temperature nanoimprint lithography. In order to study the optical properties of composites, poly(methyl methacrylate) (PMMA) was used as it has high light transmittance for most of the visible spectrum. It is also non conducting and relatively easy to process, making it possible to study both electrical and optical properties of the prepared composites.

Furthermore, poly(3-hexylthiophene) (P3HT) was employed as it is a commonly used semiconducting polymer for opto-electronic applications. It has been used in order to create devices such as photovoltaic cells, organic field effect transistors, gas sensors...\cite{18,19,21} In this work, it was also used in conjunction with carbon nanotubes in order to see if it is possible to affect the P3HT conductivity in the same way than PS was affected. P3HT also tends to crystallize, with a crystallographic structure as defined in figure 2.1.\cite{35} The lattice parameters are defined in the figure, with $a$ from backbone to backbone ($\approx 16.8$ Å), $b$ along the stacking direction ($\approx 7.66$ Å) and $c$ between the alkyl chains ($\approx 7.7$ Å).\cite{36} The way the polymer chains are packed as well as the crystal structure of the P3HT have a huge influence on the electronical properties of the material, which makes the knowledge of its crystallinity of great importance.\cite{37,38}
2.1.2 Graphene

Graphene is a form of carbon consisting in a single atom thick honeycomb structure, shown in figure 2.2a. It has been first observed by transmission electron microscopy (TEM) in 1948, and has been isolated and characterized for the first time by Novoselov et al in 2004.\textsuperscript{39,40} It is a zero-bandgap semiconducting material, and its electronic properties are sensitive to defects in its structure.\textsuperscript{41} It has a high electron mobility $\mu$, with values of $\mu \approx 2.6 \cdot 10^4 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$.\textsuperscript{42} Single layer graphene has a transmittance of 97.7% on the visible spectrum, and each additional layer adds another 2.3% opacity.\textsuperscript{43} It is used in multiple applications, including in chemical sensors, photovoltaic devices, phototransistors, memory devices...\textsuperscript{31,44–47}

In this work, it was used as a substrate after being deposited on silicon. The graphene was prepared by collaborators using a chemical vapor deposition process on copper, before being transferred on the silicon substrates.\textsuperscript{48} A P3HT film was then deposited on it from solution and either patterned or simply annealed. The crystallinity of the polymer, as well as its electrical properties, were then measured, in order to establish the influence of the processing parameters on the polymer characteristics.

2.1.3 Carbon nanotubes

Carbon nanotubes were discovered by Iijima in 1991.\textsuperscript{49} They consist in rolled sheets of carbon, and can exist as single-wall carbon nanotube (SWNT) or
Figure 2.2: (a) Graphene sheet presenting the chiral vector, as well as (b) single wall and (c) multi-wall carbon nanotube. In (a), $a_1$ and $a_2$ are unit vectors of the graphene sheet. $C_h$ is the chiral vector defined as $C_h = n \cdot a_1 + m \cdot a_2$.

multi-wall carbon nanotube (MWNT), where respectively one or several graphene sheets are rolled into each other, as shown in figure 2.2.

It is possible to specify two unit vectors $a_1$ and $a_2$ based on the graphene sheet which define a coordinate system within the graphene plane, as shown in figure 2.2a. Nanotubes can be constructed from planar structure by generating a vector $C_h$ by a linear combination of $a_1$ and $a_2$ as $C_h = n \cdot a_1 + m \cdot a_2$ where $(n,m)$ are positive integers and $|m| < |n|$. The sheet is then rolled so that both extremities of the chiral vector $C_h$ are in contact. The $(n,m)$ pair defines what is called the chirality of the nanotube. Nanotubes of the type $(n,n)$ are called armchair nanotubes while $(n,0)$ are called zigzag nanotubes. It should be noticed that the chirality of the nanotube has a direct relation to the tube diameter $d_t$, as it defines the length of the chiral vector and therefore the tube circumference. Indeed, $d_t = |C_h|/\pi = a \cdot \sqrt{n^2 + m^2 + n \cdot m}$ where $a$ is the lattice constant.

The chirality is an important characteristic as it determines the electronic properties of the nanotube. A way to determine if a SWNT has a metallic or semiconducting behavior is to check if $(n - m)$ is a multiple of 3. If that is the case, the nanotube has a metallic behavior, and if $(n - m)$ is not a multiple of 3 then it acts as a semiconductor. It should be noted that this is true in the case of defectless nanotubes, as defects are known to affect the electronic properties of the SWNT. Interested readers can refer to Saito et al for more details.\textsuperscript{50}

Nanotubes are typically produced in bulk, with a wide, uncontrolled, range of chiralities in a mixture of both SWNTs and MWNTs. Separating SWNTs and MWNTs can be done for example by centrifugation by taking advantage
of the difference in density between the single-wall and the multi-wall carbon nanotubes. Selecting a specific chirality is however more complicated. Indeed, the production method, as well as the choice of catalyst for the synthesis, strongly influences the obtained chiralities.\textsuperscript{51} It is possible to reduce the spread of chiralities by careful control of the growth process,\textsuperscript{52,53} but most methods are focusing instead on post-synthesis chirality selection. This selection can be achieved by using appropriate surfactants before proceeding to ultracentrifugation, taking advantage of the difference in weight between the surfactant-coated nanotubes and the non-coated ones.\textsuperscript{54} A similar method is possible where the surfactant promotes the deaggregation of specific nanotubes in solvent, enabling their suspension in solution.\textsuperscript{55} Destructive methods also exist where nanotubes of specific chiralities are oxidized by laser light before being removed.\textsuperscript{56} A promising way of selecting nanotubes based on their chirality is to use DNA or polymers to selectively coat nanotubes of specific chiralities.\textsuperscript{57} It has been shown that salmon genomic DNA is useful to select (6, 5) nanotubes, while poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) can select (7, 5) tubes.\textsuperscript{58,59}

\section{2.2 Methods}

\subsection{2.2.1 Fabrication}

\textbf{Nanoimprint lithography}

Nanoimprint lithography (NIL) is a technique using compression molding of a material to generate patterns based on the mold used. Chou et al showed that this technique can be used to create small, sub-25 nm patterns.\textsuperscript{60} NIL works on thermoplastics by heating the polymer to be formed above $T_g$ before pressing a mold onto it. Depending on the polymer, solvent vapor can be used instead to soften the polymer, removing the need for heat. After enough time so that the polymer fills the mold cavities, the sample is cooled down before removing the mold, leaving the imprinted patterns. This procedure is illustrated in figure 2.3. The mold is usually made of silicon with an anti-sticking layer obtained by a silanization process.\textsuperscript{61} It is also possible to use a polymeric, flexible mold in order to reduce the use of the silicon masters, as making these can be time consuming and expensive.\textsuperscript{62} This also removes the need for the anti-sticking layer on the surface of the mold. Using this technique makes it possible to obtain a wide range of dimensions, from a few micrometers to a few nanometers, as well as making it possible to directly create photovoltaic devices with complex 3D architectures.\textsuperscript{63–65} Some features achievable using this technique include cylindrical pillars such as the one made for this work, cones, nanowires, lines...\textsuperscript{66–69} The imprinting process is fast and is a parallel process, where rows of patterns can be achieved in a single operation, compared to series process such as ion beam lithography which implies the creation of one pattern after another. This allows for mass production of wide areas on different types of substrates, making it possible to use roll to roll processes.\textsuperscript{70}

During the application of pressure (figure 2.3b), the polymer flows to fill the mold cavity. By interrupting the imprinting process before the cavity is
Figure 2.3: Nanoimprint lithography process. (a) the blue mold is placed on the soften brown polymer, deposited beforehand on the gray silicon substrate. (b) Pressure is applied and the mold is pushed down on the polymer. (c) the mold is removed, leaving the imprinted patterns.

completely filled, it is possible to make partial imprints, as shown in the paper by Ryu et al.71 Indeed, depending on the imprint parameters (pressure, temperature, time), it is possible to affect how the polymer is flowing in the cavities.72,73 Depending on the viscosity of the polymer during the imprinting, it is even possible to carry small particles along with the flowing polymer.74

2.2.2 Characterization

UV-vis spectroscopy

If one wants to make transparent electrodes, one needs to maximize the transmittance and reduce the reflectance as much as possible. Here, UV-visible spectroscopy (UV-vis) was used in order to measure both transmittance and reflectance on a wide spectral range, from wavelengths of 200 nm to 2500 nm. As the electrode was usually made on a glass substrate, it was necessary to take the glass into account when measuring the transmittance. This was achieved by splitting the incoming light in two paths, one going through a reference glass slide with the resulting measured intensity $I_0$ and the other going through the sample with resulting intensity $I$. The transmittance $T$ was then calculated as $I/I_0$ and is usually expressed in percent. The absorbance $A$ was derived from the transmittance as $A = -\log_{10} T$.

When measuring reflectance, both the reference slide and the sample were measured and compared against a reference sample, which was a polymer giving a mostly 100% diffuse reflectance over the whole spectral range. The reflected light intensity was compared to the reference intensity to give the reflectance
Figure 2.4: UV-vis measurement setups. (a) shows the transmittance measurement setup, with light coming through both the reference path (glass slide) and the sample path, allowing the measurement of the reference intensity \( I_0 \) and the sample intensity \( I \). (b) shows the reflectivity measurement setup, where this time the reference is a 100% reflecting polymer (Spectralon). The samples are placed against a reflection sphere in order to capture all reflected light. The setup shown in (b) allows for measurement of the diffuse reflection. In order to obtain the total reflection, the sample is placed at an angle against the sphere in order to capture the specular reflectance in addition to the diffuse one. Nothing is placed behind the sample, allowing light to be transmitted as well.

The data was then interpreted by comparing the values obtained for the glass slide with the one from the sample, in order to determine the effect of the transparent electrode on the reflectance values. Both the transmittance measurement configuration as well as the reflectance measurement configuration are schematized in figure 2.4.

Raman spectroscopy

Raman spectroscopy consists in shining monochromatic light, usually from a laser, onto a sample, and looking at the spectra of the reflected light. When hitting the sample, the light interacts with bonds in the molecules constituting the material, creating an electric dipole moment deforming the molecule in a periodical manner, making the molecules vibrate. When a molecule is excited, it can deexcitate following either of three possibilities:

- The bond returns to its initial vibrational state, re-emitting a photon at the same energy than the incoming photon. This is Rayleigh scattering, and is the most common deexcitation path.

- The bond returns to a vibrational state at a higher energy level than initially, releasing a photon with a lower frequency than initially received. This is called Stokes scattering.

- The bond returns to a lower energy vibrational state compared to initially,
leading to the emission of a higher frequency photon than received. This is called \textit{anti-Stokes scattering}.

The Raman spectra is constituted by measuring these shifts in frequency compared to the incoming light frequency, and is usually plotted as intensity versus Raman shift in cm$^{-1}$. More can be found in the book by Chalmers.$^{75}$

One useful application of Raman spectroscopy is to do mapping, where the sample is scanned over an area instead of at a single point. This makes it possible to localize specific components in a material, such as the presence of carbon nanotubes in a composite. It is also possible, by using polarized filters, to check for alignment of specific particles.$^{76-78}$

\section*{Electrical conductivity measurements}

Electrical conductivity measurements are critical to evaluate the electrical properties of both the electrodes as well as the nanotube-based composites. The conductivities were measured both in in-plane and out-of-plane configurations, as illustrated in figure 2.5. In order to measure the electrical conductivity, contacts were made with two electrodes, a voltage difference was applied and the resulting current was measured. The voltage difference was usually swept from -3 to +3 V in order to establish if the conductivity followed an ohmic behavior or not.

In the case of in-plane conductivity measurement, two conducting stripes of length \( L \) separated by a distance \( D \) were deposited on the substrate and the film/composite was made on top of it. In this case, instead of the conductivity, the sheet resistance was calculated as

\[ R_s = \frac{U}{I} \cdot \frac{L}{D} \tag{2.1} \]

where \( U \) is the applied voltage difference, \( I \) the measured current and \( R_s \) the sheet resistance in \( \Omega/\square \).

In the case of out-of-plane conductivity measurements, the conductivity \( \sigma \) was calculated as

\[ \sigma = \frac{U}{I} \cdot \frac{h}{A} \tag{2.2} \]

where \( U \) is the applied voltage difference, \( I \) the resulting current, \( h \) the sample height, and \( A \) the contact area. In this latter case, a flexible electrode was used in order to have a good contact with the film underneath. The electrode was made of cured polydimethylsiloxane (PDMS) with either gold or silver deposited on top. This PDMS part was then stuck under a brass cube which provided some pressure so that the electrode conformed better to the measured film, as well as to improve the stability of the system. This technique was used instead of simply evaporating a metal layer on top of the polymer film in order to avoid diffusion of the metal inside the polymer layer during evaporation, which could lead to shorts as well as changing the conductivity of the measured film. Also, in the case of patterned samples, this was done in order to insure proper contact with the top surface of the pillars while avoiding the base layer of the film. This made sure that the measured vertical conductivities were
Figure 2.5: Electrical conductivity measurement setups. (a) shows the setup for the out-of-plane conductivity measurements, while (b) shows the in-plane configuration with the two stripes deposited on the sample substrate. The voltage is swept by a sourcemeter and is measured at the same time, as well as the resulting electrical current.

dependent on the materials within the patterns. Furthermore, the side of the patterns made a high angle with the bottom substrate (close to 90°), which made it impractical to obtain good continuous coverage of the whole sample area if metal evaporation was to be used.

Atomic Force Microscopy

Atomic force microscopy (AFM) was used in order to accurately measure heights and film thicknesses for the different types of sample made. It can also be used to determine the periodicity and diameters of imprinted pillar arrays, although one should be careful to take into account the artifacts due to the scanning direction. The AFM consists in a scanning part as well as a detector. The scanning part is a tip attached to a cantilever, which is itself attached to a piezoelectric component, used to make the tip vibrate as well as to control its height compared to the surface to scan. The detector system consists in a laser which is reflected from the top of the cantilever to a four-quadrant detector. This detector is used to determine the bending of the cantilever compared to its position before scanning. A typical system is shown in figure 2.6. Achievable resolutions are in the order of 0.1 nm, depending on the configuration used as well as the quality of the tip.

The AFM was used in tapping mode, a mode in which the cantilever (as shown in figure 2.6) is oscillated close to its resonance frequency at a given amplitude. The surface is then scanned, while the oscillating amplitude is measured using a four-quadrant detector. When the tip gets closer or further away from the surface, the amplitude is changed due to the change in contact between the tip and the sample surface, and the height of the tip is modified thanks to a feedback loop so that the oscillating amplitude returns to its initial value. The image is then obtained by recording these height adjustments as
Figure 2.6: Schematics of an AFM. The tip is attached to the cantilever and scans the sample surface. The cantilever is oscillated near its resonance frequency and its position is tracked by the reflection of the laser hitting the 4-quadrant detector.

well as the tip position, resulting in a height map of the sample surface. This imaging method limits the contact between the sample and the tip, reducing damage to the sample in the case of soft materials, as well as reducing the tip wear and tear. More about AFM can be found in the book by Haugstad.\textsuperscript{79}

**Scanning Electron Microscopy**

Scanning electron microscopy (SEM) was used to observe the different types of patterns on a larger scale than with AFM, as well as to locate specific constituents in composites. In order to obtain an image, an electron beam is generated and focused through a set of electromagnetic lenses, before being scanned onto the sample, which is placed on an electrically conducting holder in order to avoid charging.

When hitting the sample, electrons from the beam are ejecting electrons from the valence band of the materials being observed, which are then detected. These ejected electrons are called secondary electrons (SE) and give information on the sample topography. Some electrons from the incoming beam are reflected back from the sample due to scattering, and can be detected as well. They are called back-scattered electrons (BSE) and give information on the sample density. X-rays are also emitted from the sample, giving information about the sample constituents. More can be read about SEM in the book by Reimer.\textsuperscript{80} This imaging technique is commonly used in materials science.\textsuperscript{81}

One use of the SEM in this project was to observe nanotube bundles within patterned composites. This involved fracturing the samples in order to access
the inside of the patterns. To avoid deformation of the polymer due to the cut, a freeze-fracture technique was used where the sample was dipped in a liquid nitrogen bath on a hard metal surface and was held onto its edge. A scalpel blade was cooled by dipping it in the liquid nitrogen bath and was then positioned on the top edge before being hit with a small hammer. The resulting cut was usually straight, as it was guided along the crystalline planes of the silicon substrate. The sample was then placed vertically in a specific holder before being placed in the SEM, allowing imaging of the section and making it possible to look for nanotube bundles and other filler material in the composites.

**X-ray Diffraction**

X-ray diffraction (XRD) is a well developed technique which can be used to determine the crystalline structure of materials. XRD takes advantage of the fact that X-rays of a specific wavelength incoming on a material at a specific angle will diffract depending on the crystalline structure of the material.

In order to have a usable measurement, it is important to have X-rays of a single, stable wavelength, so that the only non-fixed variables in equation 1.2 from section 1.2 are the angle of incidence and the interplanar distance which will depend on the studied material. The incoming x-rays should be as collimated as possible, in order to get good control on the angle of incidence and therefore the possibility of obtaining a high resolution on the XRD scan. Finally, the incoming beam should have a high flux in order to being able to limit the exposure time, allowing for faster scans as well as limited sample damage due to the exposure of the sample to the beam. These three parameters are usually combined in a figure of merit called the *brilliance*, which is defined as

\[
B = \frac{P_{0.1\%BW/s}}{\delta \cdot A} \tag{2.3}
\]

where \(B\) is the brilliance, \(P_{0.1\%BW/s}\) is the photon flux in photons per seconds, \(\delta\) is the beam spread in mrad\(^2\), \(A\) is the beam cross-sectional area in mm\(^2\). \(P_{0.1\%BW}\) refers the photons which have their wavelength contained in a bandwidth of 0.1\% of the chosen beam energy.

In this work, it was possible to get access to the Stanford Synchrotron Radiation Lightsource (SSRL) at SLAC National Accelerator Laboratory, using two XRD configurations on two different beam lines. The first one was XRD in Bragg configuration where the incoming X-ray was fixed in position and both the sample stage as well as the detector were rotating in order to record the diffraction spectrum of the sample studied. The setup was available on beam line 2-1 and is shown in figure 2.7, while a diagram of the Bragg configuration is presented in figure 1.1a in section 1.2. The detector was a point detector, which means that the sample and the detector had to be rotated between each measurement in order to construct the diffraction spectra. The setup was controlled by a computer and an example of the sample alignment as well as the measurement procedure is detailed in appendix A.

The second setup was a grazing incidence X-ray diffraction (GIXD) con-
Figure 2.7: (a) X-ray diffraction setup on beam line 2-1 at SLAC, and close-up on the sample holder in (b). The sample is placed in the red square, in a chamber with a flow of helium. The X-rays are coming along the red arrow, and the detector is placed further away along the green arrow. The goniometer is visible in the back.

The measurements were also much faster than those obtained using a point detector as a single exposure was needed to obtain the full diffraction spectrum in all directions. This type of measurement was done on beam line 11-3 on first a plate detector and later on a charge-coupled device (CCD) detector, as shown in figure 2.8.
Figure 2.8: Grazing incidence X-ray diffraction setup on beam line 11-3 at SLAC using either the plate detector in (a) or the CCD detector in (b). In the green square is the area detector, in the blue square is the sample holder and a box containing samples is lying in the red square. (c) shows the sample holder, with the sample being positioned in the red square. The plastic tubing on the left provides the helium flow to fill the chamber and the brown plastic tube on the right is for the vacuum holder. The copper wire connects the thermocouple. The X-rays are incoming along the red arrows.
Chapter 3

Results

3.1 Carbon nanotube based composites

3.1.1 Preparing the films

Making the composites involved three main steps: preparing the polymer solutions as well as the nanotube dispersions, spinning the polymer in a film on the substrates and potentially pattern them using nanoimprint lithography (NIL). The composites were based on a two layer model, where a thin, nanotube-rich layer was first spun, and a pure polymer layer was spun on top of it. This process is schematically shown in figure 3.1, while the patterning process is shown in figure 2.3 page 9. The samples were then characterized first by measuring the electrical conductivity, and then by determining their geometry by atomic force microscopy (AFM) and if needed scanning electron microscopy (SEM). UV-visible spectroscopy (UV-vis) was also used when making transparent electrodes to assess their transmittance and reflectance.

The nanotubes used during the project were mainly provided by Sigma-Aldrich and consisted in a mixture of semiconducting (mostly \((6, 5)\)) and metallic tubes, with more than 90% of the nanotubes being semiconducting. They were dispersed at diverse concentrations in orthodichlorobenzene (ODCB) by ultrasonication. They were dispersed in ODCB as it is one of the solvent where the single-wall carbon nanotube (SWNT) dispersion is the most stable. Furthermore, this solvent can also dissolve both polystyrene (PS) and poly(3-hexylthiophene) (P3HT) which were used to make the composites, making it a good choice for preparing the nanotube dispersions. The solution for the first layer used either only ODCB as a solvent, or a 50:50 ratio of ODCB:chloroform (CF) by volume. The addition of chloroform was mostly in the case of PS based solution, in order to decrease the drying time of the film during spinning and therefore reducing dewetting. The solvents used for the second layer were either pure CF, pure ODCB, mixtures of the two at various ratios, or toluene, depending on the polymer used.

The first layer should ideally only contain nanotubes. However, ODCB has a vapor pressure of 1.22 mm Hg at 20°C which means the drying time by
Figure 3.1: (a) polymer solution was deposited on the substrate before being spun to form (b) the first layer on the substrate. (c) the solution for the second layer was deposited on top and spun to form (d) the second layer, creating the double layer composite.

evaporation can be long\textsuperscript{84}. This means that a too high spin speed can simply results in the ejection of all the material, requiring a simple deposition of the solution and slow drying instead. Furthermore, when drying, the nanotubes re-aggregate, leading to a non-uniform distribution of the nanotubes on the substrate. In order to prevent the nanotubes from agglomerate during drying of the layer, a small amount of polymer (\(\approx 0.5\) weight percent (wt.\%)) was added to the dispersion prior to deposition. The deposition was then done by spin coating in order to obtain a 20–30 nm thick layer. The second layer was formed by spin coating on top of the first layer, with a polymer solution containing no nanotubes. Composites consisting of single layer of nanotubes and polymer mixed in solution were also made as control samples.

The nanotube concentration in the composites was calculated by assuming full dispersion of the nanotubes from the first layer into the whole film. This is probably not true, but it should be noted that the polymer used to make the film was the same for both layer, meaning the first layer was disturbed by the deposition of the second one, with probable intermixing between the two. At low concentrations, this intermixing was not enough to create percolating path from bottom to the top of the films, as some samples became electrically conducting only after patterning. The nanotube concentration \(\Phi\) in the composite was therefore estimated as

\[
\Phi = \Phi_{1st\ layer} \cdot \frac{h_{1st\ layer}}{h_{film}}
\]  

(3.1)

where \(\Phi_{1st\ layer}\) is the nanotube concentration in the first layer, \(h_{1st\ layer}\) is the first layer thickness and \(h_{film}\) is the total thickness of the composite. In the case of papers I and II, the nanotube dispersion was filtered in a 0.45 \(\mu\)m ethylene tetrafluoroethylene (ETFE) syringe filter prior to be mixed with either P3HT
or PS. This was done in order to limit aggregation, and can result in a reduced amount of nanotubes in the solution compared to what is calculated. This filtration was not done in papers III and IV, where the nanotubes in solution were taken using a syringe and avoiding the bottom of the vial where most of the aggregates were located. It was avoided in these later papers as it made it difficult to accurately control the nanotube concentration in the composites.

3.1.2 Patterning the composites

Once prepared, the composites were patterned by NIL. This procedure has been briefly presented on page 8 as well as in figure 2.3. Both thermal and solvent-assisted NIL were used in association with flexible molds made either of ETFE or from polydimethylsiloxane (PDMS).

ETFE molds were made by cutting a ETFE sheet and placing it on top of a silicon master. The ensemble was then placed in the thermal imprinter, heated up to 215°C and a pressure of 30 bar was applied for 10 minutes before being cooled and removed from the imprinter. The PDMS mold was made by using Sylgard 182 or Sylgard 184 which consisted in liquid PDMS and its crosslinker. The PDMS was first poured in a beaker and mixed with the crosslinker in a 10:1 ratio and then thoroughly stirred in order to make sure that the crosslinker was well dispersed in the PDMS. The beaker was then placed in a desiccator under vacuum for about 30 minutes so that air bubbles created while stirring were removed from the solution. The beaker was then taken out and its contents were slowly poured over the silicon master which was placed in a Petri dish on aluminum foil. The dish was then placed in an oven and heated at 150°C for about 5 hours before cooling slowly. The crosslinked PDMS and the master were then taken out of the dish and the PDMS was then carefully detached from the master, resulting in the PDMS copy. It should be noted that the polymer copy was a negative of the silicon master, meaning that the features later created in the composites were reproductions of the features of the silicon master. Once the mold was ready, the imprint was done by using the polymer copy as a mold, placed on top of the composite. In the case of thermal NIL, the imprint temperature and pressure depended on the polymer to be patterned. In this work, it was no more than 150°C for the PS, and around 200°C for P3HT, while the pressure used varied between 5 and 20 bar.

Room temperature NIL used solvent vapor instead of heat in order to soften the polymer to be patterned. A typical setup uses a home-made imprint chamber which is shown in figure 3.2. The mold was fixed to the piston while the composite was placed in the chamber. The chamber was then closed and solvent vapor was introduced while the piston was held in its upper position, preventing contact of the mold on the composite so that the polymer was fully exposed to the vapors and could soften. After some time determined by trial and error, a weight was placed on the piston which was moved down so that the mold contacted the composite. The solvent vapor was then replaced with a nitrogen flow in order to dry the polymer and to harden it, before demolding the sample. When patterning P3HT and depending on the patterns to imprint, solvent vapor by itself was not enough to fully soften the polymer. In this case,
the second polymer layer of the composite was obtained by spin coating at the chosen speed for very short amount of time, typically one or two seconds, so that the extra material was ejected while the film remained wet, and was then immediately placed in the chamber in contact with the mold. Solvent vapor was then introduced and could still reach the polymer by diffusion through the PDMS mold, allowing the polymer to stay soft for longer times.

3.1.3 Characterizing the composites

Once prepared, the composites had to be characterized in order to measure their geometrical, optical and electrical properties. Geometrical characterization was achieved by AFM and SEM, although AFM was usually performed last as it was needed to make scratches in the sample in order to determine the residual layer thickness of the imprints, which made it a destructive method. AFM allows for a precise determination of the patterns height, and is a way to reconstitute the 3D topography of the samples. SEM makes it possible to measure patterns lateral dimensions such as periodicity and diameter, as well as looking at the uniformity of the patterns. It is also a way to look for filler material within composites. Figure 3.3 shows the AFM and SEM of a 400 nm nanopatterned P3HT-based composite. Artifacts can be seen quite clearly on the 2D AFM image, where the slope is lower on the right edge of the pillars, which corresponds to the scanning direction. This is due to the close to 90° angle between the bottom surface and the pillar lateral area, which can be seen more accurately in the SEM picture where this asymmetry in the pillars is not
visible. This too high angle results in partial imaging of the tip by the sample instead of the other way round.\textsuperscript{85}

Electrical measurements of the composites were done using a sourcemeter, which allows for sweeping of the applied voltage difference and recording the resulting electrical current. In order to establish electrical contact, the samples were stuck on a brass plate using silver paste, while the top electrode was placed on a brass cube using silver paste, as shown in figure 3.4. These measurements were also done on composites containing various amounts of nanotubes, in order to determine the percolation threshold. Indeed, carbon nanotubes have been shown to present a percolation behavior, meaning that electrical conduction occurs only above a specific nanotube loading, the percolation threshold.\textsuperscript{86} This threshold depends on the type of nanotubes used, as well as the matrix material and the processing conditions. This type of conductivity evolution as a function of the loading as defined in equation 1.1 in section 1.1 can be seen in figure 4 from paper IV. In an article in preparation, a percolation threshold for a sample patterned at 150$^\circ$C with nano-pillars showed a percolation threshold of $\approx 1.8 \cdot 10^{-5}$ wt.% SWNT in polystyrene, compared to a value of $\approx 2.5 \cdot$
$10^{-2}$ wt.\% in the case of a random network. It should be noted that the values for the critical exponent $t$ as defined in equation 1.1 were 1.3 in the case of the non patterned network, and 1.65 for the nano-pattern. The value for the random network suggested a 2D percolating behavior, but this was not so clear for the nano-patterns, as a value of 1.9–2 was expected in the case of a 3D network.\textsuperscript{3} It has been shown previously that the values obtained for $t$ can show a wide variation, as can be seen in the article by Bauhoffer et al.\textsuperscript{87} Non universal values for the critical exponent have been reported as early as 1979 for specific non-homogeneous conductors distributions.\textsuperscript{88} One model by Balberg involving tunneling which can occurs between conducting components in the composite has been showed to lead to non universal values of the critical exponents. It has been successfully tested experimentally by using carbon black as a conductor in polyvinylchloride (PVC), which gave a critical exponent value of 4, and other measurements gave a value of 2.8.\textsuperscript{89} Other models are based on either a conducting domain where spherical holes are randomly placed (Swiss-cheese model) or a non conducting media randomly filled with interpenetrating conducting spheres (inverted Swiss-cheese model). Both these models allow for non-universal values of the critical exponents, at the exception of 2D percolating systems in the Swiss-cheese model where the critical exponents were found to have their universal value of 1.3.\textsuperscript{90,91} Equation 1.1 can therefore be used mostly to determine the percolation threshold, but determination of the dimensionality of the system cannot be assessed in a reliable manner.

The measurements showed a strong increase in conductivity when patterning the composites, compared to smooth composites with similar loadings, as shown in the included articles, and more particularly papers III and IV. The main hypothesis is that this increase is attributed to the redistribution of the nanotubes within the composite due to the flow of polymer occurring during the patterning, as it has previously been shown that it is possible to carry small particles along the polymer flow during patterning.\textsuperscript{74} A first way to determine nanotube redistribution is to use X-ray photoelectron spectroscopy (XPS) to measure the evolution in carbon content at the surface of the samples. For this measurement, P3HT was used as this polymer contains sulfur in the chain, which allows to measure the ratio of carbon content to sulfur. It is expected
that as the nanotubes migrate to the composite surface during imprinting, the values of carbon to sulfur ratio (C/S) should increase in patterned areas compared to non patterned composites. This has been shown in paper II: a pure P3HT sample containing no nanotubes had a C/S value of ≈12.2, while a non patterned composite showed a ≈12.1 values, namely no nanotubes migrated to the surface. After patterning, a micro-patterned sample showed a C/S value of ≈21.1 and a nano-patterned composite showed a value of ≈18.1, suggesting a migration of nanotubes toward the top surface of the patterned composites.

Furthermore, Raman spectroscopy was done in order to localize the nanotubes in a micro-patterned composite. This technique is commonly used to characterize nanotubes either by themselves or within composites. A HeNe laser with a 633 nm wavelength and a 20 mW power was used to record the spectra, and a typical spectrum of carbon nanotubes is shown in figure 3.5.

Carbon nanotubes Raman spectra show different features from which of main interest are the radial breathing mode (RBM), the G band and the D band. They are described here based on the article by Dresselhaus et al. The RBM are peaks in the range 100 to 500 cm⁻¹ and correspond to bond stretching where the carbon atoms move radially under the Raman excitation. The position of these peaks can be linked to the nanotube diameter, as the mass of the atoms along the circumference is proportional to the tube diameter. The relation between the peak position \( \omega_{\text{RBM}} \) and the tube diameter \( d_t \) is

\[
\omega_{\text{RBM}} \approx \frac{C}{d_t} \tag{3.2}
\]

where \( C \) is a constant which depends on the type of substrate and the surrounding media, as well as the tube-tube interactions. This constant is around 248 cm⁻¹·nm in the case of nanotubes simply deposited on a SiO₂ substrate. In this thesis, the nanotubes were embedded in a polymer matrix, which makes
Figure 3.6: Raman map showing the position of carbon nanotubes in a micro-patterned composite. (a) shows the 2D map, with darker areas where the signal from the nanotubes had a higher intensity. (b) is a 3D reconstruction of the map, with the height corresponding to the signal intensity.

It is difficult to have a clear analysis of the RBM features, so the tracking of the nanotubes was done on the G and D bands instead, which have the additional advantage of having a stronger Raman signal. The D band is usually linked to defects in the tubes, and is induced by disorder. It is located at around 1350 cm⁻¹ and has an overtone, called G' band, at 2700 cm⁻¹. Its position can give an information on whether the nanotube is semiconducting or metallic. The G band is positioned at around 1580 cm⁻¹ and is constituted of two components: G⁻ at ≈1570 cm⁻¹ and G⁺ at ≈1590 cm⁻¹. Both components can give information about the nanotubes: the frequency of the G⁺ band is sensitive to charge transfer to the nanotubes, while the line shape of the G⁻ band depends on the metalliclicity of the carbon nanotubes and its position depends on the tube diameter. It should be noted that the position and shape of the different Raman features can be affected by the nanotube aggregation state.  

In order to track the nanotube position in the patterned composites, the sample was placed on a controllable stage and Raman spectra were recorded while the stage was moved between each measurement. By associating each spectra to its position on the sample, and by tracking the intensity of the G band, it was possible to establish a map showing the location of the nanotubes within the PS-based composites. Polystyrene was used as a matrix as it didn’t show fluorescence as was the case when using P3HT, making it possible to see the signal from the nanotubes without saturation of the detector. This was done on a micro-patterned sample, as the spot size (∼0.86 µm) was too big to give any usable data on the nano-patterned samples. Such a map is shown in figure 3.6, with a distance of 200 nm separating the position of each spectra, which resulted in oversampling as the spot size was bigger than the distance between the measurement positions.

It can be seen from the map that the nanotubes migrated within the patterns, furthering the idea that the imprinting process helped displacing and reshaping the SWNT network. This redistribution is further supported by the electrical conductivity data, which suggests a vertical reorientation of the electrically conducting nanotube network, as measurements done using a non-conductive, PS matrix showed conductivity occurring after patterning. Several studies showed that a vertical polymer flow is happening when making verti-
A partial imprint of a 1.5 µm high pillar in polystyrene was achieved. Its examination in AFM (figure 3.7) showed the filling profile of the polymer in the mold, with filling starting mostly vertically along the edge of the patterns. By using polarized Raman microscopy, it is possible to estimate if there is any vertical alignment of the nanotubes in the patterns when scanning the composites from the side. This is done by controlling the incoming polarization as well as the outgoing light using polarized filters. Here, the light was arriving normal polarized, and the outgoing light went through a normal polarized filter so that only normal polarized light reaches the detector. The sample is then rotated so that the spectra are recorded for two orthogonal positions. Rotation of the sample is preferred to changing the polarized filters in order to avoid the difference in light losses which can be incurred by using a different optical setup. Once the spectra are recorded, a ratio is calculated between the intensity recorded in the vertical position where the polarization is parallel to the pillar height (perpendicular to the substrate surface) and the horizontal position, where the polarization is perpendicular to the pillar height (parallel to the substrate surface). A value of unity means that the sample is homogeneous, and that there is no particular orientation of the nanotubes, while a value above one (resp. below) suggest vertical (resp. horizontal) alignment of the nanotube network. These measurements were achieved for a micro-patterned composite, as well as for a random network (non patterned sample). The laser light was hitting the side walls of the pillars in the case of the micro-patterned sample, and the film cross section for the random network. The nano-patterned composite was not examined this way due to the too small dimensions of the pillars. The ratio obtained for a composite patterned at 110 °C has a value of 1.59, indicating vertical alignment of the network. However, it should be noted that the standard error is important (0.70) in spite of multiple measurements on multiple pillars, suggesting some disparity between the patterns. The composite patterned at 150 °C gave a ratio of 1.34, with a standard error of 0.27. The alignment is not as strong as the 110 °C-patterned sample, but the lower variation (lower standard error)
also indicates less inhomogeneity within the sample. The random network gave a value of 0.48 (standard error 0.34), meaning that the nanotubes are mostly parallel to the substrate. This makes sense when one considers the polymer flow during spinning of the film, where the polymer flows along the surface of the substrate at high speed in a lateral direction, therefore dragging the nanotubes along the substrate surface as well.\textsuperscript{101–103}

## 3.2 X-ray diffraction experiments

### 3.2.1 Measurements

In parallel to the percolation experiments, X-ray diffraction (XRD) measurements were conducted at synchrotron facilities in Stanford Synchrotron Radiation Lightsource (SSRL) on two specific beam lines using two different configurations. One was 11-3 which uses an area detector to record the diffraction patterns obtained using a grazing incidence configuration, and the other was 2-1 which uses a point detector recording spectra obtained in Bragg configuration. These setups are presented in more detail in section 2.2.2.

The samples were mostly P3HT or some other specialty polymers. They consisted in films of different thicknesses as well as patterned samples, prepared on silicon substrate or on graphene lying on silicon. They were measured using grazing incidence X-ray diffraction in order to be able to see all the crystalline orientations of the film in a single exposition, at the exception of the diffraction lying in the Bragg configuration. The incident angle of the incoming X-ray with the sample surface determines the penetration depth of the beam in the film, depending on the material, allowing for probing either the top surface of the film, or its bulk.\textsuperscript{104} Here, an angle value of 0.13° was found to penetrate the whole film while a value of 0.08° allowed for probing of the top \(\approx\) 10 nm in the case of P3HT. An example of grazing incidence X-ray diffraction (GIXD) patterns obtained using this technique for a P3HT sample on a hexamethyldisilazane (HMDS)-treated silicon substrate is shown in figure 3.8. On it are visible the diffraction patterns of crystal planes in nearly all directions in the film. Indeed, the diffraction patterns recorded along the vertical direction (along \(\chi = 90^\circ\)) are not directly representative of the specular diffraction, due to the orientation of the sample and of the detector, which remains vertical and perpendicular to the incoming X-ray beam, preventing the Bragg condition to be satisfied for \(\chi\) angles taken between 0° and \(\theta_B\), with \(\theta_B\) being the angle corresponding to specular diffraction. This is why some data is taken out of the detector image, leading to the black area visible in figure 3.8b and c. This allows for comparison of the crystallinity of different samples made using different parameters and techniques, in order to see their influence on the crystalline structure of the samples. The knowledge of this structure is essential as it has a strong influence on specific properties of the films. Combined with other conductivity measurements, it was possible to explain the difference in vertical charge transport in a P3HT film prepared on different substrates as a result of the different crystallinities.\textsuperscript{105}

Furthermore, it was also possible to observe the crystalline structure of films
Figure 3.8: GIXD patterns of a P3HT film on a HMDS-treated silicon substrate. (a) shows the patterns as recorded by the image plate. (b) shows it after the Bragg reflections from the vertical direction are removed, and (c) is a close-up on one quadrant of the detector, as the image is symmetrical. The bottom half of the image shows no diffraction patterns, as they are not visible due to the sample holder. The scale bar shows the counts in logarithmic scale, with the brighter area representing the stronger intensities. The $Q_z$ and $Q_{xy}$ coordinates are values of the scattering vector length as defined in equation 3.3 for the vertical ($\chi = 0^\circ$, out-of-plane) and horizontal ($\chi = 90^\circ$, in-plane) directions. The different peaks visible from P3HT are indexed in (c).
while heating and cooling, as the exposure time was quite short (60 s using the image plate, 40 s using the charge-coupled device (CCD) detector). For these measurements, the stage was heated and the temperature was measured using a thermocouple. The temperature was changed step-wise and the sample was exposed at each step. The oxidation of the film was mitigated by filling the sample chamber with a flow of helium. It was possible to see the influence of the substrate on the evolution of the crystallinity of the polymer while cooling by comparing between a film on a silicon substrate and one on graphene.\textsuperscript{106}

Depending on the material to investigate, as well as what peaks are targeted, it might be needed to move the detector along the beam direction. A detector close to the sample will allow for visualizing diffraction peaks occurring at high diffraction angles, while a detector further away will allow for better resolution of the peaks at low diffraction angles. These distances will depend on the detector dimensions. Here, a detector distance of $\approx 400$ mm when using the MAR345 image plate, and a distance of $\approx 350$ mm with the CCD detector from the sample was sufficient to both observe the 100 diffraction peak from P3HT as well as its 010 diffraction. For each detector position used, the setup had to be calibrated. Indeed, the detector was probably not perfectly perpendicular to the beam direction, and its distance from the sample might be different from what was specified in the control software. In order to do so, a Lanthanum hexaboride (LaB\textsubscript{6}) sample was placed on the sample holder instead of the sample to be examined. It was then aligned and its diffraction pattern was recorded. By knowing what its diffraction pattern should be, and at which position its diffraction peaks were expected to be, it was possible to recalculate the detector position and orientation, therefore correcting the measured data for the misalignment of the detector. This made it possible to extract accurate information on the peaks position from the data obtained from the samples with the detector at this particular position. The detector orientation calculations were done directly by the software provided to us (WxDiff, programmed by Stefan C. B. Mannsfeld for SSRL), but more details about a similar procedure can be obtained from the supporting information of the article from Lilliu et al.\textsuperscript{107}

In parallel, XRD measurements were performed in Bragg configuration, using a two-circle goniometer and a point detector (beamline 2-1). In this configuration, the incoming beam had a fixed direction, and both the sample and the detector were rotated. In the Bragg configuration, while the sample was rotated by an angle $\theta$, the detector was rotated by $2\theta$. At each position, the sample was exposed to the X-rays for some time, usually 1 s, although it depended on the intensity of the diffracted peaks. This meant that the measurement duration for each sample was much longer than in the grazing incidence geometry using an area detector, but the achievable angular resolution on the spectra was better and didn’t depend on the detector resolution. This was useful in the case of sharp peaks which could appear as a few pixels on the area detector but which were more detailed using the goniometer and the point detector. In order to save time, a fast scan was performed on a wide range in order to have a preview of most of the diffraction patterns. Then, more detailed scans were made focusing on selected features in order to be able to accurately determine
Figure 3.9: Specular diffraction spectra of a micro-patterned P3HT film on silicon. (a) shows the scan of the full range, and is replotted in (b) using a logarithmic scale to make the indexed peaks visible. (c) is a high resolution scan of the 100 peak, and (d) is a scan of the 010 region. (a), (b), and (c) have a 1 s exposure time per point, while d has a 60 s exposure time per point.

the crystalline properties of the sample. Depending on the type of sample, a series of measurements could take from $\approx 15$ min up to $\approx 45$ min per sample, to be compared with the $\approx 2$ min when using the GIXD setup. An example of such spectra is shown in figure 3.9.

### 3.2.2 Analysis

XRD is a way to determine the crystalline structure of a material, with the ability to extract information about crystals such as the interplanar distance or the coherence length. The data obtained by the measurements consists in spectra, usually plotted as intensity versus a position either in pixel in the case of an area detector, or a detector position in $2\theta$. Such information needs to be converted to render it independent on the measurement conditions. Indeed, the peak position will depend on the detector position in the case of GIXD, as well as the incoming X-ray wavelength in all cases, following Bragg’s law shown in equation 1.2 in section 1.2. This is why the scattering vector length $Q$ is introduced, defined as:

$$Q = \frac{4 \cdot \pi \cdot \sin \theta}{\lambda}$$

with $\theta$ being the angular coordinate and $\lambda$ the wavelength of the incoming X-ray in Ångström. This means that instead of having to report diffraction data as well as the wavelength used to record it, it is enough to communicate the
Figure 3.10: P3HT crystalline orientations. (a) shows a face-on configuration, where the chain backbone is parallel to the substrate. (b) shows an edge-on configuration, with the alkyl side groups being perpendicular to the substrate. The face-on configuration favors an out-of-plane charge transport, while the edge-on configuration is advantageous for in-plane charge transport.

data using $Q$ values instead, as the resulting peak positions in $2\theta$ can be extracted from it for any wavelength. The calibration done using the LaB$_6$ when collecting GIXD data makes it possible to directly convert the pixel position as $Q$ values. From there, the interplanar distance can be directly extracted as:

$$d = \frac{2 \cdot \pi}{Q} \quad (3.4)$$

The angle of inclination $\chi$ is also defined relative to the vertical direction, with $0^\circ$ being defined as the vertical direction, and $90^\circ$ in the horizontal plane, as shown in figure 3.8c. By examining the peak positions along this angle, it is possible to determine the texture of the material, and therefore to determine how the polymer chains are oriented in the film. The direction perpendicular to the plane of the film ($\chi = 0^\circ$) is called “out-of-plane”, while the one parallel to the film surface ($\chi = 90^\circ$) is called “in-plane”.

Here, this information was used to determine the polymer chain orientation of P3HT, based on the positions of the 100 diffraction peak. If the 100 peak is located in the out-of-plane direction, then the polymer chains are “edge-on”, while if this peak is out-of-plane, then the chain is “face-on”, such as shown in figure 3.10. It has been shown before that this difference in chain orientation leads to difference in electrical conductivity. Knowing this specific crystalline orientation depending on the processing conditions is therefore important, in order to be able to choose the appropriate conditions depending on the preferential direction for the electrical conductivity in the film.

From these measurements, it is possible to determine the interplanar distance of the crystals, as exposed in equation 3.4. This was done for a wide range of samples, as well as for films on silicon or graphene during cooling, in order to observe the evolution of the sample crystallinity (onset, orientation and spreading) as a function of temperature. The Scherrer’s formula, presented in equation 1.3, was also used to determine the crystallites coherence length.
based on the diffraction peaks full width half maximum (FWHM). However, the crystalline structure can present some internal disorder, which leads to a peak broadening on the XRD spectra. It is possible to separate the contributions of the coherence length and of the internal disorder to the peak FWHM by defining the paracrystalline parameter $g$ as: \(^{109,110}\)

$$g^2 = \frac{\Delta^2}{\langle d \rangle^2}$$  \hspace{1cm} (3.5)

where $\Delta^2$ is the variance of the interplanar spacing defined as:

$$\Delta^2 = \langle d^2 \rangle - \langle d \rangle^2$$  \hspace{1cm} (3.6)

It is possible to approximate the value of $g$ by simply using the peak position expressed in $Q$ and its FWHM $B$ as: \(^{111,112}\)

$$g = \sqrt{\frac{2 \cdot \pi \cdot B}{Q}}$$  \hspace{1cm} (3.7)

The measured peak FWHM $B$ can be written as:

$$B^2 = B_c^2 + B_g^2$$  \hspace{1cm} (3.8)

where $B_c$ is the contribution from the crystalline coherence length and $B_g$ is disorder induced and can be approximated as: \(^{107}\)

$$B_g = \frac{(\pi \cdot g \cdot h)^2}{d}$$  \hspace{1cm} (3.9)

with $h$ being the order of diffraction corresponding to the $(h00)$ plane. The coherence length can then be calculated normally by using $B_c$ in the Scherrer’s formula instead of $B$ as directly measured on the instrument.

Another type of measurement which was done using a point detector is called “rocking curve”. In this case, a regular $\theta - 2\theta$ scan was first done in order to locate the peak position in Bragg configuration. Then, the detector was fixed at the $2\theta$ position corresponding to the peak position and the sample was rotated along $\theta$, as shown in figure 1.1a. This allows measuring the dispersion in orientation of this specific set of crystalline plane from the vertical direction. \(^{113}\) Such a curve is shown in figure 3.11.
Figure 3.11: Rocking curve for the 100 diffraction peak plotted in 3.9c. The detector was fixed in position at $2\theta = 3.56^\circ$ corresponding to the position of the 100 peak, and the sample stage was rotated around $\theta$. 
Chapter 4

Conclusion and outlook

The main objective of this project was to integrate carbon nanotubes within a polymer matrix in order to increase its electrical conductivity at low filler loading. This was achieved by taking advantage of the polymer flow occurring during nanoimprint lithography, in order to vertically orient the carbon nanotubes contained in the polymer matrix. The nanotubes were dragged along the polymer flow during the filling of the mold under pressure, resulting in the creation of an interconnected network of SWNT allowing for vertical charge transport in the resulting composite. Furthermore, depending on the patterns used for the imprinting process, it was possible to reduce the reflectance of the film compared to a non patterned sample, while keeping the light transmittance above 96% in the case of a nanostructured PS-based sample, as has been shown in paper I.

This patterning process also resulted in the possibility of using ultralow nanotube loading and still obtain electrically conducting composites, while at similar loadings their non-patterned counterparts were insulating, as shown in the case of PS and P3HT in paper II. Furthermore, this nanoimprint procedure led to an increase in conductivity compared to non-patterned films even at higher loadings, with rises of between 1 and 2 orders of magnitude being reported when using P3HT as the matrix material, as exposed in paper III. Not only was this true when using thermal NIL, but this was also demonstrated when using room temperature NIL, where the polymer film was soften by the use of solvent vapor, as shown in paper IV.

Further studies are still required in order to apply this technique to specific applications, such as within photovoltaic devices. This work has been started, and preliminary results look promising. Other types of conducting filler can be used, with silver nanowires being a good candidate due to their easy production process and their high intrinsic conductivity. Moreover, the interaction between the nanotubes and the matrix material can be investigated, as it has been shown that the processing parameters can lead to different crystalline configurations, which affect the electrical conductivity of the film.

Furthermore, it has been shown that the electrical conductivity of P3HT can be affected by the substrate on which the film is lying due to changes in
its crystalline structure, as presented in paper V. The influence of graphene on the conductivity of the material was further explored in paper VI, where it was shown that even reduced crystallinity of the P3HT resulted in improved charge transfer on graphene compared to silicon. More work is needed however in order to integrate graphene in the structure of a device, in order to examine the consequences of these improved electrical characteristics on the efficiency of a working photovoltaic device.
Chapter 5

Summary of appended articles

**Paper I:** Nanostructured networks of single wall carbon nanotubes for highly transparent, conductive, and anti-reflective flexible electrodes

Highly transparent patterned composites were made of SWNT embedded in PS. The samples were micro- and nano-patterned, and their optical properties were measured, as well as their electrical conductivities.

Contribution: all experimental results, Raman spectroscopy, electrical conductivity measurements, UV-vis spectroscopy.

**Paper II:** Nano-engineering of SWNT networks for enhanced charge transport at ultralow nanotube loading

Micro- and nano-patterned composites were made using either PS or P3HT as the matrix material, with carbon nanotubes as filler. The electrical conductivity of the different samples was measured and proved to be as high as eight order of magnitude higher than random networks at the same filler concentration.

Contribution: experimental results for the polystyrene based samples, electrical conductivity measurements, Raman spectroscopy.
Paper III: SWNT nano-engineered networks strongly increase charge transport in P3HT

Nano-patterned composites were prepared with SWNT as the filler material and P3HT as the matrix at SWNT loadings ranging from 0.03 wt.% up to 3.00 wt.%. The vertical electrical conductivity of each patterned and non-patterned composite was measured, and an increase of as much as ≈100 times was observed for the patterned film compared to the random network.

Contribution: all experimental results, conductivity measurements

Paper IV: Ordered and highly conductive carbon nanotube nano-networks in a semiconducting polymer film by solution processing

Nano-patterned SWNT:P3HT composites were produced using both thermal and room temperature NIL, and the resulting electrical conductivities were compared to non-patterned films. The room temperature patterned samples showed the highest conductivities, which was hypothesized to be due to debundling of the nanotubes, as shown by SEM.

Contribution: all experimental results, scanning electron microscopy, atomic force microscopy, electrical conductivity measurements.

Paper V: Enhanced vertical charge transport in a semiconducting P3HT thin film on single layer graphene

Thin P3HT films on graphene have been prepared and the resulting crystallinity has been investigated using GIXD, as well as their vertical charge transport and charge mobilities. The thicker (50 nm) films on graphene showed an improved charge vertical charge transport compared to thinner (10 nm) films or to both thick and thin films on silicon. This was due to the different crystalline packing orientation.

Contribution: X-ray diffraction measurements.
**Paper VI:** Reduced crystallinity and enhanced charge transport by melt annealing of an organic semiconductor on single layer graphene

P3HT films on graphene have been annealed at either 200°C or 240°C (below and above the melting point) and the resulting crystalline structure as well as the charge transport properties have been measured. The film heated above its melting point showed a higher charge mobility, even though it was less crystalline.

Contribution: X-ray diffraction measurements.
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Bibliography


Appendix A

Measurement how-to on beam line 2-1
When the beam line is set up and ready to be used, the lead plate protecting the detector can be removed, and the absorber slits should be introduced as to limit the direct beam exposure on the detector by typing:

```
abs ins 1101
```

Do not forget to deactivate the automatic insertion/removal of the slits with `abs off`.

Once the sample is positioned on the sample holder in beam line 2-1 (two circle goniometer), the X-ray can be introduced in the chamber. In order to measure data on this beam line, it is first necessary to align the sample in order to make sure that the $\theta = 0^\circ$ position corresponds to the sample surface parallel to the incoming beam and cut the beam half-way through its height. To achieve this, the detector $tth$ is first placed in the beam path using:

```
mv tth 0
```

The sample is then positioned vertically by displacing by a distance $XX$ mm using:

```
mvr gony XX
```

The counts on the detector are then checked using `ct`, and the sample moved up or down accordingly, in order to reach approximately half of the maximum intensity reported by the detector. A file series can now be created so that the alignment data is clearly identifiable and is separated from the measurement data:

```
newfile alignment
```

A more precise positioning can then be executed using a line-up scan `lup` as:

```
lup gony -0.5 0.5 80 1
```

where -0.5 and 0.5 are the start and end positions, with 80 points of 1 s exposure each. The center position $XX$ corresponding to half of the intensity reported by the detector can then be reached by:

```
mv gony XX
```

Parallelism of the sample surface to the incoming beam can then be checked by rotating the sample using a line-up scan:

```
lup th +0.5 0.5 80 1
```

where `th` corresponds to the motor controlling the stage orientation, with its position corresponding to $\theta$ in degrees. The position $XX$ at which the signal reaches its maximal intensity is then picked and the sample is positioned there using:

```
mv th XX
```
If this maximal intensity is very different from the value obtained when positioning the sample vertically, it is necessary to redo a line-up scan of the stage with the gony motor, as explained before.

Once the sample is parallel to the beam, cutting it in half, its angle $\theta$ is set as the 0 position:

```plaintext
set th 0
```

It is then possible to start the data measurements. This can be automated by creating scripts and starting them using:

```plaintext
qdo script_name
```

Three scripts have been prepared for measurements in grazing incidence configuration, Bragg configuration, and for the rocking curves.

For the grazing incidence configuration, the sample angle relative to the beam is fixed and the detector is rotated using `ascan`. The script for the measurements in grazing incidence configuration is:

```plaintext
# Startup
abs ins 1101
mv tth 2
mv th 0
abs ins 0000

# Full range, preview
newfile sample-grazing-0.13-full-1s
mv th 0.13
ascan tth 2 25 328 1
# ascan motor start stop nb_of_pts exposure_time

# 100 peak
newfile sample-grazing-0.13-100-1s
mv th 0.13
ascan tth 2 5 300 1

# 200 peak
newfile sample-grazing-0.13-200-1s
mv th 0.13
ascan tth 6 9 300 1

# 010 peak
newfile sample-grazing-0.13-010-2s
mv th 0.13
ascan tth 10 20 200 2

# Moving away, resetting
abs ins 1101
```

55
In Bragg configuration, both the sample stage and the detector are rotated at the same time. The script used for Bragg configuration is:

```
# Startup
abs ins 1101
mv tth 2
mv th 0
abs ins 0000
abs on
# Automatic insertion of the absorbers is turned on due to the beam reflection which can be too high at the beginning of the scan

# Full range, preview
newfile G-1-bragg-full-1s-abson
a2scan tth 2 25 th 1 12.5 328 1
# a2scan motor1 start end motor2 start end nb_of_pts expo_time
# Be careful to pick theta values at half the tth values.

# 100 peak
newfile G-1-bragg-100-1s-abson
a2scan tth 2 5 th 1 2.5 300 1

# 200 peak
newfile Press-12-bragg-200-1s
a2scan tth 6 9 th 3 4.5 300 1

# 010 peak
newfile G-1-bragg-010-60s
a2scan tth 10 22 th 5 11 48 60

# Moving away, resetting
abs off
abs ins 1101
mv tth 5
mv th 0
```

The rocking curves are recorded by placing the sample at the position $\theta$ of the targeted peak and by rotating the detector. It can lead to high intensities hitting the detector, requiring the automated slits insertion to be turned on in the script. As the detector is rotated around the $2\theta$ position of the peak, the scan itself is no more than a high resolution line-up scan:

```
# Startup
abs ins 1101
mv tth 2
```

---

56
mv th 0
abs ins 0000
abs on

newfile G-1-rocking-100-tth3.6134-1s-abson
mv tth 3.6134
mv th 1.8067
lup th -0.5 0.5 200 1

# Moving away, resetting
abs off
abs ins 1101
mv tth 10
mv th 0