Functional Materials Assembled at the Air/Water Interface based on Carbon Nanotubes and Graphene

by

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To Father and Mather
Abstract

A driving goal of the research community in recent years has been to develop various methodologies of producing novel materials as uniform films with high transparency $T$ coupled with high conductivity $\sigma$. Most transparent electrodes are made from indium-doped tin oxides (ITO). This is due to the materials having high electrical conductivity $R_s < 100 \Omega/$sq and transparency, $T = 90\%$. However, using ITO involves several drawbacks. Primarily, it is brittle and expensive. In recent years, many candidates have been proposed as potential substitutes for ITO such as, nanotubes, nanowires, graphene and hybrids of these materials. The use of the Langmuir technique has already been shown to allow the user to produce high quality films by being able to manipulate various factors i.e. the surface pressure of the subphase and number of isotherm cycling. Here we use a modified method to produce graphene, hybrid of graphene/silver nanowires and single-walled carbon nanotubes based thin films in order to compete with ITO and viable alternative.

Single or few layer graphene can be considered an exciting pseudo-two-dimensional molecular material that potentially has a wide range of applications. A critical performance bottleneck may arise with issues in their controlled assembly into macroscopic ensembles over large areas both in two and three dimensions. Langmuir-type assembly is a particularly useful method to control and manipulate the distribution of graphene at the air-water interface via edge-edge interactions. In this study, pristine graphene suspended in organic solvent was prepared through adaptation of a previously developed process involving the non-invasive exfoliation of graphite. Successful deposition of graphene at the air-water interface was achieved by manipulating the vapor-pressure of the graphene dispersion through solvent mixing. The film density is precisely controlled by following the
pressure-area isotherm during monolayer compression/rarefaction. Moreover, the resulting assemblies can be easily transferred to glass and other substrates producing thin films with tunable electrical conductivity using the Langmuir-Schaefer horizontal deposition method. A major advantage of this process is that the conducting films require no further treatment unlike their graphene-oxide counterparts. Moreover, the physical properties of these assemblies can be easily controlled which is a precursor for graphene-based electronic applications.

Although silver-nanowires demonstrate comparable electrical conductivity and optical transmittance to ITO, challenges remain. For example, silver nanowires are expensive and in order to achieve high electrical conductivity relatively dense films are required. Moreover, the resulting films are often hazy and require a protective coating to prevent eventual oxidation. Numerous studies have investigated silver nanowires and graphene individually as transparent conductors, but little research has been done on hybrid systems of the two. We report a simple, scalable and relatively inexpensive method to prepare transparent conducting films based on silver-nanowire/graphene hybrids. We use a combination of spray deposition and Langmuir-based techniques to produce ultrathin films with controlled nanowire and graphene densities. Surface morphology of the hybrid films was observed by SEM, AFM and optical microscopies. We demonstrate that adsorption of graphene at nanowire junctions markedly affects the macroscopic conductivity without significantly reducing the optical transmittance. Our optimised films which have comparable properties to commercial ITO contains reduced densities of silver-nanowires in comparison to films made of pristine silver-nanowires with the same properties. The results indicate that these graphene/nanowire hybrid films may serve as a cheap replacement for existing technologies in electronic devices.

Another nanostructure material that has been touted for applications is carbon nanotubes. Carbon nanotubes are materials with a variety of fascinating properties related to their interesting quasi-one-dimensional electronic structure. There is considerable interest in developing economical and practical methods for producing aligned carbon nanotubes
and utilizing them in electronic components, optical waveguides and optoelectronic devices.

A method for assembling monolayers of aligned single-walled carbon nanotubes is described. Dispersions of nanotubes were prepared as a function of concentration in solutions of 1,2-Dichloroethene and the conjugated polymer, poly (n-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene). The helical structures of this conjugated polymer forms a hydrophobic cavity that becomes a suitable host for nanotube bundles and consequently enhances their dispersability. The Langmuir-Blodgett technique was used to prepare monolayers of oriented polymer wrapped nanotubes. The alignment of the assembles on the substrates is controlled by varying different parameters in the Langmuir-Blodgett process. SEM, AFM microscopies and polarized Raman spectroscopy reveal a crucial relationship between pressure cycling and the formation of aligned assemblies of nanotubes. Specifically, we have discovered that alignment can be improved if the surface pressure during deposition and the number of deposition cycles is increased. Electrical conductivity of the resulting films again show percolation-type behaviour as a function of density modification in the prepared films. The calculated percolation threshold is found to be unexpectedly high which may result from the local mesoscopic ordering of nanotubes in the film facilitated by the presence of the polymer.
Declaration

This thesis and the work to which it refers are the results of my own efforts. Any ideas, data, images or text resulting from the work of others (whether published or unpublished) are fully identified as such within the work and attributed to their originator in the text, bibliography or in footnotes. This thesis has not been submitted in whole or in part for any other academic degree or professional qualification. I agree that the University has the right to submit my work to the plagiarism detection service TurnitinUK for originality checks. Whether or not drafts have been so-assessed, the University reserves the right to require an electronic version of the final document (as submitted) for assessment as above.
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Chapter 1

Introduction

1.1 Research Background and Motivation

Smart electronics is a rapidly expanding area of electronic device research with transparent electrodes often playing critical functions in such devices [1]. Transparent electrodes are necessary components of many modern devices such as touch screens and interactive electronics. Other examples include solar cells, smart windows, and flexible lighting [1-3]. The requirements for high-performance transparent electrodes vary, mainly depending on the application, such as a stringent $\sim 20/\Omega$ sq for solar cells and large area displays. A high optical transmittance ($T$) $\sim 95\%$ and moderate sheet resistance $R_S$ of 400-600 $\sim \Omega$/sq for touch screens is also required [4].

Currently, transparent electrodes are made from doped metallic oxides, mainly indium-doped tin oxides (ITO). This is due to their high electrical conductivity $R_S < 100$ $\Omega$/sq and transparency, $T = 90\%$ in the visible range [3, 5]. ITO has been well researched and refined for over sixty years. It consists of a ratio of indium (III) oxide ($In_2O_3$) and tin(IV)oxide ($SnO_2$), with optimal electro-optic properties occurring at a 90/10 atomic ratio [1]. However, using ITO involves several challenges. It degrades over time, has a low fracture resistance (when the substrate is bent), is brittle, and can lose functionality when flexed [5-7]. Additionally, the material is expensive due to the limited quantities of indium metal and the high demand for pure indium [8]. Thus, future transparent electrodes will require flexible, transparent and conductive materials, which can be produced
at low temperature and over large areas at low cost. In recent years, there have been many candidates to substitute for ITO such as, nanotubes, nanowires, graphene and hybrids of these materials.

1.1.1 Single-Walled Carbon Nanotubes

One of the promising materials for replacing ITO is Single-walled carbon nanotubes (SWNTs), due to their electrical and mechanical properties. Individual carbon nanotubes (CNTs) were found to have mobilities in excess of 10000 cm²V⁻¹s⁻¹ and a current carrying capacity in the order of 10⁹ A/cm². Theoretical studies indicate that SWNTs can exhibit strength even greater than diamond [9].

Several groups used SWNTs thin films as transparent electrodes [10-12]. However, there are still some issues in the commercial use of SWNTs. One of the major problems is production of chemically and chirally pure SWNTs. Produced SWNTs typically contain a mixture of various materials including catalyst particles, catalyst support, amorphous or non-tubular carbon, fullerenes, and a mixture of nanotubes of various lengths, diameters, tube number, and chirality. For example, in electronic applications, it is critical not to use mixtures of metallic and semiconducting SWNTs as the resulting properties will be non-specific in nature. Metallic nanotubes will short semiconducting devices and this can dramatically degrade device performance. Many successes have been achieved in the SWNT purification and separation process [1], such as applying gas phase oxidation and acid treatment [13-15]. Also many techniques have been used to separate SWNTs by their electronic structure at the laboratory scale. For example, agarose gel chromatography [16], alternating current assisted dielectrophoresis [17] and density gradient ultracentrifugation [18-20].

1.1.2 Graphene

One of the other candidates for replacing ITO is graphene due to its outstanding electrical, mechanical and optical properties. Single or few layer graphene can be considered as a quasi-two-dimensional molecular material. Graphene shows room-temperature mobilities of about 10000 cm²V⁻¹s⁻¹ [1, 21]. A large size, defect free piece of graphene
demonstrates a $T$ of 97.7% and $R_s$ of about $60 \Omega$/sq [6]. Since graphene is a zero-gap semiconductor with a very high Fermi velocity $\sim v_F = 10^6$ m/s, individual graphene sheets have very high in-plane conductivities, and an $R_s$ value as low as $\sim 30\Omega$/sq [22]. Graphene films also show excellent thermal stability and the films remain intact after heating to 400° C in air [23]. Recently Peumans et al. [24] have shown that for highly doped graphene the $R_s$ in graphene is inversely proportional to the number of layers,

$$R_s = \frac{62.4\Omega}{N}$$

where $N$ is the number of layers.

Graphene has similar properties to CNTs due to the same $sp^2$ carbon chemistry, but has different optical properties owing to its two-dimensional character [1]. Another advantage of graphene over CNTs is its easy and low cost production from graphite, which should result in much more competitive pricing than that for CNTs. Similar to CNTs, there are several challenges associated with using graphene in commercial applications. Graphene synthesis methods such as epitaxial growth or chemical vapour deposition (CVD), produce relatively low quality graphene with multiple boundaries and incorporated defects (i.e., grain boundaries, ripples and wrinkles). This increases dramatically the $R_s$ as a result [1, 25]. Other methods include the production of pristine graphene in the solution phase via chemical routes. A critical performance bottleneck here may arise with issues in their controlled assembly into macroscopic ensembles over large areas.

Many different methods were suggested to fabricate graphene from a solution phase such as drop-casting, spin-coating [26], spraying [27], Langmuir-Blodgett (LB) [28], Langmuir-Schaefer (LS) and filtration [29, 30]. Langmuir-type assembly is a particularly useful method to control and manipulate the distribution of graphene at the air-water interface via edge-edge interactions. The physical properties of these assemblies can be easily controlled which is a precursor for graphene-based electronic applications.

### 1.1.3 Nanowires

Transparent electrodes consisting of a random network of metal nanowires have recently been explored [6]. Their amazingly high length-to-width ratio and the ability to
prepare wires of any material on any substrate with a variety of thicknesses makes them a promising candidate for future electronic and optical devices. According to the recent literature [6, 32], silver nanowires (AgNWs) have great potential for use as transparent conductors due to the intrinsically high conductivity of silver. A random network of AgNWs can lead to an $R_s$ value of less than 100 $\Omega$ and T of about 90%. As the films are made denser, the sheet resistance decreases along with the optical transparency. It has been shown that a higher DC electrical conductivity/optical conductivity ratio leads to optimised performance as a transparent electrode. Also, their mesh-like geometries present outstanding mechanical robustness up to a strain of $\sim 1\%$ when bent [2, 3] or stretched to $\sim 50\%$ strain [25, 31].

Recently, Coleman et al [32] studied in detail the percolation conductivity of transparent electrodes based on a AgNW networks. They found that the DC conductivity in thin film of AgNWs is not thickness independent and follows percolation-like behaviour at thickness approaching monolayer dimensions. Recent work by Hu et al.[25] have found that mechanical pressing or electroplating of metal can fuse the nanowire junctions, which dramatically decreases the film sheet resistance and surface roughness. Although, the AgNW networks has many potential applications, as transparent electrodes there are some drawbacks such as high fabrication cost, low breakdown voltages, high NW-NWs junction resistance, instability in harsh environments (readily reacting with oxygen and hydrogen sulphide), and poor adhesion to plastic substrates. Presently, this limits their integration into commercial devices [25].

1.1.4 Hybrid Systems of Silver Nanowire/Graphene

Another alternative candidate to replace ITO is a hybrid of the above materials. Such hybrid system will have advantages over either material independently. Previously Zheng et al. [33] used LB assembly process to produce uniform, large-area hybrid transparent films of ultra-large graphene oxide and functionalized SWNTs. The large and flat geometry of graphene improves the overall electro-optic properties of SWNTs, by providing increased percolation paths per unit mass [33]. Another study has been performed by Tokuno et al. [34] on hybrid system of carbon nanotubes and silver nanowires. They
show high conductivity as well as excellent stability in sheet resistance, when tested using a repeated bending test. The other possible combination is graphene with AgNWs to form a transparent and conductive film. As it has been mentioned, high junction resistance occurs between NW-NWs cross junctions, as well as high resistance at the boundaries between the different sheets of graphene. This may make each material alone unsuitable for transparent electrodes [25, 35]. However, in the hybrid system the graphene layer film gives the nanowires an overlying point of contact with one another, while AgNW networks also minimise the resistance inherent within the graphene. Such films show better electrical and mechanical properties compared to ITO. Studies show that there is almost no change in its resistance when bent [36].

1.2 The Primary Objectives and Aims of This Dissertation

The primary objective of this work is to understand the fundamental electrical and optical properties of Langmuir-produced films of carbon nanostructured materials at the air-water interface. By using this unique process, two-dimensional assemblies of graphene, graphene - nanowire hybrids and SWNTs have been fabricated. By modifying the assembly process it is possible to selectively tune the intrinsic physical properties of the resulting films. A secondary objective is to take advantage of the unique properties of these materials such as the high strength, high Young's modulus, high electrical conductivity and high optical transparency for use in potential applications such as transparent electrodes.

1.3 Thesis Outline

Each chapter contains an introductory section, which summarises the relevant literature pertinent to each study.

Chapter 2 provides an introduction to the properties of materials used in this work
such as SWNTs, graphene and AgNWs. This chapter also reviews the technique of making thin films of these materials via drop casting, spin coating, spraying, LB, LS and filtration. Finally, instrumental set up and the working principles of the various characterization techniques described with the aid of schematic illustrations is described. Such techniques include UV-Vis spectroscopy, resonant Raman spectroscopy, Atomic Force Microscopy (AFM) and scanning electron microscope (SEM).

Chapter 3 describes the production of pristine graphene suspended in organic solvents. Deposition of graphene at the air-water interface discussed here is done by manipulating the vapour-pressure of the graphene dispersion through solvent mixing. The chapter then goes on to demonstrate monolayer fabrication via the LS technique applied to graphene suspensions at the air-water interface. The morphology of the produced films is investigated here by the use of SEM, AFM and UV-Vis spectroscopy. $R_s$ against $T$ plots and percolation thresholds are established.

Chapter 4 is dedicated to hybrid systems of AgNWs and graphene via a combination of spray deposition and Langmuir based techniques with precise control of nanowire and graphene densities. The NW-NW junction resistance is investigated using Conductive AFM ($c$-AFM). The morphology of the produced hybrid films are observed by SEM, AFM and optical microscopy. The electrical properties and the effect of the graphene layer on NW-NW crossed junctions is analysed and explained.

In chapter 5, the dispersion of SWNTs using poly-$m$-phenylenevinylene-co-2,5-dioctoxyphenylenevinylene (PmPV) in 1,2-dichloroethane (DCE) is initially described. Following this, a description of how the Langmuir technique can be applied to produce monolayers from the dispersion with controlled density through modification of the surface pressure during preparation. The resulting films are characterised with a range of techniques including AFM and SEM microscopy as well as UV-Vis and Raman spectroscopy to develop detailed structure-property relationships.
Chapter 6 provides a conclusion of this thesis. It also investigates the problems hindering the industrial applications of the as-produced films and details plans for the future direction of the project and related projects.

1.4 References

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22. Fang, T., et al., Carrier statistics and quantum capacitance of graphene sheets and
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Chapter 2

Materials and Methods

2.1 Introduction

This chapter will provide an extensive explanation of materials, principles of equipment and methods that have been used in this research with particular focus on the structures and properties of carbon based materials such as graphene and CNTs. Fundamental properties and the behaviour of mixtures of PmPV with SWNTs were also investigated.

2.2 Materials

2.2.1 $sp^2$ Hybridized Materials

Carbon based materials have unique electronic states, which result from the hybridization of atomic orbitals. The atomic number of carbon is six and it has been listed at the top of group IV in the periodic table. Its electronic configuration in the ground state may be written as $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$. The $1s^2$ orbital contains two strongly bound electrons and four electrons occupy the $2s^2$ and $2p^2$ orbitals, hence two half-filled orbitals exist in this configuration. Since the energy difference between the upper $2p$ and the lower $2s$ is small, compared to binding energy of chemical bonds, it is believed that one electron can jump from the $2s$ to the $2p_z$ orbital [1]. Thus, the electronic configuration of carbon in the excited state may be written as $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$.

This mixing of atomic orbitals with nearly equivalent energy, and redistribution of the
energy for forming new orbitals with equal energy is called hybridisation. Hybridization is classified into three categories: sp, sp$^2$ and sp$^3$; while Graphene and CNTs are sp$^2$ hybridized, group IV elements such as Si and Ge exhibit primarily sp$^3$ hybridisation.

In the sp$^2$ hybridization, one 2s orbital and two 2p orbitals combine, resulting in the formation of three sp$^2$ hybridized orbitals. These three sp$^2$ hybrid orbitals are in a flat plane with 120° angles between each other, and one p orbital per carbon atom at a 90 degree angle to the hybrid orbitals [1, 2].

### 2.3 Structure of Carbon Nanotubes

CNTs were discovered in 1991 by a Japanese physicist, Sumio Iijima. The first synthesis of a SWNTs was achieved two years later in 1993. This discovery was followed later in 2000 by Tang Zikang and Wang Ning [4, 5] who produced a small (0.4 nm in diameter), stable single wall carbon nanotube. Generally CNTs are naturally occurring, but are irregular in size and quality. Special conditions and different synthesis methods such as laser vaporization, arc discharge, CVD, high pressure CO disproportionation process (HiPco) and other synthesis methods are required for their controlled mass production [1].

Since their discovery, CNT production has progressed considerably. CNTs have a variety of potential applications in many different areas such as medicine, optics and
electronics. Despite the many studies that have been performed, the applications of CNTs are still mainly theoretical, the results produced are not always fully understood and there still remains a strong need for better control over purifying and manipulating nanotubes. Areas where predicted or tested nanotube properties appear to be exceptionally promising are mechanical re-enforcement of materials and electronic device applications. Theoretical studies indicate that SWNTs can exhibit strength even greater than diamond and conductivity superior to copper [6].

There are several different kinds of CNTs: SWNT, double-walled nanotubes (DWNT) and multi-walled nanotubes (MWNT). Iijima was the first to observe MWNTs and SWNTs were also detected by him in 1995 [1]. A SWNT is considered to be a seamless hollow thin cylinder made by rolling a graphene sheet and connecting the sides. Its mantle is made of hexagonal networks of carbon. A SWNT is shown in Figure 2.2.

### 2.3.1 Single-Walled Carbon Nanotube

SWNTs have a remarkable properties which are related to their unique quasi-one-dimensional configuration. These properties allow the SWNTs to be easily distinguished from MWNTs. As their names implies, each individual SWNT diameter is on a nanoscale (0.4 to 1.6 nm) with lengths typically up to 2μm. Since their chemical bonding structure is similar to a sheet of graphene, they exhibit \( sp^2 \) hybridization, which makes them the strongest and stiffest material yet discovered. Other elements in group IV on the periodic table can only demonstrate \( sp^3 \) hybridization [1].

![Figure 2.2: A schematic presentation of a single-walled nanotube.](image)

The structures of these tubes are represented by two distinctive lattice indices \( (n, m) \).
CHAPTER 2. MATERIALS AND METHODS

Figure 2.3: The structure of unrolled honeycomb lattice of a CNT from graphene, shows diameter and chirality relative to the direction of the carbon hexagonal axis figure adapted from [7].

These two chiral indices are unique for each CNT with \( n \) is equal to or greater than \( m \). The CNTs can also be specified by their chiral vector \( \mathbf{C}_{h} \), which spans the circumference of each nanotube (See Figure 2.2).

\[
\mathbf{C}_{h}(n,m) = n\mathbf{\hat{a}}_1 + m\mathbf{\hat{a}}_2
\]  

(2.1)

\[
\cos\theta = \frac{\mathbf{C}_{h} \cdot \mathbf{\hat{a}}_1}{|\mathbf{C}_{h}| |\mathbf{\hat{a}}_1|} = \frac{2n+m}{2\sqrt{n^2+m^2+mn}}
\]  

(2.2)

Where \( \mathbf{\hat{a}}_i \) (i = 1,2) are lattice primitive vectors of graphene in real space and \( m \) and \( n \) are integers. Equation 2.3 shows the lattice constant.

\[
a = |\mathbf{a}_1| = \left(\frac{\sqrt{3}a}{2}, \frac{a}{2}\right) = |\mathbf{a}_2| = \left(\frac{\sqrt{3}a}{2}, -\frac{a}{2}\right) = 0.246\text{nm}
\]  

(2.3)

Hence, the CNT geometric configuration can be characterised by these two integers. In general, the tubes are split into two categories: chiral and achiral (zigzag and armchair).

The major difference between these two classes is that the achiral carbon nanotube mirror image exhibits an identical structure to the original one, whereas the chiral tube has spiral symmetry (see Figure 2.4) [1]. In the case where \( n = m \) the tube is called armchair and the chiral angle corresponds to \( \theta = 0^\circ \). If \( m = 0 \), then the tubes are referred to as zigzag and their axial chiral angle is equivalent to 30°. Finally, the tubes will be referred to as chiral.
if \( n \neq m \times 0 \), as illustrated in Figure 2.4. Also, as the name implies, a chiral nanotube exhibits chirality, in other words it is impossible to superimpose it on its mirror image [1].

![Figure 2.4: The construction of a carbon nanotube from a single graphene sheet and all possible structures of SWNTs defined by the chiral vector; (a) armchair; (b) zigzag and (c) chiral nanotube (figure adopted from [8]).](image)

### 2.4 Polymeric Nanomaterials

The word *polymer* or *macromolecule* is originally derived from the Greek *poly* and *meros*, meaning many and parts, respectively. Depending on their reaction to heat and pressure, polymers are broadly divided into two classes; thermoplastics or thermosets. Thermoplastics can be melted and reshaped at high temperatures or pressure; however, thermo sets decompose before they melt or reshape. Polymers are highly attractive materials for various applications and construction because of their ease of fabrication into complex shapes and sizes. Until the discovery and development of electrically conductive polymers, poor conductivity of carbon based polymers made their use in the electronics industry only desirable as inactive packaging and as an insulating material. This perspective is rapidly changing as a new class of flexible, noncorrosive and inexpensive
CHAPTER 2. MATERIALS AND METHODS

Conductive polymers enter into the market.

Polymers can be formulated to have specific conductivity characteristics from very low to very high conductivity often through doping. The conductivities of general materials compared to conjugated polymers are shown in Figure 2.5. Since carbon atoms in carbon double bonds are sp² hybridized, pₓ orbital overlap occurs so that a delocalized π electron cloud exists above and below the plane of the sigma bonds that form the structural framework of the polymer chain. Electrons can be excited from the valence band to the conduction band if sufficient energy is added to the system to overcome the energy difference between the two bands and photon emission occurs resulting from optically induced states. Alternatively, excited electron states can be electrically injected into the system by the application of an external electric potential. Light emitted through this process is termed electroluminescence.

**Figure 2.5**: The conductivities of general materials compared to conjugated polymers

Conjugated polymers, with high luminescence efficiencies are ideal candidates for use in opto-electronic applications such as LEDs, solar cells or effective laser materials (plastic lasers). One notable class of this fluorescent semi conjugated polymer is *polyphenylene vinylene* (PPV) and its family of related polymers, containing PPV-based structures in the main chain or the side chain. PPVs provide the advantages of high oxidative and thermal stability as well as the ability of tuning the emitted light through chemical modification [8].

However, PPVs display poor processability because of their low solubility range. This disadvantage is overcome by the introduction of PmPV, the alternate *meta-phenylene* linkage leads to a reduction of the conjugation along the backbone.
2.4.1 Conjugated Polymer CNT Composites

One of the most challenging tasks faced when working with CNTs is their low solubility in common organic solvents and water, due to non-covalent forces between individual tubes. However, non-covalent functionalization of CNTs is a potential approach to overcome this problem. Surfactant, oligomers, biomolecules, and amphiphilic polymers (heterogeneous with both hydrophilic and hydrophobic parts) (see Figure 2.13a-b) are suitable candidates to de-bundle nanotube aggregates in aqueous solution by wrapping around or adsorbing onto them, through electrostatic interaction or using a combination of van der Waals and complementary electrostatic interactions. The advantage of most non-covalent approaches is that they do not destroy or alter the intrinsic electron structure of CNTs. However, wrapping amphiphilic polymers around CNTs is a good way to solubilise them in water but this method is not good enough to solubilise them in organic solvent [12]. One other promising solution could be the \( \pi-\pi \) interaction between \( \pi \) electrons of CNTs and the correlated \( \pi \) electron rich components such as conjugated polymers.

PmPV, whose structure is a variation of the more common PPV, is a good candidate for use as this shows a promising solution for dispersing SWNTs in organic solvents. PmPV has exhibited high-binding affinity to CNT sidewalls via \( \pi-\pi \) stacking of its conjugated backbone and van der Waals interaction between PmPV and the surface of the SWNTs, thus aiding dispersion of nanotubes in organic solvents. SWNTs doping of PmPV exerts a notable impact on the variety of PmPV properties, for instance the electric conductivity increases almost 8 to 10 times due to the introduction of conductive paths within PmPV. Furthermore, PmPV is highly luminescent in the violet and blue region (380-475 nm) of the visible spectrum, and PmPV/SWNT composition could be a good candidate to use as a photovoltaic device [9, 10].

![Figure 2.6: Schematic presentation of a PmPV molecule](image.png)
2.5 Graphene and 2D Materials

Bulk graphite has been studied for decades. Recently there has been enormous interest in order to produce a single layer of carbon atoms. Graphene is a 2D material in which carbon atoms are bonded together in a hexagonal lattice. It can be viewed as an individual atomic plane extracted from graphite, as unrolled single-wall carbon nanotubes or as a giant flat fullerene molecule (see Figure 2.7). A few such layers stacked on top of each other are still considered graphene; it takes at least 10 layers before a sample becomes graphite [11, 12].

Graphene is a potential candidate for a number of applications, this is because graphene has proved to have exceptional properties, including: very fast electron transport, the highest mechanical strength of known materials, greatest thermal conductivity (anomalous Quantum-Hall-Effect). The mechanical properties and great thermal conductivity are due to the covalent carbon-carbon bonds, this is equivalent to the bonds held in diamond and giving graphene similar mechanical and thermal properties as diamond [14, 15]. The extraordinary electronic properties are a direct consequence of the peculiar band structure of graphene, a zero band gap semiconductor with two linearly dispersing bands that touch at the corners of the first Brillouin zone [16, 17]. Figure 2.8a shows the 2D hon-

Figure 2.7: A pictorial representation of graphene, when rolled into a tube, graphene forms 1D carbon nanotubes, and when in a ball shape it forms 0D fullerenes (adapted from [13]).
Chapter 2. Materials and Methods

Figure 2.8: (a) A top view of a graphene lattice with lattice vectors $a_1$, $a_2$ and unit cell [20]. (b) The graphene $\pi$ and $\pi^*$ band structure over the complete Brillouin zone [22].

eycomb of graphene and the unit cell which contains two subtleties A and B. The even numbers of electrons per unit-cell makes it impossible to say if the system will behave like a metal or a semiconductor [18]. The lattice vectors of the unit cell can be written as:

$$a_1 = a_0 \sqrt{3} \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right)$$  \hspace{1cm} (2.4)

$$a_2 = a_0 \sqrt{3} \left( -\frac{1}{2}, \frac{\sqrt{3}}{2} \right)$$  \hspace{1cm} (2.5)

Where $a_0 = 1.42^{\circ}$ denotes the bond length of the nearest neighbouring C atoms, so the length of the lattice vectors is given as $a = |a_{1,2}| = \sqrt{3}a_0$ [20, 21].

2.5.1 Graphene Synthesis

After the experimental discovery of the first isolated graphene sheet, led by Andre Geim and Kostya Novoselov [13], several techniques have been used to synthesize mass production of graphene sheets. At the moment, three major practical methods have been suggested to produce graphene including: mechanical exfoliation, liquid exfoliation of graphite, CVD and Micromechanically cleaved graphene. The first method, mechanical exfoliation of graphite crystals, which is also known as the ‘Scotch tape’ or peel-off method begins with graphite spread over a defined area of the tape and folded several times upon itself. The area of the tape, which is covered by very thin layers of graphite
is then pressed onto the surface of the substrate and the tape is lifted off very slowly. Although, this technique simplifies the process of finding single graphene sheets and has produced the highest quality samples, the production of graphene on the large scale with this method has limitation. The probability of finding individual graphene sheets of good quality is often low limiting this fabrication scheme to devices for research purposes.

### 2.5.2 Growing Graphene

In CVD growth process, carbon atoms stick to the surface of a metal substrate, such as nickel (Ni) and copper (Cu), under high temperatures. Once a carbon atom occupies a position on the surface of the substrate it pushes other carbons to the side, creating a one atom thick layer of carbon [23-27]. In this method, the graphene crystallization will start at various places on the surface of the substrate before the entire area has formed a lattice. Each of the initial crystallization areas has been referred to as a nucleation site and establishes an orientation for the lattice that grows from it. As various crystal regions grow out from nucleation sites, their borders will meet and a discrepancy will probably occur between the lattice orientations of each region. This will create a definite boundary between regions. Growth stops when every region is surrounded by such boundaries (or at the edge of the substrate). At this point the regions are called domains. In CVD and epitaxial growth, large-area graphene films (up to $\sim 1 \text{ cm}^2$) of single to few layer graphene could be generated. Researchers are optimistic about extending CVD growth to silicon wafer sizes [25].

One of the disadvantages with this method is transferring the graphene layer to a substrate, which is somewhat difficult and may degrade the quality of the layer and lead to folding of the layer. Another disadvantage is that the use of high temperatures is cost-ineffective, and thus may not be suitable for large scale manufacturing. Also, domain boundaries represent defects in the crystal structure of the graphene, since along those lines the bonding of the carbon atoms does not follow the simple Bravais lattice from a repetition of the unit cell.
2.5.3 Liquid Phase Exfoliation of Graphene

Recent research proposed by Hernandez et al. [28] showed a very effective way to produce graphene by exfoliation of graphite in a number of organic solvents such as N-Methylpyrrolidone (NMP), N,N-Dimethylacetamide (DMA), \(\sigma\)-butyrolactone (GBL), 1,3-dimethyl-2-imidazolidinone (DMEU) and \(N,N'\)-dimethylformamide (DMF). Among the proposed solvents, NMP seems to have a high yield with high-quality, unoxidized monolayers of graphene produced [28, 29]. In fact, this process works for solvents which have high interaction energies with graphene equal or greater to the graphene-graphene interaction energy and also much lower than the bulk solvent-solvent interaction energy. This results in a minimal energy cost to overcome the van der Waals forces between the graphene sheets [28, 30]. Figure 2.9 shows TEM images of a graphene sheet made by the liquid exfoliation technique.

![TEM image of graphene](image)

Figure 2.9: High resolution TEM images of a graphene sheet made by the liquid exfoliation technique [28], the sheet pointed with arrows.

In this technique, low power sonication followed by mild centrifugation results in a very low concentration of single layer of graphene (0.01 mg/ml). However, it is possible to produce high quality graphene with higher concentration by increasing the sonication
time. Hernandez has shown that efficient solvents should have surface tensions equal to
that of graphene in order to minimize the enthalpic cost of mixing.

2.5.4 Bilayer Graphene

As previously mentioned, graphene has extraordinary electron mobility and other
unique features which make it a great candidate in nano-scale electronics and photonic
devices. However, not having a band gap prevents complete control over the electrical
conductivity and flexibility in design and optimization of electrical devices [4, 31].
Bilayer graphene consists of two stacked monolayers lying one above the other. As ad­
ditional layers are introduced, the structure becomes increasingly complex, resulting in
unique behaviour. Nevertheless, symmetric bilayer graphene also has a zero band gap
and thus behaves like a metal. But a tuneable band gap can be introduced if the mirror­
like symmetry of the two layers is disturbed making bilayer graphene a subject of interest
in many areas [4, 16, 32].

2.6 Silver Nanowires

Nanowires (NW) possess high length-to-width structures and singularities in their
joint density of states which allow quantum effects in NWs to be optically observed. The
ability to prepare wires of any materials on any substrate with varying thickness makes
them good candidates in the future of electronic and optical devices. For example, NWs
have been proposed for applications associated with electron field emission such as flat
panel displays [33]. Nanowires were defined as having at least two dimensions between 1
and 100 nm [34] and possessing the major advantage of relatively low optical conduc­
tivity within these networks leading to relatively high transmittance for given thicknesses.
They also can be deposited from the liquid phase, are stable under flexing, and tend to
display sheet resistance >100 Ω/sq for transparency ∼ 85% [35]. Also, Ag nanowire
meshes can potentially be deposited at much lower costs because they are processed from
solution at moderate temperatures of 180-200°C [36]. Figure 2.11 shows SEM and AFM
macrograph of AgNW networks.
Figure 2.10: (a) A monolayer graphene with no band gap. (b) Symmetrical bilayer graphene also lacks a band gap. (c) Asymmetry into the bilayer structure yielding a band gap ($\Delta$) [4].

Nanowires do not occur spontaneously in nature and require synthesis inside a laboratory environment. In the past ten years, many methods were developed for the synthesis of Ag nanowires with various levels of control over the growth parameters. The two most common techniques to synthesize AgNWs are vapour phase and solution phase approaches. These approaches have the advantages of homogeneous reactions [34]. Although, many methods exist to fabricate NWs there are limitations to assembling these NWs into highly ordered arrays over a large area. Predetermined spacing and end-to-end registry have been until now extremely challenging to control. Recent research shows
Figure 2.11: (a) SEM and (b) AFM height images of spray-coated AgNWs on glass substrate

that successful alignment and patterning of NWs would significantly affect many areas in nanoscale electronics, optoelectronics, and sensors.

Lately, several research groups have been working on assembling of AgNWs from the liquid phase. These include vacuum filtration, spraying coating, spin coating and LB techniques [35, 37, 38]. According to recent literature, among these techniques, spray coating directly onto the substrate is the most promising one; as this technique involves no additional surface treatment to the substrate. Also large-scale deposition is possible on a variety of substrates (glass, plastic and fabric) with a myriad of geometrical arrangements.

2.7 Deposition Techniques

2.7.1 Liquid Phase Deposition Techniques

There are many techniques to deposit an organic thin film onto a solid substrate including; spraying dispersion, spin coating, solution casting, or electopolymerization. Among these techniques, vacuum filtration and LB are relatively quick methods for developing smooth film morphologies.
2.7.2 Vacuum Filtration

Vacuum filtration is a technique for separating a solid product from a solvent or liquid reaction mixture. The mixture of solid and liquid is poured through a filter paper in a Buchner funnel. The solid is trapped by the filter and the liquid is drawn through the funnel into the flask below by a vacuum [39-41]. Film thickness can be precisely controlled through the filtration method by controlling the dispersion concentration. However, vacuum filtration is limited by the filter size, which is a severe drawback for large-scale applications [41-43].

2.7.3 Spray Coating

Spray coating techniques are effective ways to produce uniform thin films on a large scale. Uniformity is critical in being able to consistently produce high quality films. For this technique many parameters need to be controlled such as spraying pressure, flow rate, scan speed, height, and substrate temperature. Recently, several research groups have shown interest in using this technique over others due to its low cost and robust approach for large-size, uniform films. On the other hand, among these techniques it has been difficult to produce homogeneous thin films with controlled thickness and conductivity on the nanoscale [43]. Figure 2.11 shows SEM and AFM images of a typical respective network produced using this technique.

2.7.4 Spin Coating

Another approach to thin film fabrication is spin coating. This technique has been applied by researchers for many years due to its relatively simple process, low cost, and ability to produce films with accurate thicknesses down to the nanometre scale. This technique works by utilising centrifugal forces to remove the excess liquid from the substrates’ surface and significantly increase the evaporation rate of volatile solvents [44] (see Figure 2.12). The diagram below gives a rough idea of how the spin coating process works. The arrows represent the motion of the solution on the substrate during spinning. A crucial key in many practical applications is to control the films thickness which in
CHAPTER 2. MATERIALS AND METHODS

Figure 2.12: Key stages of spin coating process, centripetal acceleration will cause most of the resin to spread to, and eventually off, the edge of the substrate, leaving a thin film of material on the surface [44]

this technique can be adjusted by varying parameters such as the rotation speed, rotation time, and the concentration of the solution. As the film is spun, it becomes progressively thinner and more uniform. However, there are drawbacks to this process. It is not suitable for larger-scale applications, as the substrate cannot be spun at a sufficiently high rate to allow thin film formation. The whole spinning process only takes a few seconds which would make for a quick turnaround. Another point is that the process makes an inefficient use of the material introduced to the substrate, typically only 2-5% [44].

2.7.5 Drop Casting

One of the simplest methods to fabricate thin films is drop casting from solution. Here, the solution is simply ‘dropped’ onto the substrate and then the solvent is allowed to evaporate, at room or at an elevated temperature depending on the solvent boiling point, from the substrate leaving behind a thin-film. This method has a potential advantage for fabrication on a large scale but cannot provide much precision in terms of film thickness.

2.7.6 Langmuir Techniques

Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) techniques are the most promising techniques for controlling monolayer thickness also have the advantage of depositing thin films on the surface of any kind of solid substrate. An important aspect of this tech-
nique is the ability to make multilayer structures with varying layer composition through repetitive stamping.

### 2.7.7 Historical Overview

LB films have been the subject of scientific curiosity for most of the twentieth century [45]. The idea began with Benjamin Franklin who in 1774 reported the following to the British Royal Society [46]. "At length at Clapham where there is, on the common, a large pond, which I observed to be one day very rough with the wind, I fetched out a cruet of oil, and dropped a little of it on the water. I saw it spread itself with surprising swiftness upon the surface. The oil, though not more than a teaspoonful, produced an instant calm over a space several yards square, which spread amazingly and extended itself gradually until it reached the leeside, making all that quarter of the pond, perhaps half an acre, as smooth as a looking glass "[47].

Further investigations carried out by Rayleigh, Devaux and Hardy confirmed the monolayer nature of LB films [47]. Irwin Langmuir was performing systematic studies on floating monolayers of molecular films on a gas-liquid interface. This study was continued several years later by his assistant, Katherine Blodgett. A Nobel Prize was awarded to Langmuir and Blodgett for this study. However, almost half a century passed before the production of ultrathin organic films with the LB-technique was achieved by scientists around the world when they realized the practical opportunities of this unique technique.

### 2.7.8 Monolayer Materials

Surfactants with amphiphilic natures are required to form a monolayer. These molecules become trapped at the interfaces of two phases, usually liquid-liquid or sometimes liquid-gas, and cause drastic reductions in the surface tension of water molecules [46].

### 2.7.9 Surfactant

Surfactants are amphipathic compounds that lower surface or interfacial tension of a system. A surfactant molecule contains polar hydrophilic and nonpolar hydrophobic
or lipophilic groups [48] (see Figure 2.13A-B). When used at relatively low concentrations, they have the capability of adsorbing onto the surface or boundary between any two immiscible phases of a system thereby lowering the interfacial tension [49].

In general, the interaction between molecules in the interior of the substance is stronger than molecules at the surface and this is due to molecules in the interior being attracted equally in all directions, whereas those at the surface experience a net inward force. This inward force pulls molecules from the surface into the interior, to reduce the area. When a surface active agent is dissolved in a solvent, the lyophilic component of a surfactant will cause an increase in the interfacial free energy of the system by distorting the solvent-liquid structure [48].

![Figure 2.13: (a) An example of an amphiphilic molecule. (b) Surface active molecules or surfactants. (c) A spherical micelle [24].](image)

### 2.7.10 Micelle Formation by Surfactant

One of the fundamental properties of surfactants is the formation of spherical structures in the solution called micelles [23] (Figure 2.13C). Micelles spontaneously form at a given concentration called the critical micelle concentration (CMC) (see Figure 2.14). Any physical properties of the surfactant solution such as electrical conductivity, surface tension, light scattering or refractive index may be used to determine the value of CMC of the surfactant within the solution.
The development of troughs with moving barriers for forming monolayers or multilayers started in the mid-1970s. The first generation of the trough used by Langmuir, Schaefer and Blodgett was made of wax. Since then, the troughs have evolved dramatically. Today, the trough is made of Teflon to prevent any leakage of the subphase over the edges and the process is fully automated. Figure 2.14 shows the surface tension versus the log of concentration. The CMC is found at the point at which two lines intersect; the baseline of minimal surface tension and the slope where surface tension shows linear decline.

Traditionally, the cohesive forces between liquid molecules are responsible for the phenomenon known as surface pressure (or surface tension) (\( \Pi \)). One of means of measuring surface tension is the Wilhelmy plate technique. In this method, \( \Pi \) (mN m\(^{-1}\)) , is defined as the reversible work done in creating a unit area of new surface [49]:

\[
\Pi = \frac{F}{2(W + t)}
\]  

(2.6)

where \( F \) is the force, \( w \) is the width and \( t \) is the thickness. The method for measuring the surface tension is schematically represented in Figure 2.15.

Figure 2.16a shows the scheme of a trough and two moveable barriers for deposition on solid substrates. In order to form a monolayer, an amphiphilic solution is spread on the

![Figure 2.14: Surface tension versus log of the concentration of surfactant in solution [24].](image-url)
Figure 2.15: Wilhelmy Plate Method for measuring the surface tension. The plate with defined perimeter, hung from the micro balance is immersed into the sample liquid (figure adopted from [50]).

water-air interface using a micro-syringe. The solution should spread rapidly to cover the available area. Figure 2.16b shows a pressure sensor which is positioned on the Langmuir trough. Surface pressure of the water surface is measured by immersing a Wilhelmy plate across the air-water interface and measuring the force experienced by this object.

2.7.11 The Bulk Phase of Matter and the Pressure-Area Isotherm

Surface pressure is one of the most important indicators of monolayer properties of an amphiphilic substance and is given by measuring the surface tension (mN/m) as a function of the area (cm²) of the water surface available to each molecule [25]. As the film is compressed by reducing the surface area within the barriers, the Π - A isotherm will show three main phases depended on molecular interaction at the surface. When no external pressure is applied to the monolayer, the monolayer molecules mimic the behaviour of a two-dimensional gas. The energy of such a system can be described by ΠA = kT, for ideal gases, where Π is the surface pressure (mN/m⁻¹), A is the molecular area, k is the Boltzmann constant and T is the temperature. As the gaseous-like monolayer is compressed on the subphase surface, the increase in pressure will cause an additional ordering thereby inducing a two-dimensional liquid like state upon the water-air surface. The nature of these phase changes by compression of the monolayer for stearic acid is
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Figure 2.16: (a) A schematic illustration of LB trough and barriers for increasing or decreasing the available surface area. (b) Wilhelmy filter plates and a micro-balanced to measure the surface tension (II).

illustrated in Figure 2.17.

2.8 LB and LS Film Deposition Techniques

2.8.1 Transfer of Monolayer Towards Substrate

As mentioned above, the Langmuir deposition techniques are unique since the monolayer can be transferred to many different substrates [45] including those with hydrophilic or hydrophobic character. Most LB depositions involve hydrophilic substrates such as glass, quartz, aluminium and most commonly silicon. In order to make a monolayer on a hydrophilic substrate, the substrate must be immersed in the subphase prior to spreading and compressing the monolayer [47].

There are two methods of Langmuir deposition of monolayers onto solid substrates. The first and most commonly employed method, first introduced by Blodgett, is vertical deposition of a solid substrate. Figure 2.18 illustrates the vertical deposition of the first
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Figure 2.17: Surface pressure versus area per molecule isotherm for a stearic acid shows three distinct regions (gas, liquid and solid) [47].

monolayer onto hydrophilic substrate as the substrate is raised from the water.

Figure 2.18: A schematic model of LB deposition on a hydrophilic substrate.

Subsequently, a monolayer coated substrate can also be used for building up highly organised multilayers of the amphiphile solution. However, there are different techniques for vertical deposition of LB films as well. Y-type multilayer structures occur if the deposited surfactant molecules are head to head or tail to tail on both the up and down stroke of the substrate. Also, two other vertical deposition modes are possible, when the monolayer deposits only in the up or down direction, the multilayer structure is called either Z-type or X-type. The X-type multilayer structure occurs when each subsequent layer is transferred on the down stroke into the water and the Z-type formation occurs on the up-stroke position. Formation of mixed depositions is possible as well. Figure 2.19 illustrates the three different types of vertical deposition.
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Vertical dipping is not the only way of building monolayers; the second method of transferring a monolayer film to a solid substrate involves horizontal lifting, shown in Figure 2.20, also called Schaefer’s method [45]. This method is based on touching one edge of the substrate with the top of monolayer. The monolayer is transferred to the solid substrate when the substrate is lifted and separated from the subphase. The advantage of this method over vertical is that the monolayer encounters fewer disruptive forces. However, this method can only be used for the transfer of highly rigid film to the substrate. The difference between two depositions technique (LB) and (LS) has been illustrated in Figure 2.21.

Figure 2.19: 'Y', 'X' and 'Z' type vertical deposition of LB multilayers, figure adopted from [47].

Figure 2.20: LS technique for horizontal deposition of the film onto a substrate (figure adopted from [30]).
2.9 Analyzing and Characterization Techniques

2.9.1 Raman Spectroscopy

There are many techniques for analysing nano-materials, especially those incorporating carbon based materials. These include X-ray diffraction, IR and Raman spectroscopy. Raman spectroscopy is a spectroscopic technique based on the inelastic scattering of monochromatic light, usually from a laser source. It provides information about molecular vibrations that can be used for sample identification and quantification. When the incident light passes through a sample, it interacts with molecules or atoms and distorts (polarises) the cloud of electrons surrounding the nuclei to form a short-lived ‘virtual state’. This event occurs in $10^{-14}$ seconds or less. Consequently, two types of scattering can occur: elastic and inelastic.

Photons scattered elastically, called Rayleigh scattering, do so with an equal frequency to that of the incident radiation. However, it is possible to get a small fraction of photons which scatter inelastically at higher or lower energies. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample; this phenomenon is called Raman scattering.

The difference in energy between the inelastic scattered radiation and the incident radiation corresponds to transitions between vibrational energy levels of the molecules. If the scattered photons possess energies less than their initial energy, it is called Stokes scattering. A spectral analysis of the scattered light under these circumstances will reveal
Figure 2.22: (a) Comparing the relative intensity of Stokes, anti-Stokes and Rayleigh lines. (b) Energy level diagram for Raman scattering; Stokes scattering and anti-Stokes scattering.

spectral satellite lines below the Rayleigh scattering peak at the incident frequency. If the scattered photons have energies greater than the incident photons, then vibrational energy has been added to the incident photon energy in a process called anti-Stokes scattering as shown in Figure 2.22. The Raman Effect is the basis of Raman spectroscopy and was pioneered in 1928 by the Indian physicist, C. V. Raman. Figure 2.22a shows that the relative intensities (indicated by peak height and width) of anti-Stokes lines are much less than Stokes lines and they are both significantly less than Rayleigh lines.

Higher amplitude signals in Raman spectroscopy can be detected when incident or scattered photons are in resonance with the excited electrons. These two resonance phenomena are called incident resonance and scattered resonance respectively. The incident laser energy should be equal to the separation energy between two electronic states. The following equation, Equation 2.7, gives the difference in scattered resonance and incident
Figure 2.23: Micro-Raman spectrometer scheme equipped with confocal microscope used for Micro Raman 3D imaging. Acronym in photo LD: laser driver POL: polarization rotator USB SMD: two axis stepper motor controller M1 and M2: motorized flip mirror L1, L2: focusing lenses SH: sample holder, FN: Notch filter.

resonance [1, 2, 51].

\[ E_L = \Delta E + \hbar \omega (\text{Scattered resonance}) \]  \hspace{1cm} (2.7)

\[ E_L = \Delta E (\text{Incident resonance}) \]  \hspace{1cm} (2.8)

Where \( E_L \) is the energy of incident laser beam and \( \hbar \omega \) is photon energy [2, 52].

2.9.2 Polarized Raman Spectroscopy

Raman spectrum provides information relating to the molecular shape, orientation and vibration symmetry within crystal lattices, liquid crystals or polymer samples. Polarized Raman uses a polarized laser excitation and a polarization analyser, the spectra acquired with the analyser set can be used to acquire spectra, either parallel or perpendicular to the excitation laser. The ratio of the peak intensity of the parallel and perpendicular
component can be used to calculate the depolarization ratio $\rho$:

$$\rho = \frac{I_\perp}{I_\parallel}$$ (2.9)

Where $I_\parallel$ is the intensity of the scattered light whose polarisation is parallel to the polarisation of the excitation light and $I_\perp$ is the intensity of scattered light whose polarisation is perpendicular to the polarisation of excitation light collected by the system [53].

### 2.9.3 Scanning Electron Microscopy

SEM is a type of electron microscope that uses the intensity of mostly secondary electrons (SE) and back-scattered electrons (BSE) to produce a magnified image. The electron beam hits the sample and interacts with atoms within the 3-dimensional space in the specimen known as the interaction volume. The scattering event of the electrons travelling through the interaction volume can be divided into two general classes; inelastic scattering and elastic scattering. In inelastic scattering, electrons scatter within the target material, losing energy and changing direction with each atomic interaction. During this event, secondary electrons, backscattered electrons, and X-rays are ejected from the sample. Backscattered electrons are elastically scattered from the nuclei of atoms in the solid. Detectors collect X-rays, backscattered electrons, and secondary electrons and convert them into a signal. Figure 2.24 show a schematic of the typical SEM set up.

![Figure 2.24: A schematic diagram of a scanning electron microscope [27.]]
2.9.4 Atomic Force Microscopy

AFM provides many advantages over conventional microscopy techniques. For example, SEM can only image conducting or semiconducting surfaces; however, AFM has the advantage of imaging almost any type of surface, conducting or non-conducting in a range of environments as opposed to a vacuum. The information is gathered with a mechanical probe consisting of an elastic cantilever with a sharp tip on the end and is capable of making measurements in all spatial dimensions presented in Figure 2.25 is a schematic of the typical AFM set up. AFM is generally operated in three modes: contact mode, semi-contact mode, non-contact mode. Contact mode AFM imaging monitors the bending of the cantilever due to changes in the sample surface with atomic-scale sensitivity by an optical lever system. A laser beam directed onto the cantilever is reflected via a mirror to a position sensitive photodiode. A piezoelectric ceramic scanner controls the motion of the cantilever by an electronic feedback mechanism. Although contact mode achieves the best resolution, in order to study soft materials such as polymeric thin films, a non-destructive method is required. Semi-contact mode, sometimes called intermittent-contact mode, can be employed and operates by detecting the oscillations of the cantilever at a frequencies close to its free resonant frequency given by:

\[ v = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \]  

(2.10)

Where \( k \) is the spring constant and \( m \) is the mass of the cantilever. Non-contact AFM, maps topography by lightly tapping the surface with an oscillating probe tip excited by a piezo-electric driver, where the cantilever oscillates above the surface of the sample.

2.9.5 UV-Visible Absorption Spectroscopy

Absorption spectroscopy is a very common procedure for identifying compounds measuring the concentrations of solutions or dispersions. This process indicates some interactions of the light with the sample by measuring the attenuation of a beam of light at a given wavelength after it passes through a sample. In this technique, the instrument measures the intensities of the input \( I_{in}(\lambda) \) and output \( I_{out}(\lambda) \) light to identify the absorp-
Absorbance is directly proportional to the path length, $b$, and the concentration, $c$, of the absorbing matter. The measurement of an absorption spectrum is based on Beer's Law given in Equation 2.11:

$$A = - \log\left(\frac{I_{in}}{I_{out}}\right) = \varepsilon bc$$  \hspace{1cm} (2.11)

Where $\varepsilon$ is a constant of proportionality, called the molar absorptivity of the solution.

---

**Figure 2.26:** Measurement principle of light absorption spectra by changing the wavelength over the required range.
Absorption spectra of ultraviolet and visible radiation of organic molecules are restricted to the certain functional groups, chromophores, by exciting a ground state electron into an excited state. The spectrum of a molecule containing these chromophores is complex because the superposition of rotational and vibration transitions on the electronic transitions gives a combination of overlapping lines. This appears as a continuous absorption band. These are the transitions of interest in the study of PmPV given the presence of the phenyl group in the polymer structure.

2.9.6 Fluorescence Spectroscopy

Fluorescence is the emission of light from an aromatic molecule. Fluorescence spectroscopy is used in a number of chemical and biological applications and is especially applicable to low concentration range studies because of its inherent sensitivity. Fluorescence often quantifies unknown concentrations, determines excitation lifetimes, and detects fluorescent species [10].

$I_{flu}(\lambda)$ represents the intensity of the fluorescence light emitted by as a function of

![Fluorometer Diagram](image.png)

**Figure 2.27:** A simple fluorometer contains basic spectroscopic components. A light source passes through an excitation filter or diffracts off a monochromator to allow one wavelength region of light to irradiate the sample which then emits in all directions. Emission filters or separate monochromator then select light of the wavelength of interest and directs it into the emission detector. Emission detectors are usually placed at right angles to reduce detection of scattered light emanating from the solvent and cuvette.
emission wavelength. Molecular emission occurs when molecules in an excited electronic state radioactively decay to their ground electronic states. To excite to the higher electronic state, molecules must first receive an amount of energy equal to the difference between excited and ground state energy levels. Emitted fluorescent light occurs at lower frequencies than the excitation light because while the molecule is in the excited electronic state, vibrational relaxations transfer energy to their environment through heat. In this study, optical spectroscopy (absorption and emission of light by matter) is used to detect the dispersion states and concentrations of carbon nanotubes and polymers. A sample's optical spectrum can reveal its electronic transition energies, concentration, extinction coefficient and interactions with its environment.

2.9.7 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is one of the most powerful techniques for determination of molecular composition and structure by detecting the vibrational transitions of a molecule. This technique has advantages of measuring solid, liquid and gaseous sample and it could collect all wavelengths, NIR to FIR spectra. In infrared spectroscopy, IR radiation is passed through a sample as molecules absorbing specific frequencies matching the transition energies of bonds or chemical groups. Infrared spectroscopy probes molecular motions that involve a change in a bond’s dipole moment.
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2.10 References

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Chapter 3

Density Controlled Conductivity of Pristine Graphene Films

3.1 Introduction

Graphene, a two-dimensional (2D) honeycomb lattice structure of carbon atoms, possesses intriguing properties. Its micrometer-scale ballistic-type electrical transport [1, 2] opens up the possibility for many new applications such as field-effect [3] and spintronic devices [4] as well as chemical sensing [5]. It’s intrinsic strength, modulus [6] as well as thermal conductivity [7], far exceeding that of diamond [8] or carbon nanotubes (CNTs) [9], have inspired the fabrication of high-performance functional composite materials [10, 11] and electronic circuits [12, 13]. In order to fully utilize graphene’s unique properties there are two bottlenecks to overcome; namely (i) the controlled production of high-quality graphene with a selected number of layers in large quantities and (ii) the controlled uniform deposition of graphene over large areas. Several methods have been developed to produce high quality graphene including micromechanical cleavage [14], epitaxial growth [15, 16], chemical reduction of exfoliated graphene oxide [17-19], CVD growth [20] and liquid phase exfoliation of graphite [21, 22].

However, only the latter method appears to be presently suited for mass production of high-quality un-oxidized graphene that can be fully dispersed in a wide variety of organic solvents [23]. Good control over the chemical purity of the sheets is essential for
the efficiency of graphene-based electronic devices and sensors, and different approaches to achieve this have been reported. Mono-or multilayers of 2D pristine graphene and graphene oxide (GO), can be assembled from solution using conventional layer-by-layer (LbL) assembly [24-27], by vacuum filtration [28, 29] or by spray coating [23].

The assembly of materials at the air-water interface using the Langmuir process is another way of fabricating thin films. It can be realized by spreading a dispersion which has been previously dispersed in an organic solvent onto a water subphase, evaporating the solvent and finally compressing the floating monolayer. The vertical or horizontal transfer to a substrate can be achieved using the LB [17, 30-32] or the LS [33] techniques respectively. The LB and LS methods facilitate the formation of thin films with controlled thickness and a high degree of structural order. There have been several reports already of using these techniques to produce films of GO, which can then be thermally or chemically treated to form graphene, however the need for this final step is not ideal [17, 31, 33].

Here, a method to produce pristine graphene thin films using the LS approach were shown. This method requires no post-processing treatment. Typically, solvents that have been shown to efficiently exfoliate graphene have low vapor pressure and are hence not ideal for use in the LS process. Therefore a mixed solvent strategy were used, which not only facilitates efficient liquid phase exfoliation of graphene but modification to the solvent mass ratio manipulates the vapor pressure so as to be more amenable for the process. The resulting dispersions can be successfully used as a pre-cursor to the self-assembly of pristine graphene at the air-water interface which can be subsequently transferred by the LS technique onto a solid substrate. The technique allows for the deposition of pristine graphene flakes over large areas and for control over film density as well as the number of layers in the film. Through careful control of density, by following the pressure-area isotherm during monolayer compression, it is possible to precisely tune the electrical conductivity. Our results point to the potential of the LS deposition technique to prepare high quality graphene films on various substrates which potentially could be suitable for a range of applications including thin-film flexible electronics, optoelectronics and sensors.
3.2 Experimental Methods

3.2.1 Graphene Dispersion

The graphene dispersion was prepared as described elsewhere [22]. Briefly, as-produced sieved graphite powder (Aldrich product 332461, batch number 06106DE) was added to N-methylpyrrolidone (NMP) (spectrophotometric grade, 99.0%) to give an initial graphitic concentration of 0.1 mg/ml. This mixture was sonicated using low power bath sonication (Model Ney Ultrasonic) for 30 minutes. The resulting dispersion was then centrifuged (using a Hettich Mikro 22R centrifuge) for 90 minutes at 500 rpm. The resulting supernatant was used for further processing. The final dispersed graphene concentration in NMP was calculated to be 0.876 mg/ml (from the absorbance at 660 nm using an extinction coefficient of 3620 L/g/m). 1 mL of the resulting NMP dispersion was mixed with 100 mL of chloroform (Sigma Aldrich) and sonicated using bath sonicator (fisher scientific FB15051) for 60 minutes, followed by centrifugation (Eppendorf 5702) for 90 minutes at 4000 rpm - 2500 G. The supernatant was then bath sonicated under chilled conditions (ice bath) for a further 30 minutes. The final dispersed graphene concentration in NMP/chloroform mixture was calculated to be 0.007 mg/ml.

3.2.2 Langmuir-Schaefer Deposition of Graphene

For LS deposition of graphene, a commercial deposition trough (NIMA Technology, Model 612D) was used. In order to form a monolayer at the air-water interface, the graphene dispersion in a chloroform/NMP mixture (8-10 mL) was spread onto the water subphase (ultra-pure Millipore water) with a microliter syringe utilizing drop-by-drop deposition technique. The pressure-area isotherms were obtained after 10 min waiting time to let the remaining solvent evaporate (see Figure 3.1). The surface tension was determined by suspending a Wilhelmy paper plate completely wetted by water. Measuring the downward force on it during compression of the monolayer by moving two opposing barriers towards each other at the speed of 15 cm²/min. Thin films of graphene were then transferred onto glass substrates by LS horizontal deposition technique at various surface pressures (ranging from 0 to 40mNm⁻¹), using a transfer speed of 3 mm/min. Prior to
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3.2.3 Characterization

The length distribution of graphene flakes in NMP was evaluated statistically using a transmission electron microscopy (TEM) by drop casting the dispersion onto a holey carbon TEM grid. The length distribution of graphene in NMP/chloroform mixture as well as thickness distribution of graphene flakes in both, NMP and NMP/chloroform was evaluated statistically using an AFM. AFM topographic analysis of the dispersions as well as LS graphene films deposited on glass substrates was performed in a semi-contact mode using NT-MDT AFM (Moscow, Russia). The AFM probes used (NT-MDT) had an average spring constant of 11.8 Nm$^{-1}$. Samples were prepared by spin-coating the dispersion onto freshly cleaved mica at 3000 rpm for 10 seconds.

The current-voltage characteristics have been obtained using a Keithley Model 4200. The final specific conductivity calculated from the resistance and thickness of the film. All sample thicknesses were measured using AFM. Gold electrodes $\sim 70\ \mu$m thick were evaporated using Kurt J. Lesker evaporator on top of LS graphene films. The distance between electrodes was 4mm. The width (W) and length (L) of each electrode was 1 mm and 8 mm respectively (see Figure 3.2). The transmittance data of LS films was obtained

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**Figure 3.1**: Schematic image of a Langmuir trough, graphene monolayer were spread at air/water interface by using a micro-liter syringe.

the film deposition, substrates were cleaned by rinsing them thoroughly with de-ionized water followed by sequential sonication in de-ionized water, isopropyl alcohol (IPA) and methanol for 5 minute in each solvent.
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3.3 Results and Discussion

3.3.1 Dispersion and exfoliation of graphene in high and low boiling point solvents

The graphene dispersion in NMP has been prepared by the method of liquid phase exfoliation of graphite [22]. The choice of solvent was dictated by its ability to achieve suspensions of high quality, defect-free, and un-oxidized graphene at relatively high concentrations[34]. Histograms of the size distribution of flakes as obtained from TEM analysis are shown in Figure 3.3a. As can be seen, graphite is almost completely exfoliated to multilayer structures with less than 5 layers in NMP. The average flake size is \( \sim 500 \) nm.

Representative TEM images of the flakes observed are shown in Figure 3.3b where graphene monolayers (with well-defined edges) as well as multilayers can be easily distinguished. It should be noted that a small number of larger objects (a few tens of flakes thick) was also present in the dispersion. The high dispersion efficiency of NMP is attributed to its ability to match the surface energy of graphene. Consequently, the NMP-graphene interaction is balanced with the exfoliation energy resulting in a minimal energy...
cost to overcome van der Waals forces between the graphene flakes [22, 35]. Since NMP is completely miscible with chloroform [36], the initial graphene dispersion was diluted down to a ratio (NMP/chloroform) of 1:100 as described in the experimental section. To estimate the size distribution of graphene flakes after dilution, AFM analysis was performed and histogram analysis of length (Figure 3.3c) and thickness (Figure 3.3d) of more than 150 graphene flakes were obtained. It can be seen that a large population of flakes are single-layered as shown on the representative AFM topography image and height profile in the inset of Figure 3.3d. However, flakes consisting of two-layers, three layers and multilayers are also present. The average flake major axis is 305 nm which is smaller than
those observed in the initial NMP dispersion. Narrowing of the flakes length distribution as well as the thickness maybe due to further dilution and additional ultracentrifugation of the already exfoliated flakes [37].

The use of the NMP/chloroform mixture to facilitate the spreading process is not a new concept, and has been successfully used previously for the deposition of conducting polymers [38, 39]. Such a mixed-solvent strategy is required for the following reasons. Firstly, the LS deposition technique requires the use of a low boiling point, water immiscible solvent. This is because the spreading solvent must evaporate within a reasonable period of time to avoid residue being present in the condensed material [40, 41]. NMP is highly miscible with water and its vapor pressure at 20 °C is very low so, on its own, is inappropriate for the deposition of graphene. When a nonvolatile solute such as NMP is added to a volatile solvent such as chloroform, the vapor pressure of the solution will be lower than that of the pure solvent as determined by Raoult’s Law. The vapor pressure of chloroform and NMP at room temperature is 21.3 kPa and 0.039 kPa, respectively. The total vapor pressure will lie between the vapor pressures of the pure components, and can be determined by the mixture composition according to the following formula 3.1 [42]:

$$p_{\text{mixture}} = p_A^X A + p_B^X B$$

A dilution of the graphene dispersion in the solvent mixture also enables complete spreading of graphene over the interface. The use of a more concentrated graphene dispersion results in poor spreading due to large graphene flakes being hindered from accessing the water surface. If a dilute solution is used, the monolayer is laterally homogeneous and the isotherms are independent of spreading conditions, compression speed and are nearly free of hysteresis.

The presence of a small amount of NMP is also critical. As shown by O’Neill et al.[23] the dispersion and exfoliation of graphene in solvents can be predicted by using
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• chloroform

21.3 kPa

chloroform/NMP mixture used

\[ P^0 = 21.04 \text{ kPa} \]

water

1

0.5

Mole fraction of NMP

\[ P' = 2.3 \text{ kPa} \]

0.039 kPa

\[ P_{\text{NMP}}^0 \]

Figure 3.4: The total vapour pressure of the NMP/chloroform mixture calculated using Raoult’s law

the Hansen solubility parameters (HSP) consisting of a dispersion force component (D), a polar component (P) and a hydrogen bonding component (H). Good quality graphene dispersions can only be achieved for solvents that possess HSPs matching well with those for graphene [23]. Chloroform is one of the least successful solvents, probably due to its polar component \[ \delta P = 3.1 \text{ (MPa)}^{1/2} \] which is located at the edge of the acceptable values for solubilization of graphene (3-17 MPa^{1/2}). It is widely accepted that the HSP for a solvent mixture is a linear function of composition [43] according to the following formula:

\[
\delta_{\text{mixture}} = \Sigma \Phi_{n,\text{comp}} \delta_{n,\text{comp}}
\]  

(3.2)

where \( \Phi \) is the volume fraction for each solvent present. Therefore, due to presence of NMP in chloroform, HSPs are shifted towards greater graphene solubility. The resulting dispersion is stable with no precipitation occurring even after a week (inset of Figure 3.4c).

To quantify the relative amounts in the mixture of chloroform and NMP used for our experiments vibrational spectroscopy can be used. Fourier transform infrared (FTIR) is a particularly useful technique in this regard as the vibrational modes of graphene are inactive. FTIR spectra of the NMP/graphene as well as the mixture of NMP and chloroform has been performed (See Figure 3.5). The peaks around 1670 cm\(^{-1}\) are associated with NMP and are assigned to \( \text{C=O stretch} \) [44]. When the mixed system is analyzed the presence of NMP is clearly seen. The relative ratios of NMP to Chloroform can be taken
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Figure 3.5: FTIR spectra of NMP and the NMP mixture with chloroform directly from the spectra by analyzing the reduction in the peak for the NMP feature in the pristine and the diluted sample respectively.

3.3.2 Spreading of Graphene Films at the Air-water Interface

As water has a high surface tension at room temperature, when a solution of graphene dispersed in a water-insoluble solvent such as chloroform is placed on the surface, it rapidly spreads to cover the available area. During solvent evaporation, graphene sheets tend to assemble into 2D films. If the graphene concentration per unit area is low, the distance between adjacent graphene flakes is large and their interactions are weak. At this point, the monolayer can be regarded as a 2D gas that has one interface with the aqueous phase and the other with air and thus has little effect on the surface tension.

When the available surface area of the monolayer is reduced by moving a barrier across the water surface, the graphene flakes start to exert a repulsive force on each other initiating a reduction in surface tension. During compression, the monolayer undergoes
phase transitions from gas to liquid to solid phases before collapsing, yielding a surface pressure-surface area (density) (π-A) isotherm. A typical Langmuir compression isotherm of a graphene monolayer is shown in Figure 3.6 with distinct phase changes and a collapse pressure above 39 mNm⁻¹.

![Figure 3.6](image)

**Figure 3.6:** (a) Representative surface pressure-area (Π-A) isotherm of graphene monolayer deposited from chloroform/NMP mixture at the air-water interface. (b) A corresponding photograph of a Langmuir trough showing a dense graphene monolayer with a glass substrate above the surface ready for a Langmuir-Schaefer deposition.

A compressed graphene monolayer can be considered to be a 2D solid film that is strong and rigid and does not exhibit typical monolayer collapse behavior. As can be seen in the photographs in Figure 3.7a taken perpendicular to the optical axis, the packing density of graphene flakes can be manipulated by altering the surface pressure during the compression/expansion cycle. At a Π=0 mNm⁻¹, graphene flakes are separated from each other forming multiple discrete monolayer islands of various sizes with a surface of a few μm². The presence of these islands is probably a consequence of the large volume of graphene dispersion deposited (10 mL). At lower volumes (below 5 mL), the graphene monolayer is not visible on the water subphase and is difficult to investigate optically until large surface pressures are reached. By compressing the barriers, the monolayer is densified resulting in the multiple discrete islands becoming connected and thus reducing the free space. Compression of the film up to the Π = 40 mNm⁻¹ results in merging of the monolayer islands into a continuous closely packed monolayer.

It should be noted that the interfacial area can only be reduced to a point where graphene flakes resist packing into a higher density state due to the hard limit dictated by
Figure 3.7: (a) Optical photographs of a graphene monolayer film at the air/water interface deposited from chloroform/NMP mixture as a function of surface pressure taken perpendicular to the optical axis. (b) Π-A isotherms of two sequential compression-expansion cycles.

The molecular cross-sectional area. Further compression from this point compromises the stability of the interface and leads to film collapse defined as the movement of graphene flakes from the interface into the bulk resulting in their transition to an out-of-plane geometry.

It is possible to reversibly tune the density if the target surface pressure is not more than 25 mN m\(^{-1}\). For example, Π-A isotherms of two sequential compression-expansion cycles (0-15 mN m\(^{-1}\)) are shown in Figure 3.7b. During the first compression-rarefaction cycle, a minor degree of hysteresis was observed, but this effect was essentially absent during further recompression.
Typically, the monolayers formed contain graphene flakes of various thicknesses ranging from single layered graphene to multilayered structures. Due to the variation in thicknesses, they are not able to overlap, leading to reversible density alterations of the monolayers during several compression/expansion cycles. It is likely that the presence of a negligible amount of residual NMP also aids the spreading by acting as a molecular lubricant, which is slowly squeezed out under applied surface pressure and assists in the increased reversibility of the monolayers during repetitive compression/expansion cycles. The reversibility has also been observed by Cote et al. [31] for GO deposited onto a water subphase from a water/methanol mixture. However, in their situation it is due to the presence of electrostatic repulsion between adjacent flakes.

3.3.3 Langmuir-Schaefer Deposition of Graphene Monolayer Films

The LS technique is used to transfer graphene monolayers from the air/water interface onto a solid substrate. When the graphene monolayer is spread onto the water and compressed to a desired density the substrate is lowered onto the graphene covered interface. Once contact is made the substrate is then retracted resulting in the graphene monolayer being transferred onto the substrate. The choice of LS method over LB was dictated by the fact that LS is more appropriate for the transfer of highly rigid monolayers because the floating monolayer is subjected to less disruptive forces than in the LB method [41].

Figure 3.8a shows a representative AFM height image of a dense graphene film deposited from the maximum surface pressure of ~40 mNm$^{-1}$ which is just before the point of monolayer collapse. The transferred film is homogenous and free of microscopic voids over its entire area. The line profile in Figure 3.8b along the yellow horizontal line in Figure 3.8b shows an average thickness of 15 nm with the majority of the flakes being no thicker than 3 nm.

By following the Π-A isotherm, monolayers at different surface pressure ranging from 0 - 40 mNm$^{-1}$ deposited on glass substrates are shown in Figure 3.9a-e. A film deposited from the gas phase (at = 1 mNm$^{-1}$) is low in density and contains large voids. The deposition at higher Π results in the formation of denser films and consequently fewer voids, until the maximum surface coverage is reached at ~ 40 mNm$^{-1}$.
3.3.4 Electrical Properties of Langmuir Graphene Films

While the resulting films are electrically conducting, the absolute conductivity depends on the density of graphene which is controlled by the Langmuir process. In order to analyze this dependence the surface coverage as a function of $\Pi$ can be obtained di-
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rectly by processing AFM height images using ImageJ software as shown in Figure 3.10.

In order to analyze the surface coverage as a function of pressure (P), ImageJ software was used to directly process AFM height images as shown above. For this reason, 'Mean' method thresholding, that utilizes the mean of grey levels as the threshold, was used to section an image by setting all pixels whose intensity values are above a threshold to a foreground value (graphene flakes) and all the remaining pixels to a background value (glass substrate). Figure 3.10 shows a typical AFM and corresponding threshold image. Here, the black regions represent the substrate, while white regions represent the graphene flakes.

Figure 3.11a demonstrates threshold images of samples at different surface pressure. The electrical conductivity of the growing graphene islands at increased surface coverage can be analyzed using percolation theory given by:

\[ \sigma = \sigma_0 (S - S_c)^n, S > S_c \]  \hspace{1cm} (3.3)

where S is the occupation probability of a conducting area on the substrate (also known as fractional coverage), S_c is the critical value of fractional coverage and n is the critical exponent of the electrical conductivity. In such networks, the ability for electrons to flow requires the formation of conductive pathways through the material. This, in turn, requires a critical density of connections for effective passage of current. As can be seen

Figure 3.10: Analysis of graphene surface coverage using ImageJ software analysis of an AFM image
in Figure 3.11b when the surface coverage reaches ~20% the graphene flakes form islands consisting of loosely packed flakes linked by a small set of inter-cluster connections. As this stage, the percolation is dominated by tunneling of charge carriers from one flake to another and the surface coverage is insufficient to allow the formation of fully-connected pathways. As the surface coverage increases, the film conductivity also increases due to the inter-flake distance reducing until one approaches 100% coverage at which point the conductivity mechanism is ohmic in behavior (as evidenced by I-V characteristics). The best-fitting curve to the data using percolation-type power law scaling is shown in Figure 3.11b yielding a critical exponent $n = 8.95$, a conductivity coefficient $\sigma_0 = 46 \text{ S/m}$ and a formation of the percolative network at $S_c = 9\%$ respectively. Such a high value of a critical exponent $n$ has been previously reported and may be associated with the large distribution of junction resistances at flake-flake interfaces [45]. The highest conductivity for a single layer thin film of graphene obtained by LS is $\sim 19 \text{ Sm}^{-1}$ which is expectedly low compared to the intrinsic conductivity of the individual graphene flakes. Since the films produced consist of graphene flakes of varying thickness, as observed by AFM, the broad distribution of their thicknesses requires charge transport parallel and perpendicular to the graphene sheets. As reported by Nirmalraj et al.[46], the inter-flake resistance is linearly dependent on the graphene thickness. They showed, by connecting a monolayer graphene flake with a bi-layer graphene the resistance at the intersection of $\sim 550-650 \Omega$ was measured. However, when a monolayer graphene was connected to the tri-layer graphene, the resistance jump at the intersection was as high as 6.5 k.

Repetitive stamping of a substrate on the floating monolayer enables the formation of thicker films. As shown in the inset of Figure 3.11b, bi-layers and triple-layered films deposited at the highest surface pressure of $\sim 40 \text{ mN m}^{-1}$ yield a conductivity of $\sim 30 \text{ Sm}^{-1}$ and $\sim 65 \text{ Sm}^{-1}$ respectively. The conductivity can be further enhanced by increasing the number of layers however the transparency would have to be sacrificed. Since the film's transmittance is strongly dependent on the graphene density (see Figure 3.12a), it decreases exponentially as the conductivity increases as shown in Figure 3.12b. One layer of graphene with a conductivity of $\sim 4.8 \times 10^{-6} \text{ Sm}^{-1}$ has a 95% transmittance, while a graphene film of the highest density has a conductivity almost four times higher
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Figure 3.11: (a) Thresholded AFM images of LS films as a function of pressure showing
the change in packing density (here the black areas show the background while the white
areas represent the graphene flakes.) (b) The change in the electrical conductivity as a
function of surface coverage (inset: electrical conductivity as a function of number of
layers deposited).

(4~19 \times 10^{-6} \text{ S/m}) while the transmittance is lowered by only \sim 10\%. Additionally, for
highly dense graphene films it is possible to tune the conductivity without significantly
sacrificing their transmittance. The above results point to the process as being ideally
suited to the preparation of large area electrically conducting graphene assemblies. We
have shown that the transfer of the films formed at the air-water interface to solid sub­
strates is simple and results in solid films of reproducible physical properties. Unlike
GO thin films our systems require no further chemical or thermal treatment to produce
electrically conducting arrays. Interestingly, the controlled deposition of such conduct­
ing assemblies at the air-water interface may have a range of applications in their own
right without transfer to a substrate. For instance, differences in the extent of proto-
nation on either side of water-hydrophobe interfaces are deemed essential to enzymatic catalysis, molecular recognition, bio-energetic transduction, and atmospheric aerosol-gas exchanges and could be easily measured using our floating graphene electrodes. Another application that these films would be ideally suited to is to understand the role the ocean plays in the biochemical cycles of climate modifying gases such as carbon dioxide. The influence of monomolecular films on the gas exchange process is essential. The graphene layers could be used as proxies for biogenic slicks which are prevalent to coastal waters and gas exchange rates could be better determined by dynamically measuring changes in conductivity which we are currently investigating.

Figure 3.12: (a) Representative photograph of the resulting thin film on glass at three different surface pressures. (b) Transmittance versus conductivity for monolayer graphene films.
3.3.5 Raman Spectroscopy of Graphene

There are many methods to characterize graphene, including atomic force microscopy (AFM) and electron microscopy; however, the identification and counting of graphene layers is a major hurdle. AFM measurement has been so far one of the most direct ways to distinguish the number of layers, but this method has some limitation, such as a very slow throughput and it may also cause damage to the crystal lattice during measurement. Furthermore, an instrumental offset of 0.5 nm (caused by different interaction forces) always exists, which is even larger than the thickness of a graphene monolayer. Therefore, researchers have turned to more improved ways to identify different layers of graphene without destroying the crystal lattice [47]. Raman spectroscopy and imaging is another candidate for non-destructive and quick inspection to provide information on the graphene sample quality, its total accumulated charge and the thickness and thereby the number of graphene layers [48]. The unusual dispersion of $\pi$ electrons in graphene means that, using laser excitation from the visible window of the spectrum, the process is always in resonance [22, 47].

3.3.6 Raman Spectroscopy for Characterization of Graphene Layers

In graphene, Raman active modes arise from the $\Gamma$ and $K(K')$ point of the Brillouin zone, providing useful information on the defects and layer stacking. Ferrari et al. have proposed to use Raman spectroscopy as a simple and efficient way to confirm the presence of single layer graphene [47]. Their work shows two prominent features appearing in the Raman spectra of graphene, both of which are strongly connected to graphite. The first feature is the G-band (at $\sim 1582 \text{ cm}^{-1}$ for graphite) corresponding to the in-plane vibration of $sp^2$ carbon atoms. This feature will be upshifted by approximately $5\text{cm}^{-1}$ in single layer graphene. The G-band intensity increases almost linearly as the number of layers increase enabling researchers to determine the thickness of multilayer graphene from the G-band intensity [47, 49].

The second spectral feature is the 2D band at about $\sim 2700 \text{ cm}^{-1}$. This feature occurs in the second-order Raman spectrum and is the second order mode of zone-boundary phonons. This feature is extremely sensitive to the number of layers of graphene. In
particular, the shape of the 2D band, could identify the number of layers from single layer, to bi-layer to few (less than five) layers. However, it is not possible to distinguish more than five layers from that of bulk graphite using Raman spectroscopy. In single layer graphene, this feature is very sharp and highly symmetric; however, in bilayer and multiple-layer graphene, due to the change of electronic structure of graphene, this feature becomes much broader.

Figure 3.13 shows the dependence of the 2D band on the number of layers. As the figure shows (Figure 3.13a) the Raman spectrum of a single layer graphene sheets shows very intense Lorentzian peaks. In bilayer graphene 2D band show four Lorentzians peak (Figure 3.13b) which are related to the four possible double resonance scattering processes. As the number of layers increase, the peak shape converges to that found for graphite where only two peaks are observed (Figure 3.13e) [49].

![Figure 3.13: Dependence of the 2D band on the number of layers (picture adopted from [50]).](image)

A Raman spectrum of graphene has more features than G and 2D. For example, the presence of defects in graphene could make another feature called the D band to occur at $\sim 1350 \text{ cm}^{-1}$. As expected, this feature is observed at the sample’s edges [47]. Also, the M band at $\sim 1750 \text{ cm}^{-1}$, is strongly dependent on the number of graphene layers, only appears in bilayer and few layer graphene samples [51].
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Figure 3.14: Comparison of the Raman spectra of graphene with two, three and many layers (more than 3), measured at 514 nm. The number of layers is estimated based on the peak intensities, ratio of the G-band and 2D-band peaks and Lorentzian peaks.

In these experiments, Raman spectroscopy was used to analyze the distribution of flakes (in terms of the number of layers) typically present in the resulting films. Figure 3.14 shows a typical Raman spectra of LS films of pristine graphene obtained at several arbitrary points on the film. As the figure indicates, the produced films contain different types of flakes (2, 3 and many layers). These findings confirm our hypothesis that the inherently low conductivity of our graphene films relative to pristine graphene flakes is due to the large distribution of layers in a typical films. As discussed previously, the conductivity of the graphene flake varies with the size and structure [52], hence the presence of graphene with a different number of layers will markedly lower the macroscopic conductivity of the produced films.

3.3.7 Collapse Mechanism of the Film

Compression of the film, results in transition from gas phase to a solid phase. Once the isotherm reached $\Pi = 40 \text{ mN m}^{-1}$ the monolayer form a continuous packed film (see Figure 3.6b). Further pressure of the monolayer (above 40 mN m$^{-1}$) will cause scrolling of
Figure 3.15: Photograph of a collapse monolayer of graphene at the air-water interface.

the monolayer. Figure 3.15 shows macroscopic fibers appeared near the closing barriers. Further increasing the surface pressure will cause the micro fibre to expand toward centre of trough. This phenomenon is reversible, and by expanding the barrier, the wires gradually will fade from the surface. Previously, Braga et al. showed bending the graphite sheet will caused increasing in elastic energy (decreasing stability) while the van der Waals interaction energy of overlapping regions of the graphite sheet will cause decreasing in free energy [53, 54]. Here, the compressing force applied by the moving barriers will bend the graphene sheets.

3.4 Conclusion

Here, a successful assembly of pristine graphene at the air-water interface have demonstrated. The resulting water-supported monolayers can be made by deposition from solvent mixtures with controlled vapor-pressure. The edge-to-edge repulsion between the layers prevented them from overlapping during compression which is facilitated by the
presence of small quantities of a high boiling point solvent NMP. The monolayers respond pseudo-elastically to compression and rarefaction with little hysteresis.

The resulting monolayers can be readily transferred to a solid substrate with density continuously tunable from dilute, close-packed to over-packed monolayers of interlocking sheets using the Langmuir-Schaeffer method. The resulting deposited films are electrically conducting with absolute conductivity controlled by the preparation process. Most importantly, unlike similar films prepared using GO the films require no further treatment with their electrical conductivity defined by the inter-layer junction resistance. Moreover, multi-layer films can be prepared by consecutive layer by layer assembly. The study shows that the LS technique is a simple but effective method to prepare macroscopic films of pristine graphene with controlled physical properties which is a precursor for graphene-based electronic applications.
3.5 References


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Chapter 4

Silver Nanowire/Graphene Hybrids for High Performance Inexpensive Transparent Electrodes

4.1 Introduction

ITO is one of the most used materials in applications where there is a need for transparent and conductive thin films, due to its low sheet resistance ($R_s \sim 100 \Omega/\text{sq}$) and high transmittance ($T > 90\%$) [1]. However, ITO suffers from several important drawbacks, such as high cost, brittleness, and the high processing temperatures required [2, 3]. Alternatively, CNTs and graphene have recently been used successfully in several applications such as in Light Emitting Diodes (LED) [4, 5], solar cells [6], sensors [7], and most importantly in transparent electrodes [8]. Although these materials show great potential and are possibly a low-cost solution for the applications mentioned above, they have not yet achieved sheet resistance and transmittance comparable to ITO. Therefore, the search for alternative materials for transparent conducting electrodes still needs to be continued [2, 8, 9].

AgNWs are another potential candidate to replace ITO [10]. High electrical and thermal conductivities, as well as excellent optical transmittance of AgNW networks make them one of the most promising materials to be used as transparent electrodes in op-
toelectronic applications [8, 10-12]. Lee et al. [13] has pioneered the development of this material. Since then, many groups have reported using AgNWs to produce flexible, transparent, and conducting thin films [6, 8, 14-17]. There are many techniques available to fabricate AgNWs such as vacuum filtration [10], LB [18], drop casting [13, 15, 19], Meyer-rod-coating [15, 20] and spray deposition [8, 9, 21].

Previously Groep and co-workers produced AgNW thin films by vacuum filtering aqueous dispersions of AgNWs onto a cellulose membrane achieving $T$ of 85% and $R_s$ of 13 $\Omega$/sq. [14]. More recently, Hu et al. reported the use of the Meyer rod coating technique to produce AgNW thin films with $T = 80\%$ and $R_s = 20 \Omega$/sq [20]. Scardaci et al. reported large-scale deposition of AgNWs with spray coating. They showed $T = 90\%$ and $R_s = 50 \Omega$/sq for their deposited films [9, 21]. When one compares the results of all of these studies a key conclusion is that regardless of the preparation methods, the resulting morphology in terms of nanowire density, the type of nanowire used and the inter-wires junction characteristics were crucial parameters. And there are directly affect the optical and electrical conductivity of the resulting thin films.

In transparent conductor research, it is critical to compare the performance of new materials against known standards. Transparent conducting materials are generally compared using figures of merit (FoM) [22]. A FoM is determined by comparing the transmittance to the electrical conductivity and relates how they are affected by the physical properties of the electrode. The optical properties of a thin film can be analysed using the Lambert-Beer law which relates optical transmittance to the thickness of the material:

$$T = e^{-\alpha t}$$  \hspace{1cm} (4.1)

Where $\alpha$ is the absorption coefficient and $t$ is the film thickness. For a bulk-like metal system it is well recognised that the optical transmittance can be directly related to the electrical properties of the material as light transmission is determined by the interaction of impinging photons with the plasmonic states in the metal. Hence the above expression can be modified and the $T$ can be directly related to the sheet resistance $R_s$:

$$R_s = (\sigma_{DC, \omega t})^{-1}$$ \hspace{1cm} (4.2)
Where $\sigma_{DC,B}$ is the DC conductivity of a thick (bulk-like) network. It is also possible to write Equation 4.1 independently of $t$ to relate the optical and electrical characteristics of the material independently of the thickness:

$$T = e^{-\alpha/\sigma_{DC,B}R_s}$$  \hspace{1cm} (4.3)

However in nanostructured transparent conductors, where the electrode material is no longer considered as a homogeneous bulk material but rather a connected network of particles [21-23], the following Equation (Equation 4.4) is used to calculate $T$:

$$T = \left(1 + \frac{Z_0}{2\sigma_{Opt}}\right)^{-2}$$  \hspace{1cm} (4.4)

where $Z_0=377$ $\Omega$ is the impedance of free space, and $\sigma_{Opt}$ is the conductivity of such a network in the presence of an alternating electric field (optical conductivity) [23]. Equation 4.4 can be rewritten to directly relate $T$ and $R_s$:

$$T = \left(1 + \frac{Z_0\sigma_{Opt}}{2R_s\sigma_{DC,B}}\right)^{-2}$$  \hspace{1cm} (4.5)

Surprisingly when one approaches the monolayer limit and the electrode structures are very thin the networks tend to have sheet resistances considerably higher than predicted by equation 4.2. This is because, for thin networks, the DC conductivity is no longer thickness independent but follows a percolation-like thickness dependence [9]. According to percolation-like behaviour, $\sigma_{DC} \propto (t - t_c)^n$, where $t$ is the estimated thickness of the network, $t_c$ is the minimum thickness required to form the first conducting path, and $n$ is the percolation exponent. This leads to a new relationship between $T$ and $R_s$ which applies to very thin, transparent networks.

$$T = \left[1 + \frac{1}{\Pi} \left(\frac{Z_0}{R_s}\right)^{\frac{n+1}{1-n}}\right]^{-2}$$  \hspace{1cm} (4.6)

Where $\Pi$ is the percolative FoM:

$$\Pi = 2\left[\frac{\sigma_{DC,B}}{\sigma_{Opt} \sigma_{Opt}^n}\right]^{\frac{n+1}{1-n}}$$  \hspace{1cm} (4.7)
Here, $t_{\text{min}}$ is the thickness below which the DC conductivity becomes thickness dependent and $\Pi$ is a dimensionless number. It is clear from analysis of the above expression 4.7 that large values of $\Pi$ give low $R_s$ coupled with high $T$. Hence a high value of $\Pi$ but low values of $n$ are desirable to achieve low Resistance coupled with high transmittance [9, 21]. Thus achieving the highest value for the ratio of optical conductivity to electrical conductivity is a driving goal in producing functional electrodes.

Although AgNW networks demonstrate comparable electrical conductivity and optical transmittance to ITO thin films, some challenges remain, such as reducing wire junction resistance, eliminating parasitic lateral current flow which is due to gaps between silver nanowires. Moreover, mechanical robustness and flexibility of the AgNW thin films need to improve [24]. Additionally, AgNWs are currently very expensive (~$5/mg) and their adhesion to most substrates is poor [8]. Another disadvantage relates to issues with chemical stability. AgNWs can easily oxidize by exposing to air and water for an extended period of time which results in the marked increase in the $R_s$ and increased haze of the film [25]. In order to reduce junction resistance between wires and consequently achieve high electrical conductivity, heat treatment is usually required [16]. However, such temperature treatments is likely to damage certain substrates, which is not desirable as well as being an expensive post-fabrication process [15, 16, 26].

While numerous studies have investigated AgNWs and graphene individually as transparent conductors, little research has been done on the hybrid systems of AgNWs/graphene. Recently, Yun et al. [27] made a layered system of AgNW networks and GO to make a flexible thin film with a transmittance of 86% and a sheet resistance of 150 $\Omega$/sq, by thermal annealing at 150 °C. Zhang et al. also fabricated AgNW films coated with a GO layer by spin-coating [16]. They have shown that both the electrical conductivity and the chemical stability of AgNW were enhanced after being coated with a GO layer. Their GO-coated NW film remained stable upon heating to temperatures up to 275°C. Another hybrid system was made by Kholmanov et al. [28], with a goal of minimizing the influence of the line defects and the line disruptions of graphene grown by CVD. Subsequently, a hybrid system has been made by spin coating AgNW dispersions from Isopropyl Alcohol (IPA) on the graphene film. They obtained a $R_s$ of $64 \pm 6.1 \Omega$/sq.
and $T$ of 93.6%. This experiment employed high quality graphene which is expensive to produce and is hardly scalable using traditional CVD processes. In another study, Ahn et al.[25] prepared AgNW/graphene hybrid transparent electrode by dip-coating reduced graphene oxide onto the AgNW film. In a recent report by Chen et al. [29] they have shown a hybrid system of CVD grown graphene intimately wrapped around AgNWs by depositing both on the bottom and top sides of the network. In their study they were successful in reducing the graphene $Rs$ from 770 to 22 $\Omega$/sq with $T$ about 88%. They have also demonstrated that hybrid films with graphene on the bottom of AgNWs networks is not effective and moreover that markedly low $Rs$ is achievable in an inverted structure, where the SLG is on top of the AgNW network [29]. All the above studies suggest that there is potential for using hybrid systems of nanowires and graphene to produce functional hybrid structures. Although, in each case there are fundamental limitations. Most of the work has been relied on graphene grown by CVD. This is an expensive process that requires high-temperature growth followed by complicated post processing. Moreover, as of today, there are major issues in the realisation of CVD as an up scalable process to produce high quality graphene in commercially viable quantities.

In the following section, a novel and inexpensive method for making AgNW/graphene hybrid materials will be described. To move away from using CVD grown graphene as an active material in the electrode a process was introduced that is solution processable that is scalable. A two stage process was used whereby the initial step involves the spray deposition of AgNWs on glass as a function of density. This was followed by the deposition of liquid exfoliated graphene using the novel Langmuir-Schaefer deposition methodology. The selected adsorption of individual graphene flakes at nanowire junctions or as bridges between nanowires results in a markedly reduced resistance in the resulting electrode structures. The novel approach described should lead to the development of cheaper electrode structures.
CHAPTER 4. SILVER NANOWIRE/GRAPHENE HYBRIDS FOR HIGH PERFORMANCE INEXPENSIVE TRANSPARENT ELECTRODES

4.2 Experimental Method

AgNWs were purchased from Seashell technologies as suspensions in IPA. The initial solution concentration was 20 mg/ml and was diluted down with IPA to the final concentration of 0.2 mg/ml as described elsewhere [9, 21]. The diluted solutions were bath sonicated in an ice bath for 30 min using the sweep mode. Figure 4.1 shows a photograph of a vial containing a typical dispersion of AgNWs in IPA. Due to the nano-scale dimensions and aspect ratio of the individual wires visible light undergoes appreciable elastic scattering which is indicated by the opaque quality of the dispersion. The dispersions are stable for extended periods with no appreciable sedimentation witnessed over days.

![Figure 4.1: A photograph of the nanowire dispersion](image)

4.2.1 Spray Deposition

Initially, AgNW films were sprayed down manually onto clean glass substrates. The cleaning procedure is the same as explained in the previous chapter (see Figure 4.2). Here, three different densities (low, medium and high) were fabricated using the airbrush-spraying deposition method. Although it is difficult to exactly quantify the exact densities
in each case, as discussed below their resulting films under each regime can be easily distinguished by the resulting electrical properties. The deposition pressure was in the range of 30-50 psi. However, for the optimum system (section 4.4.7) a fully automated spraying technique was used to deposit AgNW on to glass substrate.

![Spray nozzle](image.png)

**Figure 4.2:** Our spray system comprises an airbrush (Harder & Steenbeck GmbH), which is vertically mounted onto a controlled plate, movable in x and y directions.

### 4.2.2 Welding process

In order to reduce wire-wire junction resistance and to improve the conductivity of the produced films the sprayed film were annealed in the vacuum oven at ~100°C for 10 hours. Although this is well below the melting temperature for bulk Ag, due to the high surface area of the nanowires, surface sintering occurs which allows for local welding.

### 4.2.3 Langmuir-Schaefer Deposition of Graphene

Finally, in order to make hybrid systems, Langmuir films of liquid exfoliated graphene dispersion in a chloroform/NMP mixture (15 ml) was spread onto the water subphase
(ultra-pure Millipore water with an electrical resistance of 18 MΩ) with a microliter syringe utilizing a drop-by-drop deposition technique. The surface tension is determined by suspending a Wilhelmy paper plate that is completely wetted by water, and measuring the downward force on it during compression of the monolayer by moving two opposing barriers towards each other at the speed of 15 cm²/min. Thin films of graphene were then transferred onto glass substrates by LS horizontal deposition technique. The pressure-area isotherms were obtained after 10 min so as to let the remaining solvent evaporate. Initially graphene was deposited onto AgNW networks (prepared at the different densities) formed at two different surface pressures (Ω) (15, 25 mNm⁻¹) using the transfer speed of 3 mm/min. In order to analyse the effect of graphene deposition at very low graphene densities the procedure was modified slightly. In this modified approach, the graphene Langmuir film were prepared at lower Π (5, 3, 1 and 0 mNm⁻¹) followed by three compression and expansion cycles at barrier speed of 15 cm²/min. Subsequently the graphene film were deposited onto prefabricated AgNWs films prepared with three different densities (low, medium and high).

4.3 Characterization

The surface morphologies of AgNWs, annealed AgNWs and the hybrid films of AgNWs/graphene were observed by, SEM, AFM, c-AFM, and optical microscopy. In addition, the effect of welding as well as graphene deposition on electrical and optical properties was studied by current-voltage (I-V) measurements as well as UV-Vis spectroscopy. All results were compared to the initial characteristics of the pristine AgNW films.

LS deposition of graphene was performed by using a commercial NIMA deposition trough (NIMA technology, model 612D). AFM topographic analysis of AgNWs as well as the hybrid film of AgNW/graphene films was performed in a semi-contact mode using NT-MDT AFM (Moscow, Russia). The AFM probes used (NT-MDT) had an average spring constant of 11.8 N.m⁻¹.

The I-V characteristics were obtained using a standard two-probe technique (Keithley
Model 4200). Silver paint was applied at the edges of the rectangular glass substrates with a conductive film on top (see Figure 4.3). Four different samples were prepared for each individual experiment and the values reported are the average values. Optical transmission spectra were obtained using a Carry 5000 spectrometer.

![Figure 4.3: Schematic diagram of the sample with contacts](image)

### 4.4 Results and Discussion

#### 4.4.1 Spray Deposition of AgNW

The spray deposition of AgNW requires careful optimization of the process and involves controlling the concentration of AgNWs in the dispersion, spray deposition pressure, flow rate, scan speed, distance from the substrate, and substrate temperature [9, 21]. AgNW in IPA dispersions were used and sprayed down with the same method as described in the previous section, with three different densities (low, medium and high). In order to make a AgNW conductive network, wires have to form a continuous percolating network and large scale aggregation needs to be avoided. This can be controlled not only by the number of spray repetitions but also by the solution concentration [9]. Here the desired network density (low, medium and high) was achieved by a variation in the number of layers of NWs. Figure 4.4a shows a SEM of low density AgNW networks (high $T$), obtained by two layer deposition. Figure 4.4b shows 3 to 4 layers deposition, while Figure
4.4c shows the network with many layers deposited resulting in a low \( T \) (more than 5). The insulating glass substrates appear as black areas due to charging and low secondary electron emission from these regions, and the conductive NW networks correspondingly appear white. As the film thickness was increased, networks became denser, and as a result the substrate is less visible in the micrographs. It is evident that the uniformity of network improves with increasing density of the AgNW networks [15].

The mean \( T \) versus \( R_s \) is plotted in Figure 4.5. As discussed above the relationship between the optical and electrical properties of the resulting networks can be analysed in terms of two regimes namely the percolative and bulk-like regimes. In the above figure the dependence has been fitted to equations 5 and 6 respectively (dashed and solid lines). Lyons et al. have demonstrated similar data for AgNW networks with the transition from percolative to bulk occurring at an obvious cross over point. Above \( R_s = 30 \, \Omega/\text{sq} \), the behaviour corresponds to the electrical percolation defined process and below \( R_s = 30 \, \Omega/\text{sq} \), it follows a bulk-like trend. The crossover between these regions occurs for networks with \( T = 92.5\% \).

Figure 4.6 shows the experimental results of \( T \) versus \( R_s \) for sprayed AgNW networks prepared using the automated system. Here measured data shows percolative and bulk-like regimes as expected. The crossover between these regions occurs for networks with \( T = 93\% \). In the region designated blue the nanowires form a monolayer percolated network. In the regime (designated by red) the conductivity is dominated by bulk-like transport. At point a, although the conductivity mechanism is transitioning into the bulk regime the
transmittance is still above 90% making the films viable as electrodes. Obtained results show that it is possible to control the $T$ and $R_s$ via the film thickness which makes this system desirable for different industrial applications.

### 4.4.2 Junction Resistance

The $R_s$ in AgNW networks depends on many factors such as the nanowire length, nanowire resistance, the junction resistance, and nanowire area density. Junction resistance in AgNW networks can be created as a result of nanowires sitting on each other and the possible formation of air gaps determined by intermolecular force separation. Moreover, the geometry of the system (i.e. one rod has to bend over the other to make contact) also affects the junction resistance (see Figure 4.7). Lee et al. estimated junction resistances of about 1Ω for AgNWs with diameters less than 0.3 μm$^{-2}$, using computer generated random meshes, and about 40 Ω for diameters larger than 0.3 μm$^{-2}$[13]. Hence,
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Figure 4.6: Mean $T$, plotted as a function of $R_s$ for the transparent AgNW networks studied in this work.

The formation of many parallel connections with the lowest resistance connections dominates the macroscopic resistance. In order to develop a highly conducting AgNW films, it is critical to understand the electrical properties of junctions. To measure the junction resistance in the system, as well as to check if the current flow exists out of plane as well as through it, conductive AFM (c-AFM) measurements were performed.

The main advantage of c-AFM over other methods such as scanning tunneling microscope (STM) is the ability to correlate electrical transport properties with topography [31]. The basic principle of c-AFM technique is similar to AFM contact mode. In c-AFM a metal-coated AFM tip acts as one electrode and a conductive substrate or a metal electrode on the surface of a substrate is used as the second electrode (see Figure 4.8a) [32]. In principle, the measurement can be applied in two different configurations. In both configurations, the first electrode is the conductive AFM tip and acts as a movable electrode. The first configuration, which will call the horizontal configuration, involves

Figure 4.7: Schematic image of cross junction contact resistance of AgNW Networks figure adopted from [30].
the film of interest to be deposited on an insulated substrate (see Figure 4.8a). Here the measurement is performed by applying a constant voltage between the tip and metal electrode and as a result measuring the generated current flow. The local I-V characteristic can then be collected by sweeping the voltage between the tip and the electrode. As each measurement can be effectively pixelated with the current being measured at each point the measurement results in a map of electrical characteristics as a function of x and y. The second method is set up in a vertical configuration regime. In this configuration the samples were deposited on conductive substrate which act as the second electrode [31, 32]. The vertical configuration has the ability to obtain current density - voltage curves (J - V curves), which in turn can be used to extract local hole mobilities using a space charge limited current model. Carrier mobility can then be extracted by fitting the J - V data to the Mott - Gurney law:

\[ J = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{V^2}{L^3} \]  

(4.8)

Where \( J \) is the current density, \( \varepsilon \) is the relative dielectric constant of the active layer, \( \varepsilon_0 \) is the permittivity of free space, \( \mu \) is the charge carrier mobility, \( V \) is the applied voltage, and \( L \) is the thickness of the device [32]. An important application of c-AFM is spreading resistance profiling (SRP). SRP is the resistance associated with current crowding near a point contact and can be related to the dopant concentration in a material by comparison to a calibrated standard [31].

In this work, horizontal c-AFM has been used to probe the local electron transport in AgNWs networks. Previously, c-AFM was used by Nirmalraj [33] to examine the dependence of the local junction resistance at junctions on the diameter of constituent SWNTs. Figure 4.8b AFM topography and 4.8c spreading resistance microscopy (SRM) show typical images produced for a low-density AgNW network. Here, single pass measurements was used whereby both topographical and SRM images are obtained directly and so one can easily overlap and confirm that they are from the same nanowire networks. It is interesting to note that as the vast majority of the wires are connected to the network, there is direct overlap between the images in (b) and (c) except for a few minor differences. However, in a region where a nanowire has been deposited in such a way as to be isolated
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Figure 4.8: (a) Scheme of a typical c-AFM experiment in which a Au-coated AFM tip is used to probe the generated current in the AgNW networks. AFM images of AgNW networks (a) topography; (b) SRM taken of the same section of film are shown. It is interesting to note that nanowires that are isolated from the network do not show up in the SRM image as highlighted by the dotted rectangle in each image.

from the network while it shows up in the topography image and it is not present in the c-AFM image as it would be expected. As it can effectively measure and quantify the electrical properties on specific points of an individual nanowires, it is possible to look at the change in resistance not only along the nanowire length but more importantly as one transitions across a junction.

Figure 4.9 shows SRM images for a localised region of a low density film. It is easy to show the change in electrical properties across a junction by following specific pathways. For instance, pathway 1 (Figure 4.9a) is traced (relative to the reference electrode) along a specific wire which is flat against the substrate. One can observe that as the path
transitions along the wire and through a junction formed with a wire overlapping (and sitting) on the wire there is no significant change to the current flow. The current stays approximately at 8 nA along the wire. Although there is no apparent change in the electrical properties through the junction, there is a local instability after which it recovers to the original level. Along pathway 2 (Figure 4.9b), the current is reduced as one passes through the junction formed by the original nanowire and the second nanowire that overlaps. The reduction in current is a direct consequence of the formation of the junction and the associated junction resistance. The observed change in current of $\sim 6 \text{ nA}$ corresponds to the resistance of the NW - NW junction (the current goes from 8 nA to 2 nA).

The results indicate that the electrode resistance is dominated by the resistance of the individual cross-junctions, thus finding ways to reduce the resistance of the individual junctions would be critical to improving the resistance of the film. Although this is the first clear measurement of the effect of junctions on the flow of charge in such networks it is difficult to exactly relate the change in current flowing to the resistance of the junction. The exact nature of this junction is related to the complicated set of parameters involving the tip shape, local curvature of the junction and the effective volume of the air-gap between the wires among others. This will require a further comprehensive study which is beyond the scope of this thesis. However, it is clear that in order to effectively increase the performance of macroscopic electrode structures based on such networks, once must find a method to not only control but potentially manipulate the characteristics of the junctions to produce optimised macroscopic assemblies.

Accordingly, the rest of this section is focused on describing two new methods, that it has developed to reduce inter-wire resistance. The first method involves surface annealing of individual AgNWs in the networks using a low temperature process. The second method shows that by depositing graphene in relatively low densities onto the preformed nanowire networks using the LS deposition one can effectively enhance the conductivity by several orders of magnitude. In particular, the latter process has much promise for the fabrication of low cost electrodes which may eventually compete financially with ITO and other commercially available transparent electrodes.
4.4.3 Effect of Heating on Produced Films (Welding)

Figure 4.10 shows an AFM phase image of AgNW a) before and b) after the annealing process. It is clearly visible in Figure 4.10a that if heat is not applied to the film, then as expected wires lie on top of each other with a gap in between, and the resulting connectivity between them is poor. However the low temperature annealing process introduces melting of the outside layer of connecting wires resulting in them being partly welded together (4.10b). This has been observed in other metal nanoparticle systems where one can selectively differentiate surface melting from bulk melting depending on the associated grain size within the particles [11, 30]. By investigating individual line profiles of
the wire-wire junctions, it is clear that the height of the junction is reduced once they are welded together (Figure 4.10), and hence the gap between the wires is eliminated. Further analysis of AgNW films was carried out by studying the I-V curve for each individual sample before and after annealing the sample.

**Figure 4.10:** AFM phase image of AgNW (a) Before and (b) after heating the sample. (c) current-voltage curves for two different samples before annealing (black) and after annealing (red).

Figure 4.10c shows the I-V plot before (black) and after (red) heating for two individual samples. Results indicate that the resistance drops significantly (from $170 \pm 2 \Omega$ to
64 ± 0.9 Ω) for the annealed sample compared to the not annealed one. Possible explanations for the sheet resistance decrease include; improved junction connection and better electrical contact between AgNWs. In addition, the contact between NW to substrates could also improve due to heating, which will lead to an improvement in morphology of the film. Although thermal annealing of the AgNW sprayed film allows for significant progress in reducing the resistivity while maintaining the transparency at an acceptable value for applications, high temperature processing (and sometimes even low temperature processing) cannot be applied to heat sensitive flexible substrates. For many applications, it is important to have a simple and cost effective process while maintaining the excellent properties.

4.4.4 Fabrication of Hybrid Films

To fabricate AgNW/graphene hybrids, LS deposition process was used. At first the graphene Langmuir films were produced at the the air-water interface with two different Π values (15 and 25 mN m⁻¹) (see previous chapter for more details). Subsequently, the graphene films were deposited onto the prepared sprayed AgNW films. Figure 4.11 shows the produced isotherm at air-water interface and the deposition pressure used in the experiments are marked by the letters (a) and (b) respectively. One can see from the isotherm that film (a) is produced in the region where the isotherm resembles the, solid phase, while film (b) is produced from the region of the isotherm that resembles the liquid phase. Production of hybrids from lower pressure films will be described later in this chapter.

Figure 4.12 displays the AgNW/Graphene hybrid film deposited onto three different densities of AgNW, low (a, d), medium (b, e) and high (d, f) and two different packing densities of graphene, 15 mN m⁻¹ (a, b, c) and 25 mN m⁻¹ (e, d, f). Here the graphene surface pressure was controlled by following the pressure area isotherm (see Chapter 3) for more details). The images indicate that the graphene flakes preferentially cover the AgNW junctions regardless of the density of AgNWs. For example the change in Figure 4.12a show similar junction coverage compare to Figure 4.12b. This may be because the junctions are at a higher elevation than the individual wires lying flat on the substrate and
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Figure 4.11: A typical surface pressure-pressure area curve (Π-A) for a graphene monolayer. In the beginning, with the barriers most apart, the monolayer is in the gaseous phase and more compression forces the monolayer into the liquid phase. Finally, with further compression the monolayer goes to solid phase. The LS films were taken at Surface pressure (a) 25 (b) 15 mN\text{m}^{-1}.

hence they are the first point of contact for the individual graphene flakes. The graphene affinity for the metal nanowires is markedly higher than with the glass substrate. As the figure indicates, graphene flakes cover NWs junctions as a function of their network density in low (a, d) and medium (b, e) AgNW networks, however at high density AgNW networks (c, f) the thickness of the film changes and AgNWs on the surface prevent the flakes from penetrating inside the layers.

To look more closely at how the graphene flakes are covering the junction, 3D AFM topography was performed on the cross-junction. Figure 4.13a is a representative 3D AFM height image, which was done on the low-density AgNW with the graphene deposited at a pressure 15 mN\text{m}^{-1}. As the figure shows, the graphene flakes are wrapping intimately around the junctions (marked with a dotted square). These results indicate that there is better contact between AgNW and graphene. Also it indicates that the Junction resistance is reduced due to compression of AgNW into a more planar structure by graphene force (see Figure 4.13b). Several previous studies have shown that there is a
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Figure 4.12: AFM images of LS graphene film at pressure of 15 (a, b, c) and 25 (d, e, f) \( mNm^{-1} \) on films of sprayed silver nanowires at three different density of AgNW, low (a, d) medium (b, e) and high (c, f).

relatively strong electronic interaction between graphene and metal substrates at the interface. This will be discussed further in the next section.

For further investigation of this phenomenon, SEM microscopy has been performed. Figure 4.14 shows SEM images with increasing AgNW film thickness (a) low, (b) medium and (c) high. Graphene monolayers are transferred at surface pressures equal to 25 \( mNm^{-1} \) on the AgNW film with different densities. It can be seen from these SEM images that the image with relatively high transmittance (see Figure 4.14a) has sparse networks however many graphene flakes are deposited on the glass substrate. The black background can be associated with the substrate even with deposited graphene present. As a consequence, it is insulated and charging effects are evident. However the AgNW networks covered with graphene (especially on junctions), show brighter colour than bare NWs, indicating the lower resistance at the junctions.
Figure 4.13: (a) AFM topography image of graphene on AgNW networks. (b) 3D height image of graphene flakes covering the cross wire junction of AgNW

4.4.5 Analysis of the Kelvin Probe Force Microscopy

As stated above, previous experiments using X-Ray Photoelectron spectroscopy have indicated that there is a large electronic interaction between graphene adsorbed on a metal at the interface. The resultant electronic doping (p- or n-type) will depend on the relative differences between the work functions of the metal and the graphene. Modifications to the workfunction can be locally analysed using Kelvin Probe Force Microscopy (KPFM). KPFM is a type of scanning probe microscopy (SPM) where an AC voltage is applied to measure the local contact potential difference (CPD) between a conductive tip and a conductive sample. This technique measures the work function difference, $\Phi_S = \Phi_{probe} - eV_{CPD}$, where $\Phi_S$ and $\Phi_{probe}$ are work functions of the surface and probe, respectively, and $V_{CPD}$ is the contact potential difference directly measured by KPFM. The main advantage
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Figure 4.14: SEM images of LS graphene transferred at surface pressure of 25 mNm$^{-1}$ on a film of sprayed AgNWs at various densities of AgNW networks. The number of deposited layers controls the surface density of AgNWs.

of KPFM over c-AFM is that in KPFM there is no contact between tip and the sample also no charges are injected during the measurement [34].

Although a free standing monolayer of graphene has a 0-bandgap energy and a vanishing density of states at the Fermi energy, due to the unusual electronic structure associated with the chemical structure, the valence and conduction bands overlap as conical points (Dirac) and the dispersion is approximately linear. However, when graphene is adsorbed on a metal interface it has been shown both experimentally and computationally that the electronic properties can be altered [35]. This is particularly relevant for adsorption onto transition metals as the effect varies hugely depending on the type of metal used. The extent of the interaction is primarily determined by the work function and the chemical interaction between the graphene lattice and the surface of the metal. For instance, in strongly interacting systems such as monolayer graphene grown on cobalt, the electronic modification is governed by a chemisorption process. Density functional theory calculations have recently shown that the Co dopes the graphene by 0.1 eV per carbon atom. For a system which has a weaker interaction such as Cu, Al and Au, the doping levels are smaller and estimated to be $\sim 0.04$ eV per carbon atom [35].

The sign and amount of doping can be deduced from the differences of the metal and graphene workfunctions as well as the distances apart at the interface. For AgNW at an equilibrium distance of 0.33 nm, the doping levels are calculated to be 0.043 eV per carbon atom. As the work function of the metal (4.92 eV) is higher than for freestanding
graphene (4.48 eV), it is expected that the graphene will undergo n-type doping. Using KPFM, one can determine the local contact potential difference which can be directly related to the local workfunction as described above. It is also a clear way of differentiating graphene adsorbed at metal junctions from graphene adsorbed on the glass substrate in the samples. Figure 4.15 displays topographic and corresponding phase and surface potential mapping of a typical low density hybrid film. Here KPFM has been used to determine the surface potential difference between NWs and graphene. The results demonstrate that by depositing graphene on AgNWs there is a clear change in the measured contact potential which can be directly related to the modification of the Fermi level position relative to the vacuum for both materials. The variation in contact potential difference is clearer when a line profile is plotted from KPFM data across a junction between metal and adsorbed graphene (see Figure 4.15c). This line profile demonstrates significant variation between graphene and NWs in the respective surface potential. This relates well to the discussion of resistance modification at junctions. When graphene is adsorbed at such junctions the inter-tube resistance is modified and thus may explain why the overall macroscopic conductivity is increased in the hybrid films.

In order to investigate the effect of graphene, on the NW-NW cross-junctions, the I-V characteristics before and after graphene deposition have been obtained. The representative I-V characteristic for the hybrid film with medium density of AgNWs and $\Pi$ (25 mN m$^{-1}$) of graphene is shown in Figure 4.16a. As it can be seen the slope of the I-V curve increases appreciably when graphene is present.

The change in resistance after graphene deposition as a function of initial resistance of pristine AgNW films is plotted in Figure 4.16b. As the plot reveals the change is more significant for the lower density networks of AgNWs and the smallest change is observed for the highest density networks. The reason for this is that the high density AgNW films contain multiple layers of AgNWs and therefore their surface layer will prevent the graphene flakes from penetrating through to the inside layers. In-plain thickness will cause less junction coverage, hence the number of junctions covered by graphene at pressure 15 and 25 mN m$^{-1}$ has only been calculated for low and medium density AgNW film using AFM height images. Figure 4.17 shows representative AFM height images for
Figure 4.15: (a) AFM topographic image of hybrid film; (b) the corresponding phase image; (c) contact potential difference and cross section through the contact potential difference image; (d) 3D representation of the experimental KPFM image of magnified area within the red dotted frame highlighted in image c.

The low density AgNW networks with graphene deposited at pressure 15 mNm$^{-1}$. Here covered and uncovered junctions were marked by dotted squares.

<table>
<thead>
<tr>
<th>Percentage of nanowire junctions covered by graphene</th>
<th>low density</th>
<th>Medium density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure 15mNm$^{-1}$</td>
<td>44.3%</td>
<td>55%</td>
</tr>
<tr>
<td>Pressure 25mNm$^{-1}$</td>
<td>78 %</td>
<td>89 %</td>
</tr>
</tbody>
</table>

Table 1 Percentage of cross-junction covered with graphene to the entire junction.

4.4.6 Optical Transmission

Reducing the resistance by itself is an encouraging progress point but it is important for application purposes to achieve a high conductivity together with high transparency. The percentage change in $T$ of hybrid films in relation to pristine nanowire networks has
been calculated for each sample and the average change can be seen in Table 2. The results indicate that as the graphene deposition pressure is increased the transmittance is reduced considerably. For example, low density AgNW-low density graphene hybrid shows \( \sim 100\% \) drop in resistance from M\( \Omega \) to K\( \Omega \) while its transparency is reduced from 92\% to 75\% which maybe deleterious for potential applications where transparent electrodes are needed.

Figure 4.16: (a) Current-voltage (I-V) measurement of medium density AgNWs sprayed film (black) and AgNWs/Graphene film (red) deposited at pressure 25 mN\( \text{m}^{-1} \). (b) Percentage change in Resistance after applying LS at 15 (red) and 25 (blue)mN\( \text{m}^{-1} \) against the initial resistance (\( \Omega \)) for spray AgNW films.
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Figure 4.17: Representative AFM image of low density spray coated AgNWs after LS at pressure 15 mNm$^{-1}$. The image shows the junctions and the covered junctions which were marked.

<table>
<thead>
<tr>
<th>Percentage change in $T$(%)</th>
</tr>
</thead>
</table>
| Pressure 5mNm$^{-1}$          | 6-7%  
| Pressure 15mNm$^{-1}$         | 8-9%  
| Pressure 25mNm$^{-1}$         | 12-15%|

Table 2 Percentage change in optical transparency for each sample after applying LS at pressure 5, 15 and 25 mNm$^{-1}$.

4.4.7 Compression-Expansion Hysteresis Cycles

In order to improve the transparency of the hybrids further experiments were carried out that involved using lower deposition pressures and isotherm cycling. This is explained below. As described in the previous chapter, if the graphene is deposited at a surface pressure of 5 mNm$^{-1}$ or below the surface coverage is only ~20%, and graphene flakes are present in the form of loosely connected islands. As indicated above high deposition pressure is required to achieve better coverage of junctions. However, there is another way of achieving higher surface coverage at low II by introducing an additional step to
the LS process, which is cycling (subsequent compression and rarefaction of a graphene monolayer at the air-water interface). It is thought that such a cycling procedure will force the small graphene islands to homogeneously distribute resulting in more uniform surface coverage while not adversely affecting the film morphology. Similar results have been demonstrated previously with CNTs [36].

In order to examine the effect of cycling on surface coverage, a graphene monolayer was formed at the air-water interface at $\Pi = 0 \text{ mN} m^{-1}$ and then deposited on a silicon substrate and investigated using optical microscopy. Cycling was performed three times and the resulting distribution of flakes was analysed using optical microscopy. Graphene deposited on silicon can be easily deciphered due to the relatively large difference in refractive index between the two materials. Cycling produces obvious changes in relative surface coverage. ImageJ software was used to estimate the area coverage after processing. Thresholded optical microscopy images are shown in Figure 4.18. The calculated average area coverage after cycling is $\sim 47.2 \pm 1.36\%$ which is significantly higher in comparison to what was observed for a single compression experiment (see previous chapter for more details). Graphene was deposited onto AgNW films of various densities at $\Pi$ ranging from 0-5 mN m$^{-1}$ and three compression-expansion cycles as shown in Figure 4.19.

Sheet resistance as well as optical transmittance for each sample were obtained and

**Figure 4.18:** Threshold optical microscope images using ImageJ software red are covered area and black is silicone substrate.
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Figure 4.19: Pressure area isotherm for pressure 1 and 3 mN/m\(^{-1}\). Each sample has been cycled 3 times compared with those of the initial samples before the graphene layer had been added. As the results in Figure 4.20 indicate, once graphene is present on AgNW networks, the resistivity of system will drop significantly, with only a slight drop in optical transmittance occurring. It was found that the highest improvement in \(R_s\) was seen for the \(\Pi = 3\) mN/m\(^{-1}\). However, the \(T\) of this sample was still not sufficient for the transparent electrodes applications. It has been observed that if the \(\Pi = 0\) mN/m\(^{-1}\) was used the \(R_s\) drops significantly, but the change in transmittance is minimal (<5%) as can be seen in Figure 4.20b.

Figure 4.20c shows the relationship between the optical transmission and sheet resistance for each sample before (black) and after (red) LS deposition. The figure shows the hybrids films (red) follow the same percolation regime as the AgNW networks (black). Results also indicated that by depositing graphene on AgNW networks a strong shift towards lower resistance will occur. However, there is a shift toward the lower resistance for all the samples, and this shift is more noticeable for highly conductive samples. As the figure shows, the major drop measured for higher resistance sample with 13 M\(\Omega\)/sq resistance and 98% transparency which dropped to 615 \(\Omega\)/sq. Judging from these results, it can be concluded that deposition of a graphene thin layer even at very low surface
Figure 4.20: (a) Optical transmittance of AgNWs (black) and AgNWs/graphene (red) versus wavelength and illumination time. The plot shows the total transmittance including the glass substrate (about 6%). (b) Current-voltage traces for a single AgNW sprayed film (black) and hybrid film (red). (c) $T\%$ against sheer resistance for spray AgNWs before and after applying LS layer of graphene.

pressure will considerably affect sheet resistance of the system by covering the junction.
4.5 Conclusion and Outlook

In this chapter, a spray coated AgNW with controlled density of NW has been made and the resistance and optical transmission has been measured. Two different processes were applied to reduce the junction resistance. First, the effect of welding on AgNW sprayed film was measured and then AgNW/graphene hybrid films were prepared.

In the welding process, the produced film has been placed in an oven at 100°C for 10 hours. Results indicate that heating the sample will lead to higher electrical conductivity with higher transparency, but temperature treatment is not always desired in many electronic applications. Then, a LS layer of graphene at different surface pressures (15 and 25 mN/m$^1$) has been transferred to the sprayed films and resistance along with optical transparency have been measured for each sample before and after LS layer and has been compared. A drop in resistance has been noticed in all samples but the drop was more noticeable for lower density samples where there is a much higher associated resistance in the spray-coated samples. The transparency slightly decreased for graphene deposited at low surface pressure < 5 mN/m$^1$. However, the reduction in transparency was significantly higher at transferred LS at surface pressure of 25 mN/m$^1$ (12 to 15 %). In order to find the optimum process, the graphene flakes were transferred at low surface pressures with three repeated compression-expansion cycles in the system. The produced films exhibited a low $R_s$ of 625 Ω/sq, with high $T$ of 94 % and with good repeatability. The optimised films have comparable properties to commercial ITO; thus contain significantly lower quantities of AgNWs in comparison to films made of pristine AgNWs with the same properties. This indicates that these graphene/nanowire hybrid films may serve as a cost-effective replacement for existing technologies in electronic devices.
4.6 References


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25. Ahn, Y., Y. Jeong, and Y. Lee, Improved Thermal Oxidation Stability of Solution-
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Chapter 5

Controlled Anisotropy in Carbon Nanotube Monolayer Prepared Using the Langmuir-Blodgett Technique

5.1 Introduction

SWNTs show great promise for a variety of potential applications in many fields due to their great properties such as, remarkable mechanical properties and high electrical and thermal conductivity [1]. Such applications include photonics and photovoltaic [2], sensors [3-5], and energy storage systems [6-12]. However, despite the great potential, poor solubility of SWNT in either water or typical solvents without the use of surfactants has hindered most practical applications [13]. Individual SWNTs have a strong tendency to form bundles and aggregate together because of their high surface area and strong van der Waals forces between them [14]. Studies have demonstrated that the solubilisation of SWNTs can be greatly enhanced by non-covalent functionalized adhesion of small molecules and polymer wrapping [12]. Previously, Dalton et al. [15] proposed that the morphology of CNTs in organic solvent is affected by wrapping them with conjugated polymer such as, PmPV. They speculated that this happens because of van der Waals interaction, analogous to J-aggregate stacking of aromatic systems between the benzene rings of the polymer and the hexagonal lattice structure of the nanotubes [12]. They also
demonstrated that the choice of solvent is the most important parameter, since the intermolecular interactions can be controlled by changing the polarity of the solvent [12]. Coleman and co-workers have asserted that the ideal situation for the dispersion of nanotubes would be to find a good solvent where the free energy of mixing is negative, i.e. the solution is thermodynamically stable. They have suggested that NMP and $N$-$N$-dimethyl formamide (DMF) are particularly suitable solvent for this [16-18]. Research groups around the world use the process with differing methodologies, in order to produce high quality ultrathin-films. Several methods have been reported for SWNTs deposition such as; spraying ethanol dispersion of SWNTs onto substrates [19], spin coating [20], solution casting [21], vacuum filtration [22, 23], layer-by-layer assembly [24], LB and LS assembly [18]. Langmuir deposition techniques are particularly suitable choice for developing such films. Li et al. [18] reported that aligned homogeneous LB film of SWNTs films on various substrates such as glass, silicon wafers, and flexible polymer. Giancane et al. [25] also reported highly organized structure of CNT bundles on various substrates by the LB method and demonstrated their application as photocathodes in a photo-electro-chemical cell. Most recently, Kim et al. [26] have shown a good control of packing density and alignment by combining the two methods of soft lithography and LB into a new patterning technique. The goal of the experiments described in this chapter was to form thin films of SWNTs/PmPV in DCE using LB technique. Certain LB method parameters such as monolayer pressure, barrier speed, number of Langmuir cycles and deposition speed were controlled to produce and control alignment and packing density in SWNTs/PmPV thin film [11]. The novelty of this project is to precisely control the SWNTs/PmPV density within the film, which could facilitate the fabrication of controlled functional assemblies and lead to many new applications of SWNT thin films.

5.2 Methodology

5.2.1 Preparing the SWNTs Suspension

Purified HiPco-SWNTs and PmPV were purchased from Unidym and Sigma-Aldrich respectively. Initially, 0.2 mg of PmPV was weighed and placed in a sample vial. Then
20 ml of DCE (Sigma-Aldrich) were introduced into the sample using a micro-pipette to ensure exact amounts. The produced samples were sonicated at a power level of 10 Watts (Fisher scientific FB1501) in an ice-cold water bath for 15 minutes. In the next step the suspended were mixed with PmPV/DCE solution, the mixing ratio of SWNTs to PmPV were 1 to 2. The SWNTs/PmPV solution was diluted down to several different concentrations using the DCE with concentrations ranging from 0.09 to 0.04 mg/ml (see Figure 5.1). The SWNTs/PmPV in suspension was sonicated for another 30 minutes to help separate the SWNTs and to allow the PmPV to bind to the nanotubes.

![Figure 5.1: Photographic image of suspension with different concentrations](image)

### 5.2.2 Preparing the Langmuir Film

To remove any excess PmPV, 100 ml of SWNTs/PmPV solution with concentration of 0.05 mg/ml was then filtered through Teflon filter paper (PTFE). The Teflon filter paper with the SWNT was placed in 100 ml of DCE and further bath-sonicated for 30 minutes to yield the final solution. Figure 5.2a shows the filtration setup. In order to form the monolayer at the air/water interface, the prepared solution was spread by a microliter syringe, drop by drop at room temperature (~ 21°C). Surface tension (\( \pi \)) was measured using Wilhelmy filter plates and a micro-balance (see Figure 5.2b). The plate must be completely wetted prior to the measurement to ensure that the contact angle between the plate and the liquid is zero. Spontaneous spreading will continue until the surface pressure of the monolayer is equal to the equilibrium spreading pressure. In this work 10 ml of solution were spread on the water subphase [27].
The procedure of making PmPV/SWNTs solutions was described in the above section. The pressure-area isotherms were obtained after 15 minutes of waiting time to let the remaining solvent entirely evaporate. The organic solvent (DCE) evaporated after approximately 10-15 min. To obtain the desired pressure against area (H-A isotherm), the surface tension was monitored within the compression process of the monolayer by moving two opposing barriers towards each other (Figure 5.20), with a barrier compression speed of 15 cm²/min.

A vertical deposition method (LB) was used to deposit the films. The deposition was performed with a speed of 1 mm/min. The trough, substrates and other apparatus must be kept as clean as possible. The cleaning process of the substrate consisted of rinsing it thoroughly with deionised water followed by sonication in deionised water for 5 minutes, and then repeating those steps with Isopropyl alcohol (IPA) in place of water. The quality of the Langmuir films will depend on the initial cleaning conditions. For LB deposition, the substrate had to be placed inside the water subphase prior to the monolayer spreading. Therefore, hydrophilic substrates were used. In order to make the substrates hydrophilic, they were UV/Ozone treated for 30 min in a commercial UV/Ozone cleaner (Ultra-Violet Products PR-100) [28]. In order to perform the SEM and optical transmission studies, both glass and silicon wafers were used as the substrates. During the deposition the
surface pressure of the spread film was controlled to stay at zero mN m⁻¹.

5.2.3 Characterization Techniques

UV-Vis was performed on each individual concentration of SWNTs/PmPV in DCE using carry 5000 UV-Vis spectrometer, at a wavelength range of 300 nm-900 nm with quartz cuvette, 1 mm path length. In order to observe the state of nanotube aggregation within the dispersion solution, spin-coated films of each concentration were made on silicon at a set spin revolution rate of 25 rpm and time of 20 seconds. Spin-casting allows the solvent to dry more quickly and thus prevent re-aggregation of the SWNTs, thus mimicking as closely as possible the initial dispersion state of the nanoparticles before spin-coating. AFM studies were performed on the produced films and the length and diameter distribution of the SWNTs/PmPV were measured. The Langmuir films were deposited from the ready-made SWNTs/PmPV solution by using a commercial NIMA deposition trough (NIMA technology, model 612D). The morphologies of the prepared LB films were characterized using SEM and AFM, as well as polarized Raman spectroscopy. Raman spectra were obtained using a NT-MDT NTEGRA spectrometer with an inverted microscope and a 100x objective lens. Here a polarized light source (632 nm HeNe laser) was used during the Raman scattering experiment. This type of measurement effectively measures the degree of alignment of the nanotubes along a particular axis of the sample as the absorption (and hence efficiency of the Raman scattering process) of photons in extremely anisotropic coupling strongly along the axis of the nanotube versus perpendicular. Samples of SWNTs LB film were excited with the red line (1.96 eV) of a helium-neon [He-Ne] laser. To determine the degree of nanotube alignment, polarized Raman spectra were captured using a half wave-plate to rotate the polarization of the incident beam. The samples were rotated from 0 to 90 degrees relative to the polarizer for measuring relative alignment. In order to measure the conductivity of the films, sets of gold contacts were evaporated onto the LB films. I-V measurements were implemented on each individual sample using a standard two-probe measurement (Keithley 4200). The conductivity of thin film with different film densities was investigated. In order to measure the optical transparency of the films, UV-Vis spectroscopy of each LB sample was
also performed using a Carry 5000 instrument.

5.3 Results and Discussion

5.3.1 Controlling the Aggregation State of the CNTs by Polymer Wrapping

UV-Vis absorption spectroscopy was employed to demonstrate the dispersibility of SWNTs/PmPV in the solvents. SWNTs tend to aggregate into large ropes or bundles due to their relatively high surface energy and strong van der Waals interaction [17, 29]. PmPV was the selected polymer as it has been shown as been effective at encapsulating SWNTs. The PmPV wraps around the SWNTs in a helical manner and after sonication it has been reported to be effective at isolating individual nanotubes. The polymer allows the SWNTs to be placed in solution within a solvent matrix which is essential to being able to create LB films.

This subsection will focus on the dispersion of SWNTs/PmPV in DCE. For de-bundling the nanotubes, the concentration diluted by reducing the ratio of nanotube to PmPV/DCE solution. Isolated SWNTs in the suspension absorb light proportionally to concentration, but upon aggregation, the SWNTs extinction coefficient diminishes, making the absorbance disproportional to the concentration of the SWNTs. To find the optimal concentration in which the SWNTs are individual or in small bundles, and to demonstrate the dispersibility of SWNTs/PmPV in DCE, UV-Vis was performed on each concentration of SWNTs/PmPV in DCE. Figure 5.3 shows the absorption, normalized to SWNTs/PmPV concentration, against the wavelength (nm) for each concentration from 0.04 to 0.09 mg/ml. The absorbance at the wavelength of 660 nm ($A_{660}$) was measured over the concentration range examined and divided by the cuvette length, $l$, to give $A_{660}/l$. $A_{660}/l$ was plotted against concentration before and after centrifugation. Figure 5.3 (inset), shows the extinction coefficient for the PmPV/SWNTs dispersions at various concentrations and reveals the concentration at which the onset of bundling occurs. In the concentration region just above 0.05 mg/ml, the nanotubes show a distinct drop in extinction coefficient, and this signifying that SWNTs are beginning to aggregate.
AFM studies were performed on each sample; drops from different dilutions were deposited on a clean silicon substrate by spin-casting and dried at 60 C in a vacuum oven. Figure 5.4 shows AFM images of approximately 40 nanotubes at the highest (0.09 mg/ml) and lowest (0.04 mg/ml) concentration. The SWNTs at the concentration of 0.09 mg/ml were typically found to have lengths ranging from 0.4 to 1.2 \( \mu \text{m} \), with diameters ranging from 0.25 to 2.5 nm. This is an indication of existing both de-bundled and bundled states. Diluting the dispersion to 0.04 mg/ml helped decrease the bundle size to 0.5 - 1.4 nm long and with diameters ranging from 0.25 to 0.8 \( \mu \text{m} \) (see Figure 5.5), which indicates a dispersion of individually suspended nanotubes and small bundles. Figure 5.6 shows the variation in NTs length and diameter for 0.04 and 0.09 mg/ml concentration. The concentration of 0.04 mg/ml shows a high presence of SWNTs with large average lengths compared to the 0.09 mg/ml concentration. It can be seen that there are less bundle NTs at the concentration at 0.04 mg/ml. AFM images show that SWNTs bundle
Figure 5.4: AFM height images for SWNTs/PmPV at concentrations of (a) 0.04 and (b) 0.09 mg/ml.

diameters decrease with SWNTs concentration and very small bundles were found at lower concentrations. However, a lower ratio of SWNTs to PmPV increases free PmPV in solution. The lower-concentration solutions must therefore be filtered through Teflon to remove any excess PmPV.

Figure 5.5: Typical AFM height profile of the a SWNTs/PmPV NT from the solution deposited onto a mica substrate along the line drawn across the image (inset) used for the determination of nanotube diameter
5.4 Langmuir Monolayers of PmPV/SWNTs Solution

5.4.1 The Pressure-Area Isotherm

This section is based on making Langmuir films of PmPV/SWNTs solution by means of the LB technique. As mentioned in chapter 2, an insoluble monolayer is usually characterized in terms of its surface pressure-area curve (H-A), representing the relation between the surface pressure observed and the area occupied on a liquid surface by the molecules of the film [27]. Figure 5.7 shows a typical surface pressure-area isotherm at room temperature (~21 °C), a H-A isotherm was obtained after spreading 10 ml of SWNTs/PmPV in DCE solution on the water subphase, with a concentration of 0.04 mg/ml of SWNTs/PmPV. The pressure-area isotherm is characterized by a steep rise in pressure when moving towards a reduced areas (see Figure 5.7), this indicates that a stable and condensed layer of SWNTs/PmPV was formed on the water surface. A gradual increase in the surface pressure curve was recorded as the barrier was closed and the curve...
has started rising from 450 cm² onwards. As shown in Figure 5.7, when the isotherm reached a pressure 23 mN/m further reduction in the area resulted in a a collapse of the film resulting in out-of-plane structures forming. A few distinct turning points were observed on the isotherm plot as the monolayer entered the condensed phase, reflecting different types of interactions of the single layers (gas, liquid and solid Phases).

Figure 5.7: Pressure-area (H-A) isotherm of SWNTs/PmPV on pure water. The isotherm reached pressure 23 mN/m.

Figure 5.8 shows an optical micrograph of the Langmuir monolayer formed at the water-air interface. Following the formation of SWNTs/PmPV monolayer thin films were transferred to a glass or silicone substrate. Deposition could start from any of the monolayer states (gas, liquid and solid) [27, 30], molecular organization depends on the surface pressure at which the transfer happens.
5.4.2 AFM and SEM Microscopies Investigation

The packing density of the SWNTs at air/water interface can be controlled by compressing the two barriers toward each other and reducing the trough area while monitoring the surface pressure using the Wilhelmy plate method. After compression at different surface pressures, monolayers are vertically transferred onto solid substrates.

Figure 5.9 shows the SEM images of the thin films of SWNTs/PmPV at 4 different surface pressures. The pressures at which the films were made are marked with corresponding letters on area-pressure isotherm. Figure 5.9a shows SEM micrographs of the initial gas phase at surface pressure of $\Pi = 0 \text{ mN} \text{m}^{-1}$, where the surface pressure essentially remained constant during compression. As can be seen from this image, even at such a low pressure the SWNTs form an interconnected network. However, there is very little overlap between adjacent SWNTs along their lengths. The surface pressure rose slightly at liquid phase when the second LB film (Figure 5.9b) was formed at a pressure of $10 \text{ mN} \text{m}^{-1}$. Here the film shows a better-connected network with less space between SWNTs. The SWNTs started to form a closely-packed film at solid phase with a pressure
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Figure 5.9: The resulting SEM images of LB films at the 4 different surface pressure 5, 10, 15 and 20 mN/m$^{-1}$ respectively. The images show a LB assembly of SWNTs with a tuneable density.

$15 \text{ mN/m}^{-1}$ (Figure 5.9c). $\Pi = 20 \text{ mN/m}^{-1}$ is where the film is forming a highly dense networks (Figure 5.9d) and the gaps between SWNTs become too small. This precise control of density is one of the big advantages of this method and could facilitate the fabrication of functional assemblies and lead to many new applications for such thin films.
One of the principal advantages of the methods used in this work to make LB over other techniques for thin-film fabrication is the capability of uniformly controlling the film thickness over large areas. Here the AFM images shows an average thickness of ~ 6 - 7 nm for all of the samples (see Figure 5.10).

5.4.3 Electrical Properties of the Films

Electrical characterization of the LB films is needed to explore the possible novel applications in electronics that are made possible by the high level of control over orientation and placement of molecules allowed by the LB method. There are two configurations for deposition of contacts. The first one involves the deposition of an electrode electrode on the substrate first followed by the film, while the second configuration involves depositing the electrode directly onto the LB prepared monolayer on glass (see Figure 5.11). Sputtering or thermal evaporation were used to synthesize the electrodes on which the CNT layers were deposited for electrical characterization. Figure 5.12 shows SEM images of PmPV/SWNTs monolayer deposited by the LB technique on a silicon oxide wafer with patterned Au electrodes. Silicon oxide was chosen because of its superb insulating properties to minimize the influence of the substrate on the measured I-V characteristics of the films. A dense network of SWNTs was deposited on the silicon oxide wafer. The SWNTs networks covered the area between the electrodes and were well connected.
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Figure 5.11: Schematic figure of contacts in bottom and on top

Figure 5.12: SEM images of as produced LB films on silicon oxide substrate with gold deposited electrode.

...to edges of the electrodes (see Figure 5.12). The resulting film resistances measured appeared unusually high compared to the results reported by Li et al. [18] which suggested that there was an issue with homogeneous connectivity of the film to the electrode structure during device fabrication. Hence, it was decided to use a top contact instead throughout for further studies. As such, the LB films were made on glass substrates and the con-
contacts were deposited by thermal evaporation of gold on top (see Figure 5.13). In order to increase the reliability of the electrical measurements, several gold electrodes (8 mm length with 4 mm spacing distance) were deposited on each sample. The measurement is repeated between each consecutive pair of electrodes and the resulting data points are collected and used to reliably calculate the electrical properties of the sample.

5.5 Current-Voltage Characteristics

Electrical measurements were carried out to characterize the LB films with a conventional two-probe method. LB devices were studied by measuring the current density versus voltage (-10 to 10 V). The observed results show a linear dependence of current upon voltage for all the samples, indicating Ohmic behaviour (see Figure 5.14). Moreover, the identical results obtained from different electrode pairs on different parts of the film show that the conductivity values obtained result from the electrical properties of the organic molecules in the LB array and not heavily influenced by the contact resistance.

5.5.1 Junction Resistance

Garrett et al. [31] measured modelling impedance properties of the SWNT and they have shown circuit model consisting of two Voigt elements in series corresponds well with the nature of conduction through junctions and bundles (see Figure 5.15). They also have shown higher resistance Voigt element for the junctions 3.3±0.3 (times higher), where
conduction is dominated by granular-metal type tunnelling, than the bundle resistance, where the charges are strongly localized [31]. Geometrical scaling arguments have also shown that the conductivity, $\sigma_{DC}$, of disordered nanotube films scales linearly with the number density of network junctions. In another study Nirmalraj et al. used c-AFM to measure the NT-NTs junction resistance. They have shown the junction resistance of $\sim 180 \, k\Omega$ between the bundle and the single tube [32]. They have also demonstrated that the junction resistance is strongly dependent on the size of the interconnecting bundles.

**Figure 5.14:** Current versus voltage characteristic (-10 to 10 V) for a film at pressure 2.5 and 8 mNm$^{-1}$ showing Ohmic behaviour.

**Figure 5.15:** (a) Schematic of SWNTs junction's resistance in nanotube. (b) Equivalent circuit model of the SWNT networks with parallel $R_1$, $C_1$ elements describing electrical properties of the junctions, and $R_2$, $C_2$ elements modeling the nanotube bundles.
5.5.2 Percolation Study of Produced Films

Percolation theory deals with the effect of varying, in a random system, the number of interconnections present. Percolation studies are critical to understanding the electrical behaviour of the thin films in this study. In this chapter, the interconnections are the SWNTs. For electrical percolation studies, several samples were made at different points on the pressure area isotherm curve. Identical sets of contacts were deposited on each sample, and the resistance between each consecutive pair of electrodes was measured and plotted against the surface pressure used during the formation of the film which is proportional to density of nanotubes per area of the film. Figure 5.16 shows the thresholded AFM images using ImagJ software. Since the film's transmittance is strongly dependent on the film density, it is essential to calculate the surface coverage at each different pressure. Figure 5.16 shows that at higher densities which are formed at greater surface pressures, the SWNTs better overlap, thereby increasing the occurrences at which junctions overlap and reduce resistance.

It is also evident from the data in Figure 5.16 that there is a critical pressure value, beyond which the NTs form percolation networks. The best-fitting curve to the data using percolation-type power law scaling is shown in Figure 5.16e yielding a critical exponent $n = 4.26$, a conductivity coefficient $\sigma_0 = 489$ Sm$^{-1}$ and a formation of the percolative network at $S_c = 37\%$ respectively. By comparing these results with graphene, it seems that the percolation threshold is markedly higher. Although it is not entirely clear why this should be the case. It is likely that the presence of PmPV facilitates ordering of NTs into mesoscopic low aspect ratio structures, which is evidenced by AFM and SEM analysis. In the case, the percolation threshold would be increased towards the value we extrapolate from the curve.

5.5.3 Optical Properties

Optical transparencies of each sample were measured using UV-Vis spectroscopy and absorption plotted against wavelength is shown in Figure 5.17 for each pressure.

Figure 5.18 shows $T$ (%) for wavelength 350-650 nm and indicate the transmission at 550 nm for highly packed SWNTs film is less than 90% making it a good candidate for
Figure 5.16: (a-d) Thresholded AFM images of LB films as a function of pressure showing the change in packing density (here the black areas show the background while the white areas represent the NTs). (e) Conductivity against surface coverage for LB films.

transparent electrode applications in terms of optical transparency.

5.5.4 Multilayer Structures

Figure 5.19 shows SEM images of single layer and double layers of SWNTs at surface pressure of 15 mN m\(^{-1}\). The samples imaged here have been deposited on glass substrates. The images show that depositing a second layer of SWNTs leads to higher density films.

5.5.5 SWNTs Alignment

There are many methods for the alignment of SWNTs, such as mechanical shearing, the blown bubble technique [33], and Langmuir-Blodgett [18]. As can be seen in Figure
Figure 5.17: Photograph for comparison between a clear glass and a highly dense film made at pressure of 23 mNm⁻¹.

Figure 5.18: Transmission against Wavelength for various LB film of SWNTs/PmPV.

5.20, as the barrier are moved closer to the center, the SWNT at the interface begin to align themselves perpendicular to the direction of barrier movement. This may be due to the fact that SWNTs have relatively large aspect ratio which undergoes shearing during densification. Also, both the compression and the flow-induced alignment of SWNTs are along the same direction, which would enhance the orientation. Moreover, performing
more compression expansion cycles can improve this effect. In the present experiments, the LB cycling technique has been used and the optimum alignment occurs at a surface pressure of 20 mN/m\(^{-1}\) after applying (~10) several isothermal cycles. Figure 5.20 shows the schematic image of compression and expansion of the Langmuir barrier.

Figure 5.21 shows LB film of SWNTs/PmPV, transferred after applying 10 isotherm cycles. As the (a) AFM and (b) SEM images show, highly packed arrays of NTs aligned perpendicular to the direction of movement of the barrier appear over a large area.

The 3D AFM image shown in Figure 5.22 illustrates the visual appearance of the

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**Figure 5.19:** SEM image of one and two layer LB film of SWNTs/PmPV

**Figure 5.20:** Scheme of a trough and two movable barriers for deposition on solid substrates

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Figure 5.21: (a, b) AEM topography and SEM (c, d) images of the visually appear more aligned SWNT films at lower (a, c) and higher (b, d) magnification levels.

aligned SWNTs within the film. In addition to the information provided by AFM and SEM, polarized Raman spectroscopy was used to measure the degree of SWNTs alignment in each of the LB films (Figure 5.23b).

5.5.6 Raman Spectroscopy of Carbon Nanotube

Carbon nanotubes exhibit high Raman intensities because their extended π-electron structures allow for extensive electron delocalization over the surface of the nanotube thereby increasing molecular polarizability. This makes Raman spectroscopy an extremely useful technique for the study of vibrational and rotational modes as well as the structures of SWNTs. Raman spectroscopy is a particularly powerful tool for observing spectroscopic features which provide information for low frequency modes of phonons, the pri-
mary symmetry classification of carbon nanotubes is as either being achiral (symmorphic) or chiral (non-symmorphic). The Chiral tubes show six Raman optical modes (2A1g, 2E1g, 2E2g), whereas achiral tubes display only three modes, whether they are zigzag or armchair (E2g, A1g, E1g) [10, 35].

According to these modes, there are three Raman frequency characteristic regions, high frequency, which is usually greater than 1500 cm\(^{-1}\), medium frequency, approximately between 500 cm\(^{-1}\) and 1500 cm\(^{-1}\), and low frequency, which is less than 500 cm\(^{-1}\). The center of the Radial breathing mode (RBM) peaks usually appear in wave numbers around 200 cm\(^{-1}\) [36].

**Lower frequency region**

In the following section, lower frequency regions (\(\sim 100 - 350\) cm\(^{-1}\)) will be discussed, as it is within these regions that RBM peaks appear which is corresponds to radial expansion-contraction of the SWNTs. The intensities of the peaks are dependent upon the properties of the tube i.e. whether it is zigzag, armchair or chiral. The diameter of the tube is an influencing factor as well. The frequency of RBM is inversely proportional to a diameter of tube.

**Medium frequency regions**
In intermediate regions (~ 500-1500 cm\(^{-1}\)), the frequency response is dependent on handedness and the peaks are inconsequential; they do not produce Raman spectral features of any interest. In theory at frequency (~ 1200-1500 cm\(^{-1}\)) there should not be any Raman modes, however experimental results show armchair tubes to have low intensity peaks in this regions.

**D mode**

Single crystals of graphite show one distinct line at 1375 cm\(^{-1}\), called the D mode peaks. This mode has the same origin as the graphite sheet and can be found in both graphite and SWNTs. However, the D mode of SWNTs show some additional features to those of graphite sheets; it is found in a smaller frequency region than SWNTs’ spectra and with lower laser energies, and the intensity of this D mode increases linearly with decreasing graphite crystallite size as well as decreasing with increasing laser energy (shifting at a rate between 38 to 68 cm\(^{-1}\)/eV with laser energy) \[10\]. This last aspect of SWNTs is related to the symmetry and one dimensional band structure.

**Higher frequency regions**

SWNTs’ lattices are split into the two sub-lattices, which contain A and B atoms respectively \[10\]. In A1g modes, these two regions are out of phase, in other words they move in opposite directions, whereas at low frequency the movement is in the same direction. The E2g mode usually appears around 1582 cm\(^{-1}\) and is out of phase and has the same origin as the E2g Raman active mode of graphite \[11\]. Finally, E1g has a frequency response of ~ 1585 cm\(^{-1}\). As the E1g and E2g modes have a comparable frequency response, it is difficult to discriminate them experimentally.

**G band in graphite and SWNTs**

Compared to other modes, the G band in the high frequency region is mostly related to the graphite sheets. This section explains the difference between G bands in graphite sheets and the corresponding tangential mode in SWNTs which bears the same name. Graphene sheets usually exhibit 9 vibrational Raman-active and infrared-active modes. The G-band in pristine graphite is preceded by one single Lorentzian peak at 1579 cm\(^{-1}\). This peak is involved with an optical phonon mode between the two dissimilar carbon atoms in its lattice \[11\]. This peak usually dominates the high frequency region in the
Raman spectrum.

Although the Raman spectrum of the SWNTs, especially in regard to the G band is very similar to graphite, the Raman spectrum of SWNTs possesses two distinguishing peaks resulting from carbon displacements parallel and perpendicular to the tube axis. These peaks result from the symmetry-breaking effect and phonon wave vector confinement along its circumferential direction. These peaks are usually labeled as G+ and G-, where G- is located near 1570 cm\(^{-1}\) and can be depicted at the lower frequency compared with G+ (~1590 cm\(^{-1}\)). G+ shows very little diameter dependency and is strongly associated with carbon atom displacement along the length of the tube whereas G- is associated with oscillation of carbon atoms around the edge lending a heavy radial dependency. The G- feature band is largely dependent on the electrical properties of the tube [whether they are metallic nanotubes, which exhibit both the Breit-Wigner-Fano (BWF) and Lorentzian lineshapes; or semiconducting nanotubes, which display only Lorentzian lineshape [9, 37]. This difference is due to the fact that the direction of the out-of-phase motion differs in zigzag and armchair nanotubes [11, 38].

G' mode

G' band feature is a high frequency peak dedicated to both graphite and SWNTs. These peaks arise from the second order Raman scattering process. For bundles of tubes in a high-quality sample, the intensity of this peak could be comparable with G band peaks. This peak usually appears around 2700 cm\(^{-1}\), smaller peaks usually occur around 2450 cm\(^{-1}\). This small peak is a non-dispersive second order phonon peak and it is much weaker than the 2700 cm\(^{-1}\) peak.

5.5.7 Polarized Raman Spectroscopy

The polarized Raman spectra of aligned LB SWNTs/PmPV film are shown in Figure 5.23. Figure 5.23a schematically shows the relative orientation of the polarized laser beam and the individual nanotubes within a 3-dimensional reference frame. The measurement is therefore carried out as the polarization of the laser beam (x, y polarization) is rotated relative to the NT. The angle between the laser polarization and the z axis (x axis) is represented by \(\phi(\varphi)\). Figure 5.23b shows that the intensity of both the D (1320-1400 cm\(^{-1}\)
and G (1530-1640 cm\(^{-1}\)) bands is maximized when the direction of laser polarization is parallel to the SWNTs orientation and minimized when it forms a 90 degrees angle with this axis. This is due to the sensitivity of the Raman modes of NTs to the orientation of the optical electric field with respect to the nanotube axis [39]. As demonstrated by others, this relationship can be better explained in terms of angle-dependent resonant enhancement for the SWNTs. Dependence of the intensity of the scattering for perfectly-aligned SWNTs for a parallel analyzer is

\[ I(\phi) \propto \cos^4 \phi \]  

(5.1)

where \(\phi\) is the relative angle between the electric field, \(E\), and the nanotube axis. Thus, intensity decrease (if the light is polarized perpendicular to the nanotube axis) is due to
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1.0 \times 10^6

5.0 \times 10^5

< 0

0

\phi

-5.0 \times 10^6

-1.0 \times 10^6

10 isotherm cycles

1 isotherm cycle

Voltage(V)

\textbf{Figure 5.24: I-V curve for the NT before and after alignment.}

the depolarization or the antenna effect [40].

Hence, by taking the intensity of the G band along the major axis of the film and diving it by the G band intensity perpendicular to the same axis one can obtain a so called Raman ratio which is effectively a qualitative indicator or the average alignment of the nanotubes in one direction. The calculated ratio is \sim 12. This confirms that the carbon nanotubes are aligned preferentially along the direction of the closed barrier.

Assuming the resistance of the sample is directly related to number of junctions aligning the NTs will reducing the junction as well as the resistance of the sample. I-V measurement has been done on the highly aligned samples imaged in figure iso10 and were compared to the samples that have been prepared without cycling LB film at pressure 20mNm~^{-1}. As the Figure 5.24 shows a significant reduction in overall resistance, R, of the highly packed films from $2.28 \times 10^6$ to $7.75 \times 10^5 \Omega/sq$ due to mimimization of junctions and junctions overlaps.

\textbf{5.5.8 Collapse Mechanism}

Compressing a two-dimensional (2D) film past its stability limit means that the film collapses into a three dimensional structure [41]. Further barrier compression (H 50 mNm~^{-1}) will cause the film to collapse as indicated in Figure 5.25. The results indicate that the CNTs are resistant to forming multi-layered structures which are usually
expected to form in a LB type experiment assembly. After the formation of the close pack monolayer, further compression will cause formation of some black, rod-like long folds. The rods first appear near the moving barriers due to the higher pressure build-up close to barriers. Further pressure caused by compressing the barriers, increases the number of these macroscopic wires and gradually expand them to the center of the trough. As Figure 5.25b displays, these macroscopic wires are aligned along the barrier direction. Similar phenomena have previously happened to the graphene thin film (Chapter 3). Figure 5.25b shows optical micrographs of the wires formed on the water-air interface. For further study, the wires were transferred to a silicon substrate and AFM and SEM microscopy were performed on them. AFM height image of the wires is shown in Figure

![Figure 5.25: (a) AFM image of the collapsed film on a glass surface; (b) Optical image of trough at air water interface; (c-d) SEM images of the collapsed film on a silicon wafer.](image-url)
5.25a. The AFM image reveals the structure of the wires consists of bundles of nanotubes. The structure of the micro-rods was studied by SEM. Figure 5.25c-d presents the typical SEM images of the produced micro-wires. It has been found that some micro-wires are hollow (see Figure 5.26). Such structures may have a range of further applications that we have not yet conceived. For instance, they could be used in microfluidics, building blocks in tissue scaffolds or as enhanced optical waveguides.

5.6 Conclusions

Preparation of LB films from HiPCo-SWNTs mixed with PmPV in DCE solvent has been demonstrated. UV-Vis spectroscopy and AFM analyses were used to find the best concentration at which the solution was stable and the SWNTs remained exfoliated or in small bundles with little aggregation in solution for extended periods of time. Π-A isotherms obtained at the air-water interface while using the Langmuir trough indicated that the SWNTs/PmPV solution had good surface spreading properties. LB films were prepared at different surface pressures to study the effect of surface pressure on the packing and density of SWNTs within the resulting thin films. The produced LB films were
examined by AFM and SEM. The obtained images confirmed that the packing density could be precisely controlled by varying surface pressure. I-V characteristics of the films obtained at different surface pressures were investigated. Percolation conductivity was systematically addressed as a function of surface tension. Highly aligned films were produced by varying extensional parameters such as the number of compression cycles. Degrees of SWNT alignment within the films were determined through polarized Raman. These results show dependence of the G and D band intensities as a function of the measured angle, between the polarization alignment of the excitation laser and aligned SWNTs. Two and three layer film were produced and characterized. In summation, a variety LB techniques can be employed in the fabrication of SWNT thin films to optimize the resulting electrical and optical properties thereby demonstrating the potential of such films in novel applications, including solar cells, touch screens, etc.
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Chapter 6

Summary and Future Perspectives

6.1 Summary

The main objective of the present work was to produce LS and LB assemblies of carbon nanostructured materials to be used as transparent electrodes. The produced films have shown a level of optical ($T$) and electrical properties ($R_s$) comparable to the existing commercial ITO thin films. As reviewed in Chapter 1, making transparent thin films out of ITO involves several challenges. ITO degrades over time, has low fracture resistance (when the substrate is bent), is brittle, can lose functionality when flexed and requires high temperature processing [1-3]. Additionally, the material is expensive due to the limited quantities of indium metal and the high demand of pure indium [4]. Thus, future transparent electrodes will require flexible, transparent and conductive materials that can be produced at low temperature and over large areas at low cost. Chapter 2 described the materials, techniques and instruments used in this work.

Chapter 3 showed a successful LS-based fabrication of thin films of pristine graphene. The suspension used had been made of liquid-phase exfoliated graphene in NMP and chloroform mixtures. In order to control the transparency and electrical conductivity of the resulting thin films, many parameters within the technique were precisely controlled, such as the solution concentration and spreading volume, as well as the barrier and transferring speed. The produced monolayers were transferred vertically to the solid substrates
at different surface pressures with a tuneable density. The resulting deposited films were electrically conducting, having absolute conductivities controlled by the preparation process. The highest conductivity for a single-layer thin film of graphene obtained by LS, was \( \sim 19 \text{ S.m}^{-1} \) with \( T = 85\% \), which was expectedly low compared to the intrinsic conductivity of the individual graphene flakes. The conductivity of the films was further enhanced by increasing the number of layers; however, the transparency was sacrificed. Repetitive stamping of the substrate on the floating monolayer were performed and the results showed bi-layers and triple-layered films deposited at the highest surface pressure of \( \sim 40 \text{ mN.m}^{-1} \) yield a conductivity of \( \sim 30 \text{ S.m}^{-1} \) and \( \sim 65 \text{ S.m}^{-1} \), respectively.

The relationship between conductivity and surface coverage was plotted to understand the percolation behavior of the networked system. The best-fitting curve to the data using percolation-type power law scaling was obtained yielding a critical exponent of \( n = 8.95 \), a conductivity coefficient \( \sigma_0 = 46 \text{ S.m}^{-1} \) and a formation of the percolative networks at \( S_c = 9\% \) respectively. The value of the critical exponent is often used to discuss the dimensionality of the conductive nanotube networks. While the conductivity coefficient compares well with the results obtained by Groep et al. such a high value of the critical exponent, \( n \), may be associated with the large distribution of junction resistances at flake-flake interfaces [5]. The present study has proven that the LS technique is a simple but effective method to prepare macroscopic films of pristine graphene with controlled physical properties which is a precursor for graphene-based electronic applications. Interestingly, the controlled deposition of such conducting assemblies at the air-water interface may have a range of applications in their own right without transfer to a substrate. For instance, differences in the extent of protonation on either side of water-hydrophobe interfaces are deemed essential to enzymatic catalysis, molecular recognition, bio-energetic transduction, and atmospheric aerosol-gas exchanges and could be easily measured using our floating graphene electrodes. Another application that these films would be ideally suited for is to understand the role the ocean plays in the biochemical cycles of climate-modifying gases such as carbon dioxide. The influence of monomolecular films on the gas exchange process is essential. The graphene layers could be used as proxies for bio-
genic slicks which are prevalent to coastal waters and gas exchange rates could be better determined by dynamically measuring changes in conductivity which we are currently investigating.

Chapter 4 was dedicated to AgNWs/graphene hybrid films and their applications as a transparent electrode. The chapter began with producing AgNW films using the spraying deposition method. Precise control of AgNW network densities by changing the thickness of the films (number of deposition layers) was demonstrated. The optimized film showed $R_s$ of about $30 \, \Omega/\text{sq}$ with $T = 92\%$. A well-known model [6, 7] was used to relate $R_s$ and $T$ in the percolation regime. Two methods were applied to reduce the resistivity. In the first method, the effect of annealing at low temperature was investigated. The results indicate that the $R_s$ drops significantly (from $170\pm2 \, \Omega/\text{sq}$ for the annealed sample compared to $64\pm0.9 \, \Omega/\text{sq}$ for the unannealed. Possible explanations for the sheet resistance decrease include improved junction connection meaning better electrical contact being made between wires. In addition, the contact between the NWs to the substrates could also improve due to heating, leading to an improvement in the morphology of the film by reducing the average roughness.

Further, the graphene monolayers were transferred using the LS technique at different surface pressures to existing AgNW sprayed films. AFM and SEM micrographs were used to look at the AgNW and AgNW/graphene hybrid films; the resistance, $R_s$, for each sample was measured and plotted against the $T$. The results demonstrated a major drop in the $R_s$ of AgNW films by applying graphene accompanied by a small change in $T$. The modification on the physical properties of the film after the graphene deposition is indicated by a marked shift to the left for the associated $R_s$ against $T$ curve which is advantageous for performance as transparent electrodes. This shift is more noticeable for samples where the initial AgNW density is low. For such samples, where the initial resistance and transparency are high ($R_s$ of $13 \, M \, \Omega/\text{sq}$ and $T$ of $98\%$), the deposition of graphene results in the resistance being dropped to $615 \, \Omega/\text{sq}$ and the transmittance being lowered to $T = 94\%$. This method shows the potential to offer a new low-cost approach to
fabricate high performance transparent electrode. The method could be potentially scaled up by using spray deposition to deposit graphene instead of LS technique. Using conductive atomic force microscopy and kelvin probe microscopy, we demonstrate that the change in the physical properties of the network can be attributed to the modification of junction and inter-wire resistances due to the adsorption of graphene.

The final experimental chapter (Chapter 5) demonstrated the use of the LB technique for the fabrication of thin films of single-walled carbon nanotubes (SWNTs) wrapped with PmPV in DCE. To disperse the SWNTs in DCE, PmPV was used to function as an interfacial bridge between the SWNTs and the solvent. Initially, Langmuir films were formed at the air/water interface with precise control over the relevant parameters, such as the concentration and the volume of the spreading solution, as well as the barrier and transference speeds. Fabrication was performed vertically (LB) on to glass and silicon substrates respectively. The packing density of the produced films was controlled by transferring the Langmuir film at various points of the pressure-area isotherm which modified the resulting density. The morphology of the LB films and their structure were investigated by the aid of AFM and SEM microscopies. Both AFM and SEM showed that the SWNTs/PmPV made interconnected networks even at low surface pressures. Other properties of the produced films, such as electrical conductivity and optical transparency, were measured. The films showed overall $T$ higher than 90%. The percolation threshold was calculate by plotting $R_s$ against surface pressure. LB assemblies of densely aligned SWNTs were also achieved by applying isotherm cycling. Polarized Raman studies were used to show the degree of SWNT alignment within the films. Raman ratios were achieved by taking the intensity of the G band along the major axis of the film and dividing it by the G band intensity perpendicular to the same axis. The calculated Raman ratio is $\sim 12$. This confirms that the carbon nanotubes were aligned preferentially along the direction of the closed barrier. Electrical properties of the aligned SWNTs/PmPV film were compared with the films made of random networks. The results indicated that using aligned NTs led to significant reduction in the overall resistance, $R$, of the highly packed films from $2.28 \times 10^6$ to $7.75 \times 10^5$. The produced LB films could find applications in high-speed transistors.
The mechanism associated with the collapse of the LB films at high pressures was investigated. After the formation of a close-pack monolayer, further compression will cause the formation of some black, rod-like long folds. The rods first appear near the moving barriers due to the higher-pressure build-up close to the barriers. Further pressure caused by compressing the barriers increases the number of these macroscopic rods and gradually facilitate their formation closer to the center of the trough. These macroscopic rods were formed parallel to the barriers direction and potentially could be a new method to produce macroscopically aligned fibers of carbon nanotubes for different applications.

6.2 Future work/Directions

The reliability and mechanical robustness of the produced films still needs to be examined. To do so, it would be necessary to deposit the films on flexible substrates such as polymer latex. In addition using latex substrates could expand the hybrid film applications where latex dispersions are used to produce mechanically coherent films. Some of these include paints, coatings, adhesives, caulks and sealants etc. An additional next step could be the production of electronic devices using laser patterning technology. Working with our industrial partners, we have begun looking at the potential for our transparent electrodes for application in touch screen products.

Touch screens normally used in smart phone and tablet technologies use capacitive-based sensing, whereby modifications to the local field produced when a finger comes close to the electrode is converted into an electronic signal in the device. The electrodes must therefore be efficiently pixelated. Our initial collaborative studies with the company indicate that such pixilation can be easily achieved using laser patterning technology where local modifications to the electrical properties of our carbon-based films can be induced via laser ablation.

Although the work so far has been mostly focused on one possible application, which was transparent electrode, the technique developed and the resulting films could be used for a variety of applications. Such applications include sensors and biosensors, solar cells, and transistor technology. Specifically, the produced LB films of SWNTs have
potential to be used as electrodes or transducer components in biosensors applications, due to their unique electrical and electrochemical properties. Upon exposure to target molecules, the threshold voltage of the SWNTs and graphene flakes could shift due to charge transfer between the carbon and the bio-molecules, so that target molecules can be detected simply by measuring the conductance change. In addition, individual SWNTs are extremely sensitive to their surrounding environment.

SWNTs modified with bio-recognition molecules, such as antibodies and DNA, have been successfully used to detect various targets. However, as already stated, the electrical connection in our LB film of SWNTs/PmPV is dominated by junctions resistances which are high due to the mismatch in Fermi levels of nanotubes of different diameters. This could be resolved by producing films using nanotubes of one chirality [8].

To summaries, over the last decade there has been a persistent increase in the use of devices such as smart phones, electronic books, and LCD/OLED smart TVs. All of these disparate devices include a material that is transparent to visible light and yet electrically conductive as an essential element in the device stack. Commonly used transparent electrodes are made from ITO, which is expensive due to the relative rarity of indium metal and the high energy requirements of the processes involved. In fact, the global cost of ITO alone in 2010 has exceeded $3 billion dollars [9]. Those costs are only expected to rise in future, as electronic devices find their way into new markets around the world and creating higher demand for transparent conductors. Such an increase in costs can create an escalating economic burden, especially for the people in poorer countries. In addition, the technological dependence on ITO could lead to an increase in the economic and even political power of the countries that export indium, over the world economy. According to 2010 estimates, the top five countries with the largest indium mine reserves hold about 50% of the world’s known reserves among themselves. The world as a whole can benefit a lot if we could replace ITO with carbon-based transparent conductors, such as the materials described in this thesis, which can be cheaper than ITO but offer similar performance [10]. This could pave the way towards providing and facilitating access to smart communication devices to more people, and could benefit humanity as a whole by facilitating communication, education and health services. Until then, all attempts towards
creating technologies that could lead to making cheap carbon-based electronic devices available to the people around world will stay important and any progress on that front highly significant.

6.3 References

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