

Nanoscale Large-Area Opto/Electronics via Adhesion Lithography

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The work presented in this thesis was carried out in the Experimental Solid State Physics Group of Imperial College London between October 2014 and November 2017 under the supervision of Professor Thomas D. Anthopoulos. The material documented herein, except where explicit references are shown, is my own work.

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Abstract

As the feature size of devices in the electronics industry has hit the nanoscale, device fabrication costs have rapidly increased. Whilst commercial technologies such as photolithography are able to produce nanoscale feature size, they are costly and unsuitable for large area printable electronics. To allow for up-scaling of devices considerable research is now focused on new manufacturing processes.

Alongside this, new materials such as organics, metal oxides and 2D materials have been developed, allowing for novel device applications to be realised. The ability to deposit these materials at low cost and on large area flexible substrates has been realised with solution processing techniques such as blade coating, inkjet, gravure and screen printing used to deposit materials. To compete with traditional electronics and to allow for commercial applications, however, device performance needs to be improved with reduction in feature size seen as one avenue of interest.

This thesis explores and develops the fabrication technique adhesion lithography (a-Lith). This simple process alters the adhesion forces of a metal using the unique properties of self-assembled monolayers (SAMs) to create asymmetric planar electrodes separated by sub 10nm gaps. Using this novel electrode fabrication technique in conjunction with solution processable semiconductors, highly scalable, low-cost, lateral architecture devices can be created.

First the optimisation of a-Lith is explored by looking into the influence of metal deposition on the formation of the nanogap by varying the grain size and thickness of the two metal electrodes. Both factors are found to have a large effect on resultant devices with a reduce grain size causing a reduction in device variation and increased metal thickness causing an increase in gap size. The conversion of the process from ridged surfaces to flexible plastic substrates is also investigated with annealing substrates seen to improve the adhesion of the metal thin films and increasing fabrication yield.

Solution processed materials were then used to fabricate photodiodes for various applications with copper thiocyanate (CuSCN) used to create deep ultraviolet photodiodes showing high responsivity (719 A/W) and photosensitivity (79). Next zinc oxide (ZnO) was utilised for ultraviolet photodiodes showing a high on/off ratio but slow response times. Finally poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-co-3-fluorothieno[3,4-b]thiophene-2-carboxylate] (PTB7-Th) in heterojunction structures with 6,6]-Phenyl-C71-

butyric acid methyl ester (PC₇₁BM.) and in a Schottky configurations is explored for visible photodiodes showing responsivity of 33 A/W and a detectivity (D) of 6×10^{13} Jones, with relatively fast response times (~ 1 ms). These devices demonstrate the viability of a-Lith for large area fabrication of photodiodes.

The a-Lith electrodes were then investigated in light emitting diode (LED) applications. The asymmetric electrodes were used in conjunction with solution processable polymers of varying electroluminescence spectra to create unique nano-polymer LEDs. These devices allow for high current densities to be realised due to reduced Joule heating and showed brightness tunability when device width is varied. The response time of the devices was ~ 210 μ s which enables the devices to be considered for application in the display industry and particularly high-definition optical displays. This work highlights the versatility of the a-Lith technique for LED applications.

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Chapter 1

Introduction

1.1 A Brief History of Electronics

The rapid development of technology has changed the world we live in. I write this thesis surrounded by electronics that 10 years ago did not exist. The scientific advancements that have led to this every changing landscape began nearly two centuries ago with discoveries by Alexander Becquerel in 1830 and Michael Faraday in 1833. Becquerel and Faraday both independently established that the conducting ability of a material could be modified by altering external conditions (such as light and temperature) thus demonstrating semiconducting behaviour of certain materials [1][2]. This pivotal research and those that followed changed the shape of the world we live in.

A whistle-stop tour of the subsequent key discoveries follows, with the reader encouraged to delve into more in-depth studies to understand the finer details (see references [1], [3]–[5] and those therein). Rectifying behaviour (unidirectional current) was first observed in 1874 by Karl Ferdinand Braun using metals and sulphides [1]. Cat’s whisker diodes were developed in 1906 using the naturally occurring mineral form of lead (II) sulphide (galena). Used in crystal radios in the Second World War they utilise a metal-semiconductor point contact.

The phenomenon termed electroluminescence was first perceived by Henry J Round in 1907, contacting a cats whisker detector with silicon carbide[6]. It was not until the chance discovery the pn junction by Russell Ohl in 1938 [7] (which became a part of all early solid state devices) that further developments could be made. The pn junction discovered was at the interface of two sections of a silicon crystal that had different impurities, causing one side to have an excess of positive charge carriers (holes) making it p-type and the other to have an excess of negative charge carriers (electrons) thus becoming n-type. This fundamental breakthrough was utilised in the first commercial light emitting diode (LED) to be patented by, James R. Biard and Gary Pittman in 1962 who used a p-n junction of gallium arsenide to emit infrared light [8]. The first visible light LED was created from this technology in 1962 [9], but it was not until the 1990s that the first blue LED was manufactured [10]. This then permitted advancements in white light LEDs and has allowed for the development of high efficiency devices we see today with applications in a vast number of industries. In the late 1940s the pn junction was also used to create the first photodetectors [11]. This was improved upon in the late 1950's and adapted to create pin photodiodes (with I denoting insulator) which improved device response times and quantum efficiencies [11][12]. To further reduce response time, devices have also been created using single carrier materials in conjunction with Schottky contacts. Termed due to the mid-century discovery by Walter Schottky that proved the existence of a rectifying barrier between some metals and semiconductors later called the Schottky barrier [13]. These diodes utilise the inherent band bending within the device to separate charges.

The research carried out in the 1940s, focusing on the properties at material interfaces, led to greater understanding of semiconductor properties and their use in electrical devices. This and the development of germanium led the creation of the first transistor [4]. Transistors are used in integrated circuits as fast switches for holding data and are a fundamental device for information technology. The theoretical concept of the transistor had previously been conceived, but it was not until 1947 that the first point-contact or bipolar transistor was created by John Bardeen, Walter Brattain and William Shockley at Bell Laboratories [14]. This device combined two junction diodes and was the first bipolar junction transistor (BJT). It was more stable than its predecessors and was used in early integrated circuits [3]. Another type of transistor termed a field effect transistor (FET) uses an electric field to control the conductivity of the current channel. It utilises one type of charge carrier and so is unipolar. The first theoretical description and patent of this device was in 1930 by Julius Lienfeld [15] but he was never able to practically realise it. The first working FET was created in 1960 by John M. Atalla

and Dawon Kahng. Using a metal-oxide-semiconductor interface; this type of device is known as a MOSFET. Unfortunately, due to the high contact potential of the gate electrode causing a high threshold voltage in this first MOSFET, the BJT was still favoured commercially [3]. Further development in the design of semiconducting materials and use of silicon as the gate electrode, however, increased the performance of the MOSFET and allowed it to overtake the BJT. First proposed in 1963 by Frank Wanlass, current technology is based on the CMOS (complementary MOSFET) [16]. This uses two devices with different charge carrier types to reduce power consumption in a circuit and is the mainstay of modern electronics

The first integrated circuit was demonstrated in 1958 by Jack Kilby at Texas Instruments using germanium, rather than silicon which is currently the industrial standard [13]. Half a year later Robert Noyce (one of the founders of Intel) created an integrated circuit from silicon. This proved superior to the germanium alternative with increased stability. MOS technology was first introduced commercially onto an integrated circuit in 1964 [3]. In 1974 the first true system on chip (where all components for a device are embed onto a single chip) was created by Peter Stoll and used in a Microma watch [17]. These developments led to the advent of computing technology.

In 1965 Gordon Moore (another of the founders of Intel) predicted the number of components on an integrated circuit would double every two years [18]. Even though MOS technology superseded the original bipolar junction technology, this observation called Moore's Law has been guiding electronics for decades pushing the frontiers of science and technology. This law predicts the reduction of transistor size every 18 months and has been adopted for other electronic devices, becoming an industrial driving force. Having been followed for over 50 years some now believe solid state technology as it is conceived today is at its limit and the trend of smaller device feature size is slowing. New fabrication technologies and materials are needed to continue this drive towards increasingly small devices.

Alongside these traditional technologies new generations of electronic materials based on organics, metal oxides, and perovskite materials have been researched to enable further device development. These materials have benefits including the ability to be solution processed and/or deposited at low temperature allowing devices to be created on flexible substrates and have tuneable bandgaps so can be selected for a specific function.

Seminal work in the 70s (for which Heeger, MacDiarmid and Shirakawa won the 2000 Nobel Prize [19]) showed the potential of conjugated organic materials to be used as conductors and

semiconductors [20]–[22]. They could not at the time compete with the performance of the inorganic crystalline materials used in solid state devices. It was not until the 1990s and early 2000s that these materials started to realise their true potential, when many new papers on material discoveries and device applications were published [23]–[26] .

Metal oxides for semiconductor and conductor applications were first investigated in the 2000s [27], [28]. They were attractive due to their high optical transparency coupled with high mobilities and stability. They also had the added benefits of being compatible with large area fabrication as the amorphous state of the material has similar device performance to the crystalline state [29]. The most successful of these materials indium gallium zinc oxide (IGZO) and indium tin oxide (ITO) were rapidly uptaken in the display industry as the semiconducting material for the backplane TFTs and in OLEDs as the transparent conductor, respectively.

Metal halide perovskite semiconducting materials are named because their crystal structure resembles that of the perovskite mineral [30]. These synthetic materials are a compound of three materials and are most commonly made from a hybrid of organic and inorganic materials. The selection of the different materials and their position in the structure greatly effects the electrical and optical properties, such as band gap and mobility. Lead and Tin halide based materials have been studied for use in photovoltaic applications as the active material due to their favourable light absorption. Recent investigations into these perovskites has allowed for a meteoric rise in terms of device performance for photovoltaic devices that can be solution processed, with nearly a 20% increase in efficiency for perovskite based photovoltaics in just 6 years [31].

All these materials can allow for large scale fabrication of electronic devices similar to industry packaging processes with some technologies moving into the commercial sector. Issues with performance parameters, uniformity and stability, whilst achieving low cost fabrication stills remain but, when these devices are fully realised there will be a massive step change within the electronic devices market.

1.2 Motivation

To allow for new and innovative devices made from these materials, which match device performance of traditional electronics, new manufacturing technologies that have high resolution as well as rapid fabrication are needed. Traditional techniques such as photolithography and electron beam lithography that allow for high resolution do not permit

high speed processing whereas technologies currently used for high volume manufacture such as printing do not produce high resolution. Therefore, investigation into innovative fabrication techniques is needed.

Creation of electrodes with a nanogap separation can improve device performance parameters in a variety of devices. If these electrodes can be made of dissimilar metals (which is no trivial feat) the applications in device fabrication increases massively. This can improve device parameters such as: increased speed for high speed electronics, improved sensitivity and response time in sensors and increased semiconducting performance from non-uniform materials and therefore, has uses in photodiodes, LEDs and Schottky diodes. Additionally the two electrodes made of different metals allows for the creation of diodes by simply depositing semiconducting materials on top of the electrodes simplifying the manufacturing process.

1.3 Thesis Outline

This thesis is focused on the optimisation of a technique (adhesion lithography) for creating large area nanogap electrodes made from dissimilar metals and its applications in different opto/electronic devices.

Chapter 2 remarks on the background and theory that complements the work in this thesis. Processes currently used to create nanogap electrodes are outlined and reviewed. With fundamental limitations for each technique discussed. Next adhesion theory for metals and uses in fabrication are discussed. Theory into the nature of charge transport and semiconducting properties of materials used in this thesis are discussed. Finally the working principles for metal semiconductor contact and devices fabricated are examined.

Chapter 3 explains the experimental techniques used to fabricate and analyse materials and devices used in this work.

Chapter 4 describes the technique for creating planar nanogap electrodes, a-Lith, and presents work carried out to further understand and optimise the technique. With influence of the metal deposition on the nanogap separation explored and the improvement of the technique on plastic substrates.

Chapter 5 presents photodiode devices made via a-Lith with a variety of materials to allow for different functionalities. Deep ultraviolet, ultraviolet and visible photodiodes are created by simply changing the solution processed active material placed on top of the electrodes

Chapter 6 presents solution processed polymers used in combination with the nanogap electrodes to create nano organic light emitting diodes of various colours with specific performance parameters analysed.

Chapter 7 concludes the thesis and discusses future work that could help progress the technique and devices created within this thesis

Chapter 2

Background and Theory

2.1 Introduction

This chapter presents the background and fundamental theory relevant to the studies within the thesis. First fabrication techniques that are currently used to create nanometre feature size are discussed. Next an introduction into adhesion theory is given. Materials properties and interactions are then explained. Last device fundamentals and figures of merit for devices created within this thesis are described.

2.2 Fabrication of Nanogap electrodes

Over the past few decades feature sizes have rapidly decreased in commercial electronics. In 2017 Samsung brought out a transistor with a 10-20 nm feature size with others like ARM and INTEL also producing devices of a similar quality. This feature size is, however, expected to be the last created using industrial standard silicon due to issues with quantum tunnelling [32][33]. For future devices other materials such as, germanium, indium gallium arsenide (InGaAs) or graphene are being predicted to replace silicon but these are not without their own issues.

To create these nano-features photolithography is used as the industry standard patterning technique (discussed in further detail below). This, however, is also reaching its resolution limits and it appears will be replaced with Extreme ultraviolet lithography (EUV), for the commercial manufacture of Si chips by 2020 [34]. This of course is a very expensive fabrication technique and a change in the standard industry fabrication technique will cost many 100s of millions of dollars.

Other routes to create small feature sizes include direct write techniques such as, electron-beam lithography (EBL), focused ion beam lithography (FIB), scanning probe microscopy lithography (SPM) [33]. Growth techniques such as electrochemical plating (ECP) and electro-migration (EM) are also used [35]. There are also investigations into less controlled techniques such as mechanical break junctions and on wire lithography, though these techniques are not normally scalable and often seen as only suitable for prototyping [33]. Other techniques that allow for more scalability are angled shadow mask evaporation, nanoimprint lithography (NIL) and associated techniques, and self-assembled fabrication [33]. These techniques allow for large-area fabrication, though maintaining small feature size with scalability still remains an issue. All the techniques will be explored in this section. Other techniques that utilise different adhesion forces between materials and allow for subtraction of materials to create nanogaps have also become of interest and will be discussed in depth in chapter 4, including adhesion lithography (a-Lith) which is the focus of this thesis.

2.2.1 Optical Lithography

The first integrated circuit made in the 1960s used contact lithography which is a rudimentary version of photolithography [36]. Here a mask is placed in contact with a substrate coated with a light sensitive material (photoresist) and the sample is exposed to UV light. The mask blocks the focused UV light from specific areas of the substrate. The area of the photoresist exposed to the UV light undergoes a photochemical reaction and depending on its polarity either follows the pattern of the mask or its inverse. A developer is then used to dissolve the unwanted part of the photoresist. This mask can be used to as an etch resist for materials underneath or as a lift-off mask where the material is deposited on top of the patterned photoresist and the photoresist removed taking with it the material deposited on top of it [36]. Contact Lithography has low yield and poor repeatability due to mask and photoresist damage because they are in physical contact with each other [36]. Another form of photolithography, Proximity

lithography, is also a similar process with a gap between the sample and the mask reducing damage to the sample, however the resolution is reduced due to this gap. For these reasons both of these techniques are mainly used in research and not commercially. Modern photolithography has built on these techniques overcoming their fundamental issues [36].

The photolithography used in industry and allowing for high resolution without damage is called projection lithography. This was developed in the 1970s due to better-quality optical materials allowing high quality lenses that focus the mask image onto the surface of a substrate [36]. To allow the creation of nanoscale features state of the art machines are incredibly complex with multiple lenses and steppers. Figure 2.1 shows a state-of-the art photolithography machine and the exposure process for a single mask. Advances have allowed for the resolution, R , to be determined by the diffraction limit of light (Rayleigh criterion) [37]

$$R = \frac{k_1 \lambda}{NA} \quad (1)$$

where k_1 is a constant determined by the specific process and NA the numerical aperture (measure of the ability of the optical system to collect light) are of similar values, so λ the wavelength of light determines resolution [38].

The light sources being used in state of the art tools are excimer lasers and can produce 193 nm wavelengths of light, though these light sources are the limit for tradition photolithography due to high energy sources needing other lens and mask materials. This resolution is improved via immersion of optics in high refractive index liquids and multiple sample exposure allowing for 30-40 nm minimum feature size [37][39]. Hence, nanogap electrodes can be created, but at very high complexity and cost, with limited resolution.



Figure 2.1: A photograph of a state of the art photolithography tool (TWINSCAN NXT:1980Di Step-and-Scan system copyright ASML) and example of complicated photolithography mask process

Seen as the main contender to replace photolithography EUV lithography uses 13.5 nm laser-driven Sn plasma light source. This allows for high resolution (5-30 nm), but due to EUV being absorbed by air the process must be carried out in vacuum and unlike photolithography specialist mirrors must be used to direct the light in place of lenses, increasing process costs (Figure 2.2) [38]. It is however a simpler technique as compared to photolithography due to a reduction in process steps and so has similar implementation costs. It is expected to be up-taken in high volume applications as early as 2020 [34]. EUV and Photolithography are both incompatible with the advent of low cost, large area fabrication.

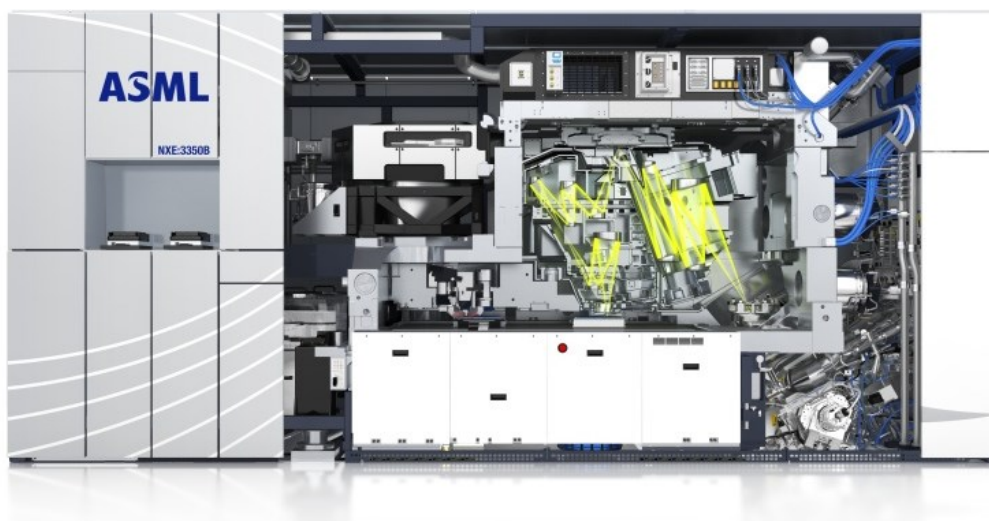


Figure 2.2: A photograph of a state of the art EUV machine (TWINSCAN NXE:3400B copyright ASML)

2.2.2 Electron Beam Lithography

Electron beam lithography (EBL) is a high resolution technique with feature sizes of 10 nm able to be realised [40]. Like photolithography it uses a resist to create a pattern though instead of using UV light to pattern the resist, a high energy beam of electrons is focused onto a sample causing a photochemical reaction in the resist. A typical setup includes an array of lenses, alignment tools and scan tools that focus, align and move the electron beam (shown in Figure 2.3).

EBL is a direct write technology so no mask is needed, but this causes low throughput and hence, although it has high resolution, EBL is normally reserved for research based devices or for creating the masks needed in other patterning techniques such as photolithography or nanoimprint lithography [36], [41], [42]. Also many techniques to create nanogap electrodes rely on EBL as a preliminary patterning technique [33].

To allow for sub 10 nm resolution work has been carried out to decrease the effects of electron scattering and reduction in beam spot size [43]. This has been successful but often the biggest issue for resolution reduction is the complications in resist stability and development [35]. Research into decreasing the fabrication time of EBL has been theorised by use of an array of electron beams [44] but industrial applications for device fabrication have not yet been realised.

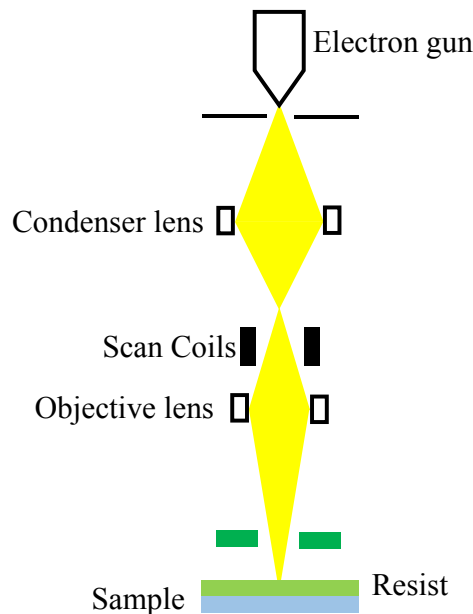


Figure 2.3: Schematic for electron beam lithography the beam emitted and focused by specific lenses and scanned across a surface to create a pattern in a specific resist

2.2.3 Focused Ion Beam Lithography

Another technique being researched to further increase device resolution is focused ion beam (FIB) lithography. It can be used in a top down or bottom up approach: it is able to sputter away atoms with a sub 10 nm resolution, can modify material using ion-induced mixing of substrate and introduce materials [45]. For nanogap electrode fabrication FIB milling is often used with the beam selectively removing an area of chosen material causing a small gap (Figure 2.4). It uses an ion beam, usually made from a liquid metal source for highest resolution, which is focused onto a surface using an array of lenses to directly write a pattern [46]. The ions hit substrate sputtering away surface material. FIB unlike photolithography and EBL does not need a resist as the ion beam directly etches the surface. This also means there are less proximity effects, allowing for higher resolution [45].

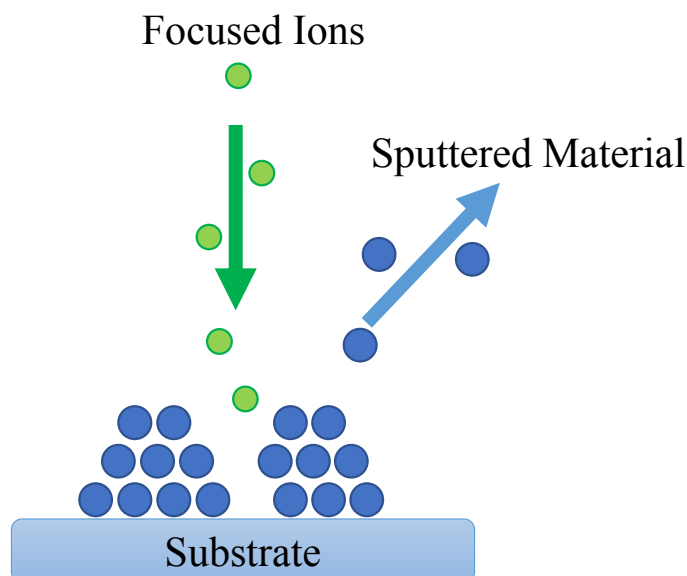


Figure 2.4: Schematic depicting principle of focused ion beam milling

Nanogap electrodes via FIB have been created as early as 2003 where Nagase *et al.* made gold electrodes separated by ~ 5 nm [47] and in 2006 improved on this by creating electrodes with a ~ 3 nm nanogap [48]. In both these reports gallium was used as the source, issues can arise when the gallium becomes implanted on the surface of the substrate [49]. This can be a problem as it changes the electrical properties of the material, also, silicon (most often a major device material) can become more amorphous with the addition of gallium [45]. Research has allowed the development of other ion sources such as helium and neon although this greatly increases

equipment costs. With these ion sources even though the ions still become implanted, they have minor effect on the electrical properties of the material. In 2013 Carl Zeiss created 4 nm separated electrodes on a gold film using a helium ion beam [50]. He ions have also be used to pattern Si and Cu showing a high resolution limit [51]. It is, however, to slow for bulk material etching and can still cause defects on the substrate surface [52]. Neon is able to sputter specific materials such as Cu and Si at a quicker rate than He but has issues with defects and bubbling on the surface [53][54]. FIB has been used to create nanogap electrodes from carbon based materials such as graphene[55] and carbon nano tubes [56]. It has also been used to pattern a resist made from C60 molecules with promising results allowing for sub 10nm resolution and reduced proximity effects, though this work is in its infancy [57].

According to recent research (see [58] and the references therein) many of the issues surrounding FIB have be resolved due to further advances in equipment technology, however this technique like EBL is seen as useful for prototyping, removal of defects from a substrate and removal of material from imbedded structures [58]. Although an invaluable tool it is not competitive when trying to produce nanogap electrodes for commercial electronic devices.

2.2.4 Scanning Probe Lithography

Patterning techniques using atomic force microscopy (AFM) tips can be used to create nanogap electrodes through many different routes and fall under the umbrella term of scanning probe lithography (SPL). The simplest form uses the AFM tip to directly write a surface, here, the AFM tip directly scratches pre-patterned metal stripes or carbon based materials. When first implemented in 1999 this technique was able to create aluminium and titanium electrodes separated by 40nm [59]. With much process optimisation in 2010 graphene electrodes separated by 10 nm were created on polymethyl methacrylate (PMMA) (used to increase the adhesion of the graphene on a SiO₂ substrate) [60]. In this simplest form of SPL gap size is limited by the AFM tip size combined with the force applied by the tip.

Another form of SPL uses conductive AFM to create nanogap electrodes by apply a bias between the tip to either pattern an electron beam resist or to separate a carbon nanotube via oxidation or breaking C-C bonds with nanogap electrodes below 50 nm being created [61], [62].

Nanogap electrodes can also be created using dip pen lithography. This is where the AFM tip is coated in a material (often a self-assembled molecule discussed further in section 2.2.10) and this is then deposited on the surface. This material can then be used as the electrode material or as an etch resist and in 2003 electrodes separated by as little as 12 nm were created from gold electrodes using 16-mercaptohexadecanoic acid (MHA) as the etch resist [63].

All of these SPL techniques are direct write technologies that allow for very fine resolution nanogap electrodes to be created. Like other direct write technologies there is a difficulty in process scale-up and although advances in research has allowed of faster patterning speeds, large area fabrication is still unattainable [64].

2.2.5 Electrochemical Plating

Electrochemical techniques use chemical deposition to decrease the size of pre-patterned electrodes. The electrodes are placed in a plating solution usually consisting of a material with the metal for deposition and a supporting electrolyte. A reference and counter electrode are then placed in the solution and a constant potential is then applied to the solution [33]. Here the gap size is normally controlled via metal salt used and measurement of the resistance between the nanogap electrodes (as the gap decreases the effective voltage for material deposition decreases slowing down deposition) [65]. This can be further controlled with the use of a series resistor with the resistor value defining the termination gap width and has been shown to create sub 10 nm gaps [66].

Asymmetric electrodes have been successfully fabricated using this technique by only plating one of the electrodes [67], [68]. In both of these cases parent electrodes were created used standard patterning techniques and a selected metal was then grown on one of the electrodes. This of course would cause differences in thickness and in any material was deposited the electrode under the second metal is likely to interfere with the device characteristics.

2.2.6 Electromigration

Nanogap electrodes created via electromigration capitalises on a process that is normally the main failure mechanism in modern electronics. The application of a current over a certain threshold value causes electromigration of the metal atoms resulting in a failure in a metal wire and a gap forming [69]. If this current and gap formation is controlled it can be used to create

a break of around $\sim 1\text{nm}$ from a metal wire and hence nanogap electrodes [70]. This technique has applications in single electron devices and has also been used to create carbon based electrodes (either from graphene or nanotubes) [35]. The reverse of this can also be used to create nanogap electrodes where the gap between electrodes is decreased by the movement of metal atoms due to an applied bias though this technique does not have as high a resolution. This technique can be used in more large area applications as a common electrode can be used to create multiple nanogap electrodes [71][72]. However stability of the nanogap shape and formation of metal clusters between the nanogap electrodes are common problems with electromigration causing high failure rate in devices. To allow for up-scaling these problems will first have to be overcome.

2.2.7 Mechanical break junctions

This technique relies on a suspended metal stripe or nanowire normally created using EBL. The stripe is then placed under mechanical stress usual via the bending of the substrate causing the stripe to fracture [69]. Most recent work shows that the electrodes can have a separation below 1 nm making them idea to test material properties of nano-materials and for the creation of single molecule devices [73]–[76]. The gap size is also highly controllable with the amount of force applied to the substrate determining the size [32]. However, this technique is mainly designed for material investigations or prototype devices as the same gap size control cannot be realised on more than one device at the same time and is therefore not capable of being used in large area fabrication.

2.2.8 Angled shadow mask Evaporation

This technique typically uses a mask fabricated via EBL with metal deposited through this mask, with the angle of the mask determining the gaps between electrodes [77]. In 2005 this technique was simplified by two groups by using a pre patterned metal on the substrate with a specific angle as the mask and evaporating the second metal at a specific angle achieving gap sizes of $\sim 3\text{nm}$ in both cases and used to analysis nanomaterials [78], [79] and also used to create memristive devices [80]. In 2014 it was used to create single electron transistors from cobalt [81]. Though the technique is only able to make similar electrodes as the second metal evaporates on top of the first electrode, it has been shown to be able to scale up onto 4 inch wafer scale patterning via precise control of the evaporation steps creating gap sizes down to

15nm [82]. This technique is heavily reliant on the grain size of the deposited metal with smaller grain sizes more favourable for smaller gaps. To fully control gap size in situ conductance measurements can be made.

2.2.9 Nanoimprint/ Soft Lithography

There are many different forms of nano patterning techniques that have arisen from nanoimprint lithography (NIL) since it was first proposed in 1995 [83]. Some of the most common are: hot embossing, thermal nanoimprint, UV nanoimprint and nano-transfer printing [84]. Each of these techniques rely on a master usually patterned by EBL or photolithography to create a mould which is then used to transfer a pattern on to the surface of a substrate [85].

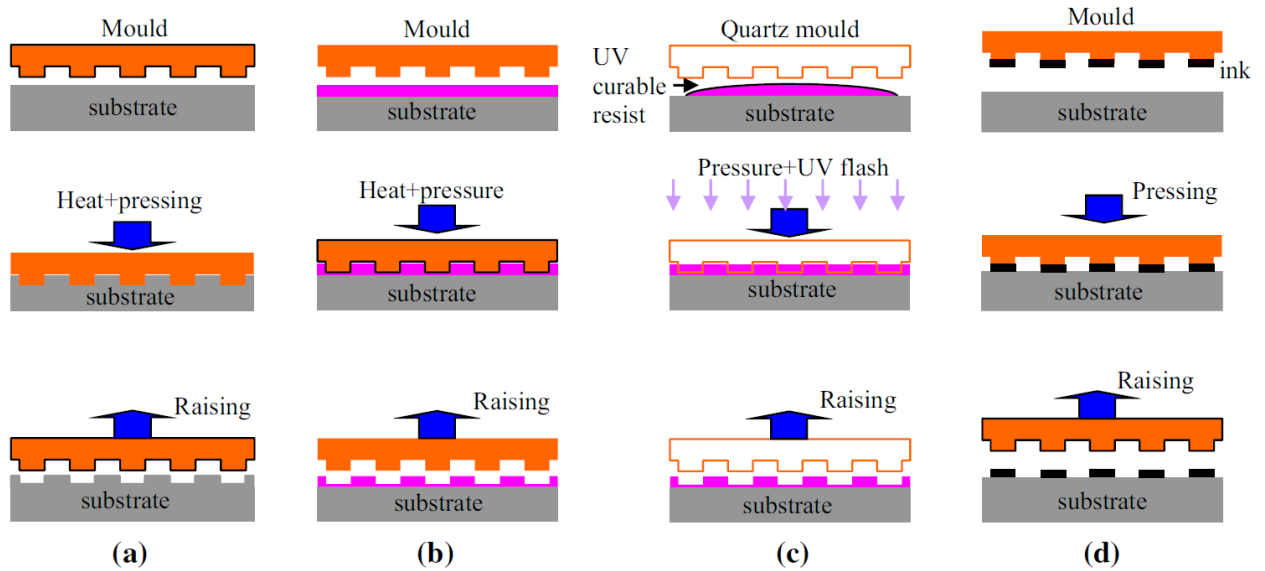


Figure 2.5: Schematics for nanoimprint lithography and extended processes: (a) Hot embossing (b) thermal nanoimprint (c) UV nanoimprint; (d) nano-transfer printing. Reprinted with permission from [84]

Hot embossing uses heat and pressure to directly pattern the substrate. The mold is brought in to direct contact with the substrate and heat and pressure are used to deform the substrate, Al films have been directly patterned using this technique using SiC molds creating separations of 100 nm [86]. Much like hot embossing thermal nanoimprint uses heat and pressure to pattern, though it is a specific resist that has been spin coated on the substrate that is patterned. This then allows of other materials to be deposited and patterned allowing for nanogap electrodes to be created. Sub 20 nm separated Pt and Au electrodes have been created using this technique [87]. UV-curable nanoimprint uses a quartz mold that is placed into contact with

a UV curable resist. UV light is then flashed through the mold curing specific parts of the resist. In 2004 Au contacts separated by ~ 5 nm were created, with the technique able to pattern a 4 inch wafer in one step [88]. In nano-transfer printing a specific mold is coated in an ink or a metal thin film. This mold is pressed on a substrate and transfers the material [89]. In 2009 Au electrodes with a separation ~ 10 nm were made on a SiO_2 substrate using AlGaAs as the mold [90], [91].

All of these techniques have applications in large area patterning and are exciting for novel applications especially because 3D structures can be made. There are however problems that have to be overcome as all of these techniques rely on direct contact between the mold and the material being patterned defects are more likely to occur as with contact lithography [92]. Also the molds are typically made from deformable materials such as PDMS which can be deformed during processing especially with temperature changes. Solutions to these problems have been found over recent years and forms of NIL are seen to be a contender as a patterning technique used to create nanofeatures in industry with current commercial systems able to create 30 nm feature sizes. These techniques also have the added benefit of being able to be processed on large area though cost of masters etc. still remain high.

All of these techniques rely on interplay of adhesive forces to create nano-features on a substrate. To further control/reduce gap size hybrid systems using NIL with other patterning techniques has shown success. [93]

2.2.10 Self-assembly

Self-assembly is the spontaneous interaction of individual components to form ordered systems. This can be carried out using either covalent or non-covalent bonds. Components can be used to form patterns by applying external conditions or spatial restrictions [94]. The benefits of self-assembly are the simplicity low cost of the method as well as the ability to allow reversible fabrication techniques. Materials used in self-assembled fabrication for nanogap electrodes include nanospheres and self-assembled monolayers (SAMs).

Nanosphere lithography is often used to pattern metal thin films by creating uniform single layers of nanoparticles that act as a lift-off mask [95]. The nanoscale metal structures are often utilised for plasmonic applications [96]. A paper published in 2017 used the self-assembly of polystyrene (PS) nanospheres to create nanogap electrodes. [97] The nanospheres

were placed on a substrate with prepatterned electrodes and etched using an O₂ plasma. A thin layer of Au with a Cr adhesion layer was then deposited on top and the nanospheres were lifted off using a solvent bath. The nanogaps were controlled by the etch time of the nanospheres with gaps from 200 nm down to 10 nm created and used to detect electrical change caused by the attachment of deoxyribonucleic acid (DNA) across the gap. This technique although simple still employed EBL to pattern the first metal reducing the likelihood of it being up taken in large area fabrication.

2.2.10.1 Self-Assembled Monolayers

A SAM is group of organic molecules that has formed an ordered molecular layer by bonding to a surface. The organic molecules usually are made of head, tail and receptor groups and are designed only adhere to a material that is compatible with its head group. When the head group has attached the tail group then organises to allow for a densely packed structure to be made. The size, shape and composition of the tail group will affect the packing. SAMs are typically very small (1-3 nm). They are very tuneable, as the head and tail group can be modified for specific applications and so are utilised for many applications in electronics including nanoscale fabrication, in nanodevices as passive or active materials and for changing adhesion forces of a surface [98][99].

The use of SAMs in the fabrication of nanogap is incredibly simple and highly repeatable [100]. They are often deposited and patterned on surfaces using other techniques such as soft lithography, inkjet printing and dip pen lithography and can be used as etch resists for photolithography and EBL to create nanogap electrodes [101]–[103] .

For substrates with prepatterned materials deposited, the substrate can be placed in a SAM containing solution, with the SAM attaching to the specific material. Using this nanogap electrodes can be created. In 2007 Yong-Young *et al.* used a hydrophobic SAM to attach to a prepatterned Au electrode and a second Au electrode was inkjet printed on top [104]. Due to the hydrophobic nature of the SAM the second metal flowed off the surface of the first and sat next to it on the surface of the substrate. This simple technique was able to create electrodes separated by 50 nm and was used to make self-aligned gate transistors. This modification of adhesion forces is also used in adhesion lithography the fabrication technique explored in this thesis [105].

SAMs are also used in devices as dielectrics [106][107], to aid film growth [108] and as semiconductors in molecular devices[109]. SAMs can also be functionalised with specific

molecules used to help improve charge injection via the creation of dipoles at the interface of a metal electrode that can reduce or increase the potential barrier for charges and effectively changes the work function (WF) of the metal [110], [111]. This ability to modify WFs is utilised in chapter 6.

2.3 Adhesion Theory

When executing most fabrication techniques, to achieve the highest resolution with the fewest defects, it is essential to understand the interaction of the different materials involved. If two materials need to be placed into contact or pulled apart, a fundamental understanding of what is happening at their interfaces is important. Whilst they are always of significance, for some fabrication techniques such as those using NIL and self-assembly, manipulation of adhesive forces is integral to device manufacture. Adhesion Lithography (a-Lith) is another method, fundamentally based on the control and manipulation of adhesive and cohesive forces. To control and perfect a-Lith both of these concepts must first be understood.

Cohesion describes interactions between the same materials and affects material properties including stress, strain, fracture rate and surface tension [112]. Strong cohesion normally results from a strong coulombic force between the molecules of the material, meaning that the molecules are strongly attracted to each other[112]. In metals this coulombic force is determined by the bound electrons, free electrons and the ions and there interactions/energies. To fracture a metal from itself these coulombic forces must be overcome. This is most easy to surmount at the grain boundaries of the metal where the cohesion is weakest.

Adhesion is a multifaceted idea, which is difficult to comprehensively define and complex in nature. It can be loosely be described as the attraction between different materials and the force required to separate them [113]. For the successful adhesion of two materials many factors must be taken into consideration including: roughness of and purity of each material, the type of bonding at the interface of the materials and the fracture potential between them [114]. Adhesion force is defined as the force required to separate two different materials. This force is affected by a weak but long range physical bonding and strong but short range chemical bonding. For a-Lith to be successful metal-substrate (usually glass), metal-metal, metal-SAM and metal-adhesive interfaces have to be understood and manipulated.

Metal-glass interfaces are governed by the nature of the metal. If the metal oxidises well (as is the case for Al) the bond strength between the metal and the glass can increase over time.[114]

For metals that do not oxidise (such as Au) the adhesion force with glass will be reliant on Lifshitz-Van der Waals interactions and will be very weak [114]. If a metal is to be strongly adhered to glass it needs to oxidise. Metals that are sputtered onto a surface, rather than evaporated, will have greater adhesion, as, the sputtered metal atoms will have a higher energy. For polymer substrates adhesion to metals is dependent on the chemical make-up if oxygen is present, the adhesion forces are normally increased. Most polymer films used in device fabrication tend to have a weaker adhesion to metals than glass substrates, this can be improved by heating of the substrate allowing for intermixing of the metal and polymer and so increasing the adhesion between the two [115].

A metal-metal interface normally has strong adhesion forces as the metals will often interdiffuse at the surface. If metals are pulled apart surface damage usually occurs causing the metals to fracture and leaving areas where the metals are still partially attached. To allow one metal to be completely removed from another, other materials need to be inserted between the metals to reduce the adhesion force between them [114].

The adhesion properties of SAMs are tuneable depending on the head and receptor groups chosen with the chemical structure determine its adhesive properties, for example a thiolated end group will strongly attach to metals such as Au due to the strong interaction of Sulphur with Au. [116] The chain length of the SAM will also change the adhesion forces, whereby if the chain length is too small the adhesion forces are too large to remove a material placed on top of the SAM. The grain size of a metal can affect the adhesion forces between it and a SAM. The larger the grain size, the less ordered the SAM will be on the surface of the metal [99]. The receptor of the SAM is also tuneable. For the one metal to be removed from another, the SAM need change the surface energy of one of the metals. The SAM needs to be to be hydrophobic in nature causing increased surface tension. The adhesion forces between the SAM and second metal need to be low so the metal can be completely removed [114]. SAMs can also be used to help characterise interfaces between materials permitting adhesion forces for specific interactions to be recorded [99].

2.4 Semiconducting Materials

To describe how semiconducting behaviour is formed in certain materials one must first understand bonding within materials. In an atom negatively charged electrons orbit the positively charged nucleus. Electrons are only able to exist at well-defined orbits with specific energy levels. Quantum mechanics dictates the number of electrons allowed at each level or state [117], with the first energy level ($n=1$) allowing 2 electron states, the second ($n=2$) allowing 8 electron states and the third ($n=3$) 8 or 18 (depending on the material). The electrons in the highest (or outermost) state are known as valence electrons. These electrons govern the majority of the chemistry of a given element. For the most widely used semiconducting element, Silicon, the $n=1$ and $n=2$ states are filled, with four valence electrons which can participate in interatomic bonding.

Materials with 3-5 electrons in their outermost shell will most often behave like semiconducting materials due to the nature of their bonding. Covalent bonding occurs when atoms share electrons to stabilise their outermost shell. However, this bonding is relatively weak and can be broken via a small change in energy (e.g. slight increase in thermal energy) allowing electrons to be freed and able to contribute to conduction [117].

When atoms are brought together the allowed energy levels change due to the presence of the electrostatic fields of other atoms. If two atoms are placed together the allowed energy levels split in two. So N number of atoms give N number of energy levels and if N is large, instead of discrete energy levels a band is formed. These bands are separated by forbidden regions where no electrons can exist as there is no electron state; these gaps are called band-gaps. The band containing the valence electrons is known as the valence band (VB) and the band above this is called the conduction band (CB). Above this there is an area called the vacuum level and this is the energy at which an electron can escape the solid completely. The VB contains the electrons involved in forming bonds between atoms and the CB is normally vacant at equilibrium [117].

Due to the less strong bonding of materials like silicon, the band gap is small enough for the electrons in the VB to escape to the CB at room temperature; this creates electron-hole pairs. Holes are the absence of electrons and contribute to conduction when the valence electrons remaining in the VB transfer to sites vacated by the electrons in the CB. This moving “position” or hole is thought of as a mobile positive charge. With both the electron and hole thought of as charge carriers with opposite charge [117].

For pure semiconductors like silicon the number of holes is equal to the number of electrons, as the process of creating an electron in the CB produces a hole in the VB. These materials are known as intrinsic semiconductors and due to the small carrier concentration they are not usable for device purposes. To increase the carrier concentration dopants are added. There are two types of dopants, donors or acceptors. In silicon the donor atom is a material with 5 electrons in the VB (such as phosphorous). If some silicon atoms are replaced with this material, four of the electrons from the VB will be used in bonding; the fifth one will be redundant, be donated to the crystal and be free to move around. As the electron is not involved in the bonding process much less energy is needed to promote it to the CB. This creates positive charged donor atoms and negatively charged free electrons. When a semiconductor is doped with donor atoms they are n-type [118]. Materials from group 3 (e.g. boron) are used as acceptor atoms for silicon. For these materials only three electrons are available for bonding with silicon, hence one valence state remains empty and can accept a valence electron from a neighbour to produce a hole in the VB. This creates negatively charged acceptor atoms and positively charge holes. When a semiconductor is doped with acceptor atoms they are called p-type [118].

To indicate the density of charge carriers within an energy diagram, a line called the Fermi level can be drawn; this represents the position in energy in which the semiconductor is filled with electrons. The Fermi level is a probability function and does not show where electrons actually lie, as electrons can only exist in the allowed bands. Its position is temperature dependant. For $T=0$ K, states below the Fermi level are occupied; those above are vacant. As the temperature increases, more electrons are found in allowed states above the Fermi level. For n-type semiconductors the Fermi level lies near the CB edge and for p-type semiconductors it lies near the VB edge [118].

Flat band diagrams offer an ideal view of the semiconductor. For materials with defects and impurities other allowed states can be found between the CB and VB. These can cause trap sites and affect material properties such as mobility of free charges and conduction [117].

Semiconductors can have direct or indirect band gaps. This mean that the CB minimum is located at zero momentum to the VB maximum (direct) or it that the CB minimum is separated from the VB maximum in momentum space [118]. Semiconducting materials used as light emitters need to have a direct band gap to allow for a photon of light to be emitted.

2.4.1 Organic semiconductors

Organic semiconductors are carbon containing compounds with the carbon influencing the bonding within the material. Carbon has 4 valence electrons, with 2 electrons in the 2s orbitals and 2 electrons in the 2p orbitals. If one of the 2s electrons is excited into a p state the orbitals can hybridise to form three sp^2 orbitals and reduce the overall energy of the system; a 2p state with an electron remains. Bonding to another carbon atom causes the sp^2 orbitals to overlap and creates strong covalent σ -bonds. The mechanical strength within a material is attributed to the formation of σ -bonds. The p orbitals in the atoms also overlap causing π -bonds which are much weaker and have a delocalised wave function [119]. The π -bonds allow conduction pathways to form in a material. Adding further carbon atoms will cause a chain of both bonds to form. The π -bonds and π^* -bonds in the material allow electrons within the p-orbitals to move freely, and cause pathways called the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) to form.

This process called conjugation causes disruption to the band structure of a material and causes a band gap to form between the HOMO and LUMO level, similar to the VB and CB seen in semiconducting and insulating inorganic materials. Similarly when at ground state, there are no electrons in the higher energy states beginning with the LUMO, but there are electrons in the lower energy states ending with the HOMO. [120]. Due to their electronic structure, organic materials do not have intrinsic free charges, with charge carriers injected via electrodes to the LUMO (electrons) or HOMO (holes)

For organic materials, charge transport is thought to occur via a combination of band-like and hopping models, depending on the amount of disorder within the material. Here, localised states trap charge carriers removing them from the current flow and affecting device performance. This is known as the multiple trapping and release model (MTR). The trap states within a material are generally caused by defects [121].

2.4.2 Copper (I) thiocyanate

Copper (I) thiocyanate (CuSCN) is a metal pseudohalide has come in to prominence in the electronics field as it is optical transparent and although an intrinsic semiconductor, it can exhibit p-type behaviour. This makes it suitable for applications such as a charge transport layer for OLEDs and OPVs. The reason for the conductivity in CuSCN is yet to be fully

established but studies have higher concentrations thiocyanate ions than copper ions creates p-type conductivity [122] with new research also suggesting individual hydrogen ions increase the holes in the material[123]. The Cu defects have the added effect of increasing the optical transparency of the material with CuSCN absorbing deep ultraviolet light.

2.4.3 Metal Oxide Semiconductors

For semiconducting metal oxides the valence band maximum is created from oxygen 2p orbitals whereas the conduction band minimum is caused by the metal ns orbitals unlike traditional semiconductors. This causes n-type behaviour to be prevalent for most metal oxides due to the effective electron mass being smaller than the effective hole mass. The ns orbitals also allow for higher charge carrier mobility, even in the amorphous state, due to their size [29]. This allows for very high electron mobility with values now advancing to near $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ even for solution processed semiconductor films [124]. The large bandgap also allows these materials to be transparent to visible light; only absorbing in the ultraviolet regime [27]. This property also prevents the thermal generation of charges suggesting there will only be small amounts of intrinsic carriers. The conductivity is attributed to defects or dopants occurring within the material with oxygen vacancies believed to cause some of this behaviour.

2.5 Devices

2.5.1 Metal-Semiconductor contacts

When a metal comes into contact with a semiconductor two types of contacts can be made, Ohmic and Schottky. Ohmic contacts form when the workfunction (WF) of a metal is aligned with either the valence band (HOMO) for p-type materials or conduction band (LUMO) for n-type materials this means there is no barrier to injection for the charge carriers and the change in current follows Ohms law where voltage is proportional to current. For rectifying junctions where the barrier is non-zero this relationship does not hold and Schottky contacts are formed. This barrier is caused by the creation of a depletion region (an area where there are no free charge carriers) due to the Fermi level of the semiconductor and metal WF aligning. This barrier height although effected by the Fermi level of the metal is also sensitive to processing conditions as they effect the surface states and reactivity of the materials.

2.5.2 Schottky Diodes

For Schottky diodes, an Ohmic contact ($WF = \Phi_{Mohm}$) and a Schottky contact ($WF = \Phi_{Msho}$) are used to create rectifying devices with low reverse currents. The energy band diagram (Figure 2.6) shows the typical flat band structure of a Schottky diode, created using an n-type semiconductor with a WF of Φ_{SC} , specific valance band and conduction band energies (E_V and E_c respectively) and Fermi level energy (E_F). The low reverse current is due to the barrier between the semiconductor and the Schottky contact (Φ_B) that is formed due to the WF offset but is also affected by surface states [118]. The barrier will increase when reverse bias is applied stopping any current flow at more negative voltages. In forward bias the barrier will lower allowing conduction through the device. There are four mechanisms that allow current to flow in these devices. Thermionic emission over the barrier is the most common form of current flow but barrier tunnelling and carrier recombination in the depletion region and neutral region of the semiconductor can also occur [118].

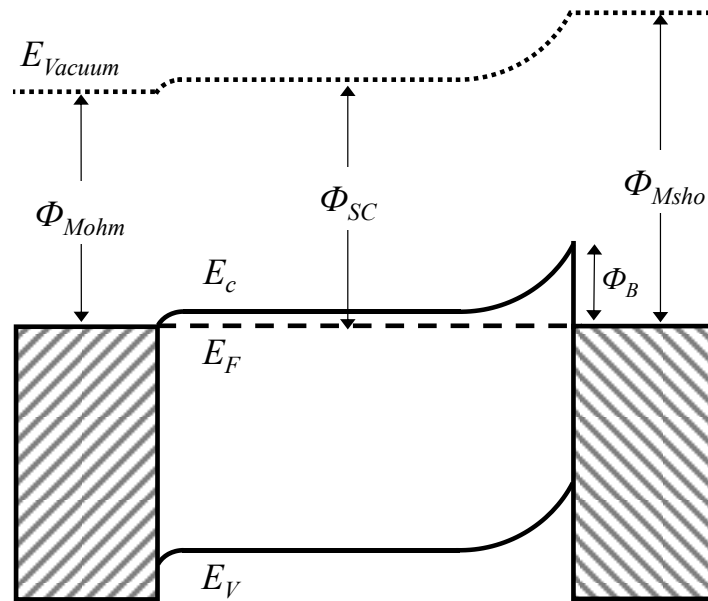


Figure 2.6: Energy band diagram of a Schottky diode formed using an n-type semiconductor with an Ohmic and Schottky metal contact.

2.5.2.1 Figures of merit

Figures of merit include reverse/off current values, rectification ratio (RR) and device turn on. The off current values indicate the effectiveness of the Schottky barrier at blocking charge carriers. The reverse breakdown of the devices occurs when this barrier is overcome allowing

current to flow. The RR is the ratio between the on and off currents at given voltages. Higher values are preferred as this allows the biggest distinction between the on and off state which is useful for device applications. The turn on of the device is also determined by the Schottky barrier height which in turn is ideally governed by the work function of the Schottky contact and the Fermi level of the semiconductor though surface states of the semiconductor will also affect this [118].

2.5.3 Solution Processed Photodiodes

A photodiode is a device where absorbed photons can excite charge carriers that then separate and create electrical currents. There are a vast number of applications for photodiodes with large area fabrication pushing towards areas such as health care such as personalised medicine and sensors for unusual locations. Active materials that are commonly used for these new applications include small molecules, polymers, and metal oxides. These materials have the advantages of being applicable to large area fabrication on flexible substrates and also allow for tunability in the wavelength detected, with the band gap of the material governing this. Different device architectures can also be implemented for a given application, with pn, pin (i denotes insulator), and Schottky structures being used according to their individual advantages. Schottky diodes are used for high speed devices due to quick charge separation whereas pn structures are often used to allow for greater device response as charges can be more easily separated. Pin structures typically have a higher response than Schottky diodes and are faster than pn junctions [118].

2.5.3.1 Operating Principle

For Schottky photodiodes a reverse bias is applied and when the light is shone on the photodiode an electron hole (e-h) pair is generated and can more easily move to the electrodes due to the large band bending in reverse bias. This band bending allows the e-h pair to separate more easily. The more this barrier is spread across the device the better the device performance as a higher majority of the generated e-h pairs can be separated [118].

For organic photodiodes the use of Schottky or single carrier based photodiode is not normally possible as the exciton formed within the semiconductor is not able to be separated into charges and often recombines, so instead heterojunctions are used. These heterojunctions use a donor (D) and acceptor (A) semiconductor to help with charge separation. The D and A have an energy offset greater than the exciton binding energy to facilitate this. These heterojunctions

can be either a bulk heterojunction where the D and A are intermixed or a planar heterojunction [125].

2.5.3.2 Figures of Merit

Performance parameters used to characterise photodiodes include: responsivity, photosensitivity, detectivity and response time. These figures of merit vary in importance depending on the desired application. With other properties such as ease of fabrication and flexibility also having to be taken into consideration.

Responsivity (R) is the ratio of the change in the current upon illumination, $\Delta I = I_{PD} - I_D$, (I_{PD} is the photocurrent and I_D is dark current) divided by the incident optical power, P , with this incident power taking the device area into account [118]:

$$R = \frac{\Delta I}{P_{inc}} \quad (2)$$

R is dependent on the applied bias and wavelength of the excitation source.

PS is the change in current due to illumination at a certain applied bias with respect to the dark current at that bias [118]:

$$PS = \frac{\Delta I}{I_D} \quad (3)$$

Detectivity is the reciprocal of the noise equivalent power (NEP) which is the minimum light power that can be detected. To allow for devices to be compared independent of area and bandwidth, specific detectivity is used as a figure of merit [118]:

$$D^* = \frac{\sqrt{AB}}{NEP} \quad (4)$$

Where NEP is [118]:

$$NEP = \frac{i_{noise}}{R} \quad (5)$$

There are three contributions to detector noise Johnson noise, flicker noise and shot noise. Devices where shot noise from the dark current is the major cause of noise, the specific detectivity can be defined as [118]:

$$D^* = \frac{R}{\sqrt{2eJ_d}} \quad (6)$$

Where the shot noise is [118]:

$$I_s = \sqrt{2eJ_d B} \quad (7)$$

Response time is defined by the rise and fall times of the photodiode. Rise time is defined as the time taken for an increase from 10% to 90% of the total value of the photocurrent. The fall time is defined as the time taken for a decrease from 90% to 10% of the maximum photocurrent. In both incidences the photodiode will be excited by a square pulse from the light source used.

2.5.4 Organic Light Emitting Diodes

Organic LEDs first used small molecules in 1987 [126] and employed polymers as active materials in 1990 [25] are now used in the billion dollar display industry as they allow for high performance appliances. The main issues effecting these technologies to allow for further development are lifetime and efficiency [127]. To overcome this, these devices normally consist of multiple layers often including; an electron transport layer (ETL) and a hole transport layer (HTL) to help improve injection into the emissive material. The cathode and anode electrodes inject electrons and holes into the device respectively. If the anode and cathode WFs are well matched to the LUMO and HOMO levels of the emissive layer some of the other layers can be omitted to reduce fabrication complexity. For most devices a transparent contact is used to allow light to escape form a device, with devices either having top or bottom light emission with the later preferred due to easier fabrication.

2.5.4.1 Operating Principle

Without externally applied biases there is a negative internal electric field within an OLED device. This is due to the large WF differences in the cathode and anode with generated hole and electrons drifting to the anode and cathode respectively. There can also be diffusion currents with in the device due to charge concentration gradients. For particular applied biases (device dependent) both electrons and holes are injected into the semiconductor where they move towards each other (through drift and diffusion) and form excitons which can then decay radiatively [128]. For highly efficient devices the injection rate of both charge carriers under an applied bias needs to be high. If these are not matched the higher mobility charge carrier may pass from the device without recombination. Ideally the current will be limited by injection from the electrodes with the devices limited by bulk transport so the current will have an Ohmic dependence at low bias and be space charge limited (SCL) for higher biases. If there are no active traps the SCL follows the Mott-Gurney law [128];

$$J = \frac{9}{8} \mu \epsilon_0 \epsilon_r \frac{V^2}{L^3} \quad (8)$$

Where μ is charge carrier mobility, ϵ_0 the free space permittivity, ϵ_r the dielectric constant of the semiconductor, V the applied voltage and L the separation between the two electrodes. This however is not a viable expression as it assumes constant trap barrier heights at varied biases which is not true for real devices.

2.5.4.2 Figures of Merit

Parameters used to assess LED performance include, response time, emission spectra, lifetime of the device and efficiency of light emission. The response time is the time taken for the device to emit light when pulsed from an off state to an on state and is important for applications that need fast switching such as displays. The emission spectra is determined by the emissive material used. The lifetime of the device is how long a device can be held under continuous operation at a specific luminance before the luminance is reduced by 50% [128].

One of the most important figures of merit for OLEDs is the quantum efficiency. Internal quantum efficiency, η_{IQE} , is determined by amount of injected charges that are able to form excitons η_{exc} , η_S ; the number of the excitons that are in the singlet state and the number of these singlet excitons that decay with fluorescent light emitted η_{fl} [128]:

$$\eta_{IQE} = \eta_{exc} \eta_S \eta_{fl} \quad (9)$$

The IQE does not however take into consideration losses that occur when the light is trying to exit the device. This can be hindered by effects such as internal waveguiding and reabsorption. The external quantum efficiency relates the amount of charge injected with the light emitted from the device [128]:

$$\eta_{EQE} = \eta_{out} \eta_{IQE} \quad (10)$$

with η_{out} equating the fraction of photons extracted from the device.

Chapter 3

Experimental Methods

3.1 Introduction

Presented in this chapter are the different experimental methods and fabrication techniques used throughout this thesis to create and characterise devices and materials. The fabrication technique, adhesion lithography was used to create all nanogap electrode devices within this thesis and discussed in detail in chapter 4. The technique uses standard laboratory techniques such as photolithography and thermal evaporation which are outlined in this chapter. The semiconductor materials used within this thesis were either deposited via spin coating or thermal evaporation. Characterisation techniques used for the materials and nanogap electrodes include optical microscopy, SEM, AFM, UV-Vis spectroscopy, photoluminescence spectroscopy and Kelvin probe. The devices were measured using a source parameter analyser and particular setups were used to characterise the specific devices (photodiodes and LEDs). Explicit details are presented within the experimental chapters for related techniques.

3.2 Device Fabrication Techniques

3.2.1 Substrate Cleaning

Substrates used for device fabrication were made from borosilicate glass (BOROFLOAT®) and polyethylene terephthalate (PET) from Teijin DuPont Films. All glass substrates went

through a rigorous cleaning process to remove contaminants and allow for successful film deposition. This procedure is as follows: First the substrate is immersed in a solution of the surfactant Decon 90 (Decon Laboratories) in DI water (100 ml:1 ml) and sonicated for 15 minutes to remove particles and organic residue on the surface. The substrate is then rinsed with DI water. Next the substrate is sonicated in acetone for 5 mins and subsequently sonicated in isopropanol for 5 mins. The IPA is then removed using a nitrogen gun. Last the substrates are placed in an ultraviolet ozone atmosphere (UVOCS[®] model T0606E) for 20mins to remove any remaining hydrocarbons. The PET films were rinsed in DI water and IPA to reduce damage to the polymer substrate they were the also placed in the UV ozone to improve adhesion of deposited materials.

3.2.2 Thermal Evaporation

Metal thin films and the organic material C₆₀ were deposited at high vacuum via thermal evaporation. This is a standard technique for film deposition where specific materials are deposited by applying a current to a metal boat which heats up and evaporates the material in the crucible (Figure 3.1). As the material heats up, the crucible shutter opens and the vaporised material then rise towards a quartz detector. When the predetermined deposition rate is reached, the substrate shutter opens and allows the vapour to hit the substrate depositing the material. The quartz crystal measures the thickness of this deposition and when the correct thickness is achieved the substrate shutter closes and the chamber vents to atmosphere. The deposition rates for the metals used in this study were varied to explore the effect on the grain size (aluminium: 0.01-1 nm/s and gold: 0.03-0.1 nm/s).

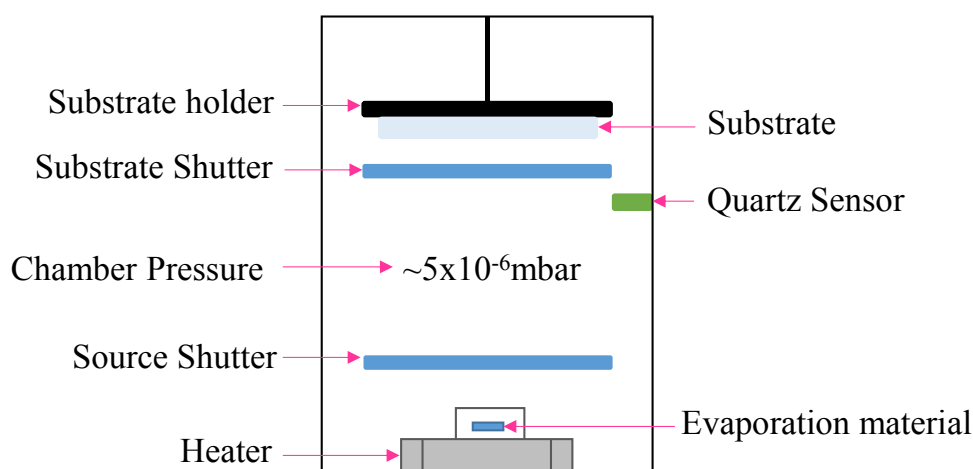


Figure 3.1: Schematic of a thermal evaporation system used for deposition of metal thin films and organic materials.

3.2.3 Photolithography

To pattern the deposited metal film, allowing for different device geometries, a rudimentary form of photolithography, contact lithography, is employed (a schematic of contact lithography is shown in Figure 3.2). The procedure used in this thesis was standard for all substrates: S1813 (Microposit®), a negative photoresist, is spin coated on to substrates at 4000rpm for 40s and soft baked at 115°C for 1 min. The sample is placed under a specifically patterned chromium mask (depending on device application) in a Kurt Lesker mask aligner (365nm mercury discharge lamp) and exposed to the ultraviolet light for 6s. The substrate is then immersed in MF-319 (Microposit®) for 40s with 20s agitation, rinsed in DI water and dried with compressed air. Commercial metal etchants are then used to pattern the thin films, the photoresist is removed with acetone and the substrates dried with compressed air.

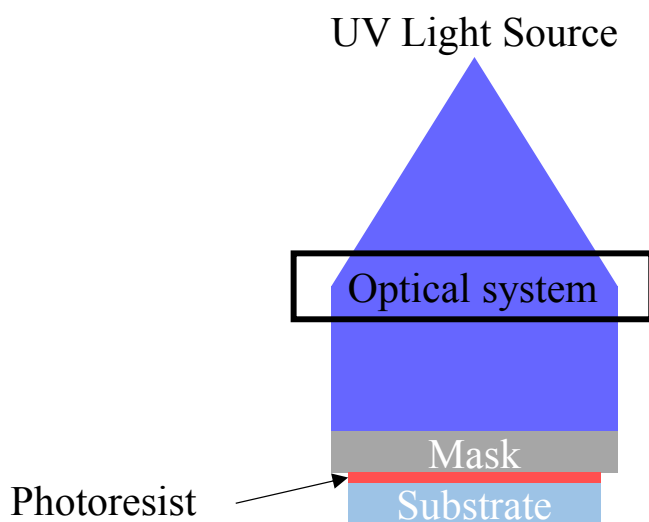


Figure 3.2: A schematic of contact lithography process. The UV light source moves through an optical system and then hits the substrate effecting the areas not covered by the mask.

3.2.4 Self-Assembled Monolayer Deposition

Self-assembled monolayers (SAMs) are organised assemblies of chains of organic molecules that have a head, tail and receptor group. The head group normally attaches to specific materials via chemical absorption depending on its chemical makeup. This procedure is quick but for the monolayers to become ordered takes significantly more time as the organisation of the tail groups is a slower process (Figure 3.3). Longer chain SAMs often allow for a denser packing

of the monolayer. In this thesis, the deposition of a SAM is carried out by the specific SAM being dissolved in a suitable solvent and then immersing a substrate in the solution overnight in ambient conditions. The substrate is then rinsed in that same solvent to remove any excess/none attached material, dried using a nitrogen gun and annealed at 70 °C for 10 mins.

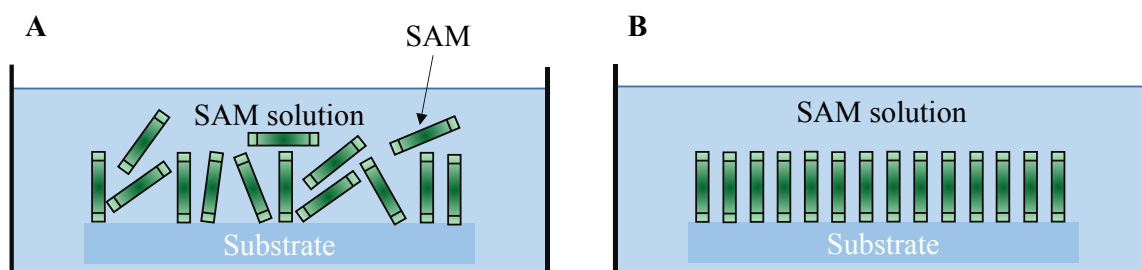


Figure 3.3: Stages of self-assembled monolayer deposition. (A) Straight after substrate immersion in a solution and (B) after a few hours (depending on specific conditions).

3.2.5 Spin Coating

Although not often used commercially, due to its inability to be sufficiently scaled up and material wastage, spin coating is still very useful in research environments due to its simplicity and ability to quickly create thin films on substrates. Spin coating deposits material from a solution onto a substrate via rotation. There are three steps to thin film formation (1) The dispensing of the solution onto the substrate (2) the initial spinning of the substrate where the centrifugal force allows for the film to be spread evenly across the substrate whilst removing excess solution and (3) the later part of the spin cycle where airflow evaporates the majority of solvent (Figure 3.4). The film can then be further annealed to remove any remaining solvent or to alter material properties/conformation. The success in creating uniform thin films at a desired thickness is dependent on a variety of conditions: spin speed, acceleration and duration and solution viscosity. This technique was used to deposit the semiconducting materials used in this thesis unless otherwise stated.

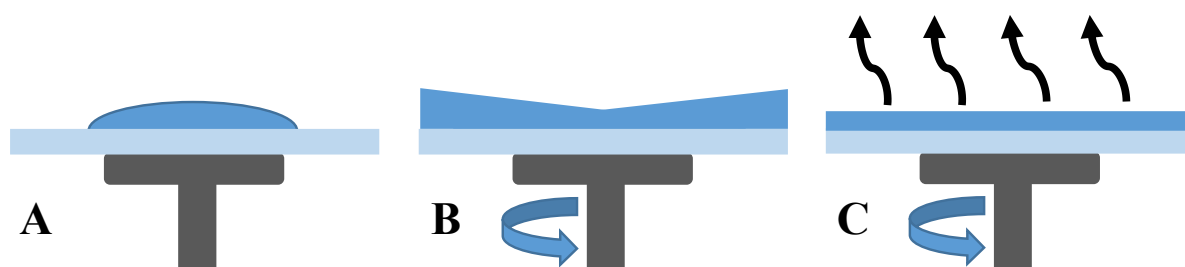


Figure 3.4: Spin coating schematic. (A) Solution is dropped onto the surface (B) The substrate is spun with specific conditions to remove excess solution and create the desired film thickness. (C) Excess solvent is removed through evaporation.

3.3 Material and Surface Characterisation

3.3.1 Atomic Force Microscopy

Tapping mode Atomic force microscopy (AFM) was used to analyse the topography of the thin film semiconductors and the gap between the electrodes fabricated via a-Lith (using an Agilent 5500 under ambient conditions). This technique uses a nanoscale tip attached to a cantilever which oscillates near to its resonant frequency. The amplitude of the oscillation is kept constant and as the tip scans across the surface if the sample surface height changes and the forces between the tip and sample will change causing a change in the amplitude. A servo will then move the tip away from the sample to keep a constant amplitude. This change will be detected by the change in position of a laser that is focused onto the tip that is then reflected onto a photodiode (setup is shown in the Figure 3.5). Phase and amplitude of the signal can also be recorded to describe surface composition and shape.

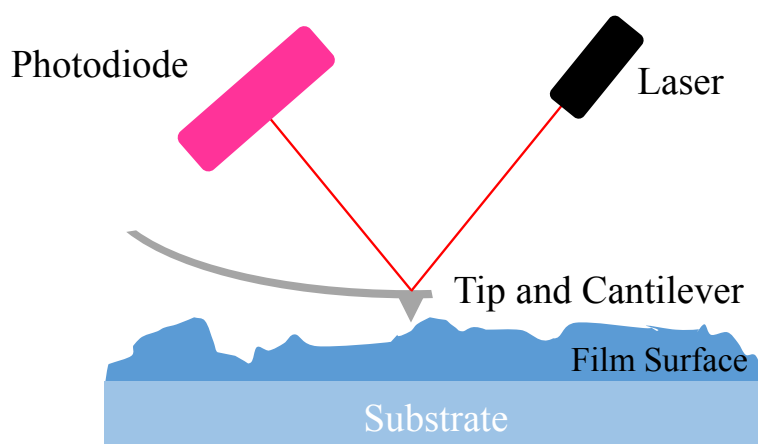


Figure 3.5: Schematic of AFM technique. As the cantilever moves across the surface of the film, changes are detected by the deflection of the laser light reflected on to the photodiode.

3.3.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) can be used to characterise surfaces and chemical make-up of particular materials and in this study it an incredibly important technique for characterising the quality of the nanogap electrodes. It uses an electron beam that is focused by specific lenses and scanned across the substrate causing electrons and X-rays to be emitted (Figure 3.6). To image the surface both secondary electrons and backscattered electrons are collected by specific detectors. The in-lens detector (inside the column) collects secondary electrons and gives topographical information about a sample. For the secondary electron detector outside the column, only topographic data is seen. A specific BSE detector can be placed near the sample to distinguish between different materials but this has poor topographic imaging. X-rays can be detected by a specific detector and used to work out the composition of a material/surface (this is known as energy-dispersive X-ray spectroscopy (EDX)). In this work SEM micrographs were taken using the in-lens detector to characterise nanogap formation in the a-Lith procedure. Before imaging 10 nm of Au was evaporated on the samples to reduce charging effects from the electron beam.

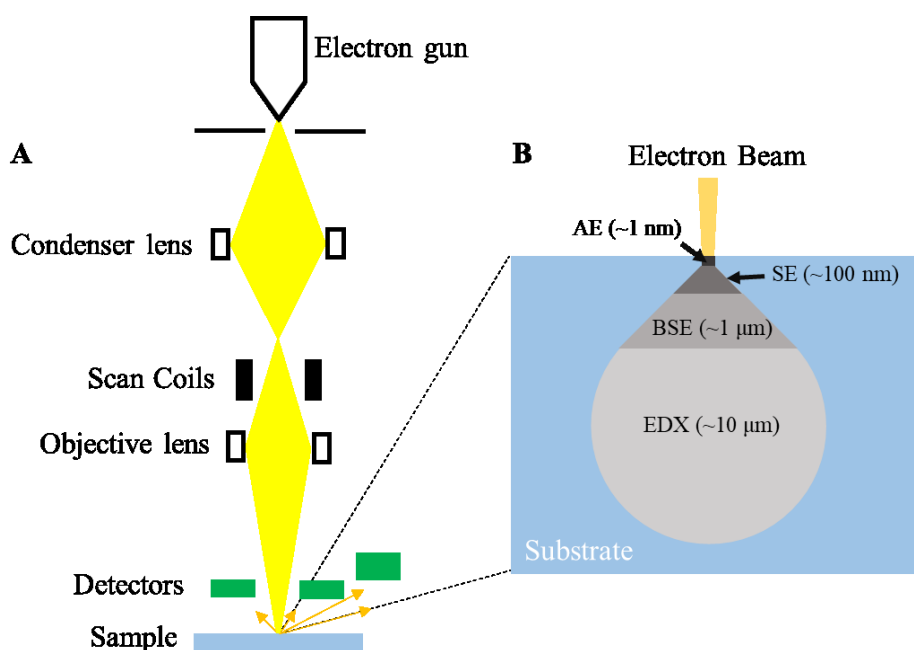


Figure 3.6: (A) Scanning electron microscope Schematic, where the beam emitted and focused by specific lenses and scanned across a surface were generated signals are used to create images via specific detectors. (B) Electron beam interaction diagram, showing how the beam reacts with a sample producing auger electrons (AE), secondary electrons (SE), backscattered electrons (BSE) and characteristic X-rays used in energy-dispersive X-ray spectroscopy (EDX).

3.3.3 Optical Microscopy

For optical microscopy a sample is placed within the microscope and an objective lens is used to magnify the image. This can be carried out in normal, transmission or dark field modes. In normal mode the light is reflected off the surface of the sample and in transmission mode the light passes through the sample. Dark field excludes the unscattered beam from an image and is used to image more transparent samples as it renders more reflective samples black.

3.3.4 Optical absorption spectroscopy

Ultraviolet-visible-near-infrared absorption spectroscopy is used to help characterise the optical properties of materials such as absorption of specific wavelengths. Monochromatic light is sent to the sample and the amount of absorbed, transmitted or reflected light can be measured. Shimadzu UV-2600 was used in this work with all samples measured being thin films spin coated onto quartz. Quartz is used as it is very transparent to all light in comparison to materials such as glass which can have strong UV absorption. Transmittance measurements were taken and converted into absorption for specific materials used in OLED and photodiode applications. The data was converted using the conversion $a = 2 - \log(\%T)$, where a = absorption and T = transmittance. Reference measurements of the transmittance of the quartz sample was also taken and removed from the material data to remove any substrate effects from the data.

The data was also used to calculate the optical bandgap of copper thiocyanate (CuSCN) used in photodetector applications. This was carried out via Tauc plots ($(\alpha h\nu)^n$ vs $h\nu$) where α is the absorption coefficient (absorbance divided by film thickness), h is Planck's constant and ν is the frequency of light. When $n = 1/2$ the bandgap is indirect and for a direct bandgap $n = 2$. The optical bandgap can be determined by finding the linear part of the graph, drawing a linear fit and finding the intersection of the line with the x-axis.

3.3.5 Photoluminescence Spectroscopy

In photoluminescence spectroscopy the material is excited near its known absorption energy which then causes the generation of charge carrier pairs. These then recombine to allow the

material to return to ground state and can cause the material to emit light. This optical emission caused by the excitation and recombination of the charge carriers is then picked up by photodetectors. This technique is used to characterise optical properties of a material including bandgap and help detect defects within a material. In this study it is used to help characterise electroluminescent materials for light emitting diodes.

3.3.6 Kelvin Probe Force

This technique can be used to determine the WF of a metal. First a probe tip made from a metal of known work function is brought into electrical, but not physical contact with a grounded sample. The tip is then vibrated creating a varying capacitor. The electrical contact forces the Fermi level of the two electrodes to align generating electrical charges at the surfaces of the metals. These charges are sensed and used to determine the surface potentials of the metal which are equivalent to the difference in the work function of the two metals. The work function is obtained from the first few layers of the metal and so the technique is extremely surface sensitive with surface structure and contamination effecting measurements. In this thesis a KP Technology scanning Kelvin Probe system SKP5050 was used to perform work function measurements. A WF was taken from a silver reference sample to calibrate the setup, from which the WFs of the metals used in this study were calculated.

3.4 Device Characterisation

3.4.1 Current-Voltage Characteristics

Devices current-voltage characteristics were studied at room temperature using a probestation. This was normally carried out in a nitrogen atmosphere to reduce degradation caused by oxygen or water. The devices are connected to either an Agilent B2902A semiconductor parameter analyser or a Keithley 4200-SCS. The devices are connected to the setup using micro-positioners to move and place the probes accurately onto the electrodes with the aid of an optical microscope. Bias is applied across the device and the resultant current is measured.

3.4.2 Photodiode Characterisation

To characterise photodiodes, devices were biased as the previous section using the same equipment. The devices were then measured in darkness and then under illumination using specific wavelength light emitting diodes (LEDs) at various currents. The optical power of these LEDs are measured using a calibrated optical power meter (PM120V Thor Labs). The wavelength of the LED was calculated using an Ocean Optics spectrometer.

For time response measurements a commercial light emitting diode is attached to a function generator (TTi TG4001 40 DDS) to create an on and off pulse. The photodiode was put under specific bias and the resulting current went via a current amplifier (Stanford Research Systems SR570) to an oscilloscope (Tektronix TPS 2024) where it was recorded.

3.4.3 Light Emitting Diode Characterisation

For an LED made via a-Lith a pulse of either current or voltage was passed through the device using a function generator (TTi TG4001 40 DDS) and the resulting time response was recorded using a standard Si photodiode biased at -2 V put through current amplifier (Stanford Research Systems SR570) and connected to an oscilloscope (Tektronix TPS 2024).

3.4.3.1 Electroluminescent Spectroscopy

In electroluminescent spectroscopy a material is placed into a device structure that allows it to be biased at values that cause it to luminesce. The spectrum of this luminescence is then recorded. This technique is used to characterise optoelectronic properties of a device. For LEDs created using nanogap electrodes standard equipment is unable to characterise the light response. A special setup was created at the nation physics laboratory by biasing the samples and using a confocal Raman PL spectroscopy with 200 nm lateral resolution to capture the light emitted from the nanogap.

Chapter 4

Optimisation of Adhesion

Lithography

4.1 Introduction

As the resolution of traditional electronics reaches the nanoscale and newer technologies demand higher performance devices, high resolution fabrication techniques that can be used in large area production have become more important [94]. New procedures that allow for this often use clever manipulations of adhesive forces to allow for subtractive or additive patterning [85]. Adhesion lithography (a-Lith) is one of these techniques (first reported in 2014 [105]) and can create planar electrodes separated by a nanogap. This fabrication technique relies on the use of self-assembled monolayers to create changes in the adhesive properties of a metal allowing for dissimilar metals separated by a nanogap to be simply produced. It opens the door to a variety of different applications using asymmetric nanogap electrodes to improve performance of many traditional electronic devices such as diodes, light emitting diodes, photodiodes and thin film transistors.

In this chapter, optimisation of the a-Lith technique is explored. Yield studies of devices are used to indicate the success of a-Lith to create nanogap electrodes. Issues with nanogap

uniformity are addressed by studying the influence of grain sizes/boundaries of the deposited metals on the nanogap. The results indicate that the deposition rate of both the metals affect the formation of the nanogap. It also reveals that there is an effect on the work function (WF) of the deposited metals and Schottky diode devices created using the different deposition rates.

Further in the chapter the effect of the electrode thickness on the formation nanogap is explored. Traditionally 40nm has been used as the electrode thickness, but thicker electrodes are expected to improve device performance for some applications. This increasing thickness, however, widens the gap between the electrodes, eliminating the expected improvement in device performance.

A-Lith is a technique that is compatible with plastic substrates and whilst it has shown some success on polyimide and polyethylene terephthalate (PET) [129], [130], it has displayed a very low yield on these plastic substrates due to changes in adhesive forces of the metal electrodes with the plastic substrates as compared to glass. In this section, improvements are made through annealing of the PET substrate.

4.2 Background Asymmetric Nanogap Electrodes

There are many methods that are used to create nanogap electrodes (discussed more thoroughly in section 2), however, these techniques most often rely on the use of metal contacts that are made from the same material, limiting their applications and not allowing the fabrication of planar rectifying devices. There are a few methods that can fabricate asymmetric nanogap electrodes, though they are often highly complex with multiple stages. One reported method includes the use of electron beam lithography (EBL) and reactive ion etching to create dissimilar metal electrodes separated by ~6 nm with Au used as the first electrode and Pt, Ti, Pd, or Al as the second electrode [131] This procedure is very convoluted with the authors noting that the process is a “viable research technique”. Another process used EBL to pattern Au electrodes with electrodeposition then used to coat one of the Au electrodes with either Cu or Co. The electrodeposition was able to self-terminate, creating electrode spacing’s of ~10 nm [67]. This technique again is not suitable for large area fabrication.

A-Lith is part of a new and interesting field in patterning where changes in adhesive properties have been used to create nanogap electrodes. This area is very new but some groups are seeing the massive potential this area of research has for large area patterning. The use of additive and subtractive technologies can offer more freedom in material choices and fewer fabrication

steps. These ideas have been exploited in techniques such as nanoimprint lithography and associated techniques but they again do not allow for asymmetric contacts.

One technique that is gaining some traction in up-scaling of the fabrication of asymmetric nanogap electrodes using change in adhesion is atomic layer lithography. This technique developed for planar nanogap metals in 2013 uses a layer of Al_2O_3 to change the adhesive properties on a metal [132]. First a metal is patterned on a substrate using focus ion beam milling (FIB) or EBL, Al_2O_3 is then deposited over the substrate and a second metal is deposited on top. An adhesive is subsequently placed on top of the second metal and peeled off. The adhesive removes the second metal in areas where the first metal is patterned on the substrate due to the height difference between the substrate and the first metal. Due to this processing, the Al_2O_3 defines the shape and width of the nanogap and so it can be easily controlled with gaps down to $\sim 1\text{nm}$ being created. This technique can be carried out on fairly large areas but is limited by the EBL/FIB patterning. The second metal is always noble metal, to allow for poor adhesion to the Al_2O_3 and aid removal. This can limit applications, though, much success has been shown in the creation of photonic structures [133]. Memristors using Au for both electrodes have also been created [134]. Some work has been carried out to remove the EBL/FIB step by replacing it with a higher throughput technique; optical interference lithography. Although successful this does reduce uniformity across the gap and is still in development stages. It is however, able to create electrode spacing of about $\sim 5\text{nm}$ [135]. In the same paper the electrodes are also transferred on to flexible substrates by using epoxy as the “adhesive”. The epoxy removes both metal layers with the first substrate used only as a carrier. This however leaves the Al_2O_3 on top of one of the electrodes causing some complication for device fabrication.

4.3 A-Lith Process

A-Lith is based on the use of self-assembled monolayers (SAMs) to modify adhesion forces between materials. A schematic of the method is shown in Figure 4.1. The electrodes are most often fabricated on glass for ease of process and repeatability.

The first step is to deposit the first metal (M1) on the substrate this is then patterned using contact photolithography. This step is done due to the limitations of equipment available and the patterning step can be substituted with high throughput technologies such as nanoimprint lithography. It is also a non-critical step in determining the gap size between the electrodes; the

only stipulation is that the edge profile created from the first metal by the patterning step is sharp. The first metal is normally aluminium (Al) due to ease of patterning and because it forms a self-passivating oxide layer of 2-3nm which is useful for specific SAM attachment.

Second, the substrate is immersed in a SAM solution. Octadecylphosphonic acid (ODPA) is chosen for metals with an oxide layer due to the favourable bonding of the phosphonic acid group to oxides. The long alkyl chain allows for good coverage of the metal without defects and its hydrophobic nature favourably tunes the adhesion forces of the metal. The substrates are rinsed in the appropriate solvent as used in the solution and dried after the immersion to remove any residual SAM that may be left on the substrate.

In the third step the second metal (M2) (often Au) is deposited using high vacuum thermal evaporation. When Au is used a 5nm thick layer of Al is evaporated beforehand (in the same vacuum process) to improve the adhesion of the Au to the substrate.

Last First Contact® adhesive glue (Photonic Cleaning Technologies) is applied to surface of the sample, using the brush provided and dried for 60 mins. The glue is then peeled away from the substrate. In areas where M2 is on top of the SAM coated M1, M2 is removed. In places where M2 is directly deposited on the substrate, however, it remains. This is able to take place due to the adhesion forces between the substrate and M2 being higher than the adhesion forces of the glue to M2 whilst the adhesion forces of the glue to M2 are greater than the adhesion between the SAM and M2 and the cohesive force of M2. The fracture of the M2 layer occurs at the Al substrate interface and results in a nanogap separation between M1 and M2. The length of the SAM decides the optimal resolution of the separation between the two metals. ODPA is around 3 nm in length. The gap size usually created, however, is slightly larger normally ~15 nm. This is due to other factors affecting the gap formation including metal deposition and the non-optimised peeling step that is usually carried out using a pair of tweezers.

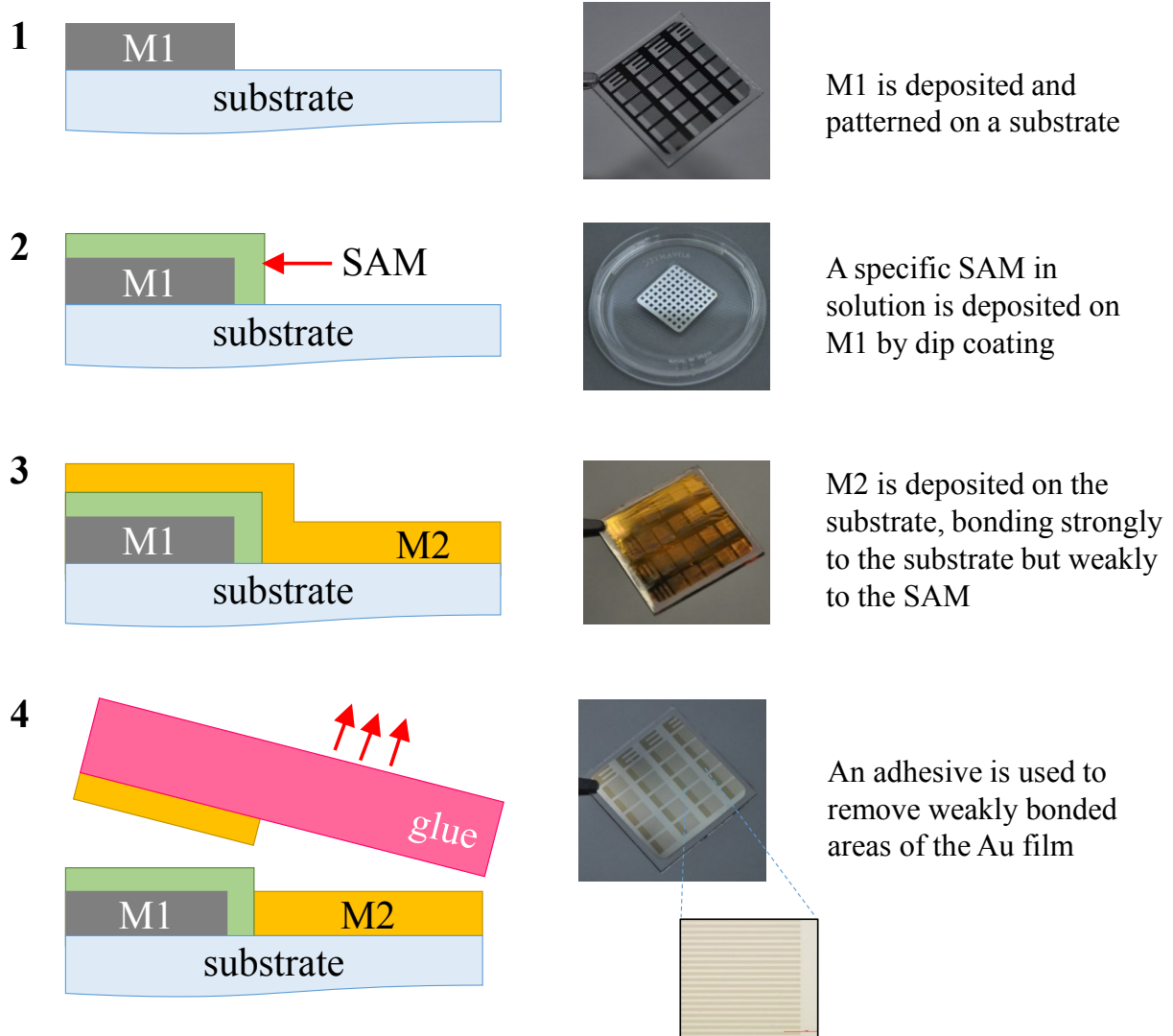


Figure 4.1: A schematic with corresponding photographs and a description of the a-Lith procedure. The samples within the photograph are 25 mm x 25 mm

To create planar devices, the substrate is then placed in a UV ozone treatment for 20 mins to remove the SAM. The resulting electrodes (Figure 4.2) can then be used to create a variety of devices by simply depositing an active material on top of the electrodes. The material and deposition technique used dictates the placement and structure of the material film and determine whether the material sits on top of the electrodes or fills the nanogap. A-Lith has been utilised in many different application including photodiodes, RF diodes, LEDs, memristors and transistors [105], [129], [130], [136]–[138] Due to the success shown in this technique, several variations have been employed where a-Lith electrodes have been used in conjunction with a SAM dielectric and molybdenum disulphide (MoS_2) to create self-aligned gate transistors [139]. Additionally, a similar technique has been reported called self-assembly

lithography. This uses functionalised CdSe quantum dots to create nanogap electrodes before characterising these same quantum dots [140].

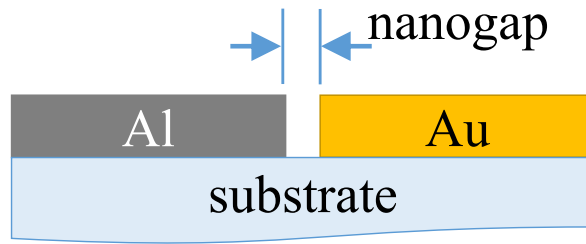


Figure 4.2: A schematic of nanogap separated electrodes created via a-Lith.

Much work has been already carried out on the early optimisation of the technique to increase the nanogap uniformity and decrease nanogap width. This includes changing the metal patterning technique and adhesive used to remove the second metal [141]–[143]. This early work has succeeded in more control of the nanogap created via a-Lith. With this optimisation, a-Lith is now capable of creating vast numbers of electrodes of different shapes (Figure 4.3) with minimum electrode feature size determined by the patterning technique of M1 allowing for electrodes, customisable for specific applications to be created.

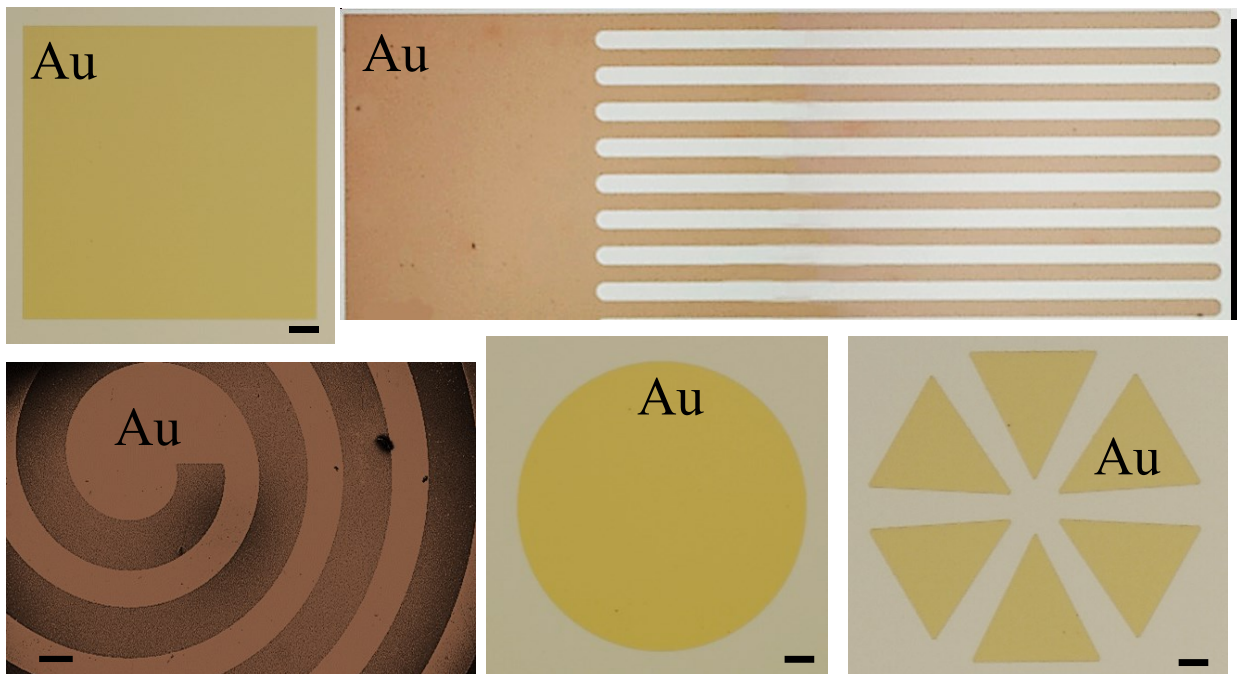


Figure 4.3: Optical and SEM (spiral electrodes) micrographs of different shape Al/Au electrodes created via a-Lith, showing the versatility of the technique. Scale bars: 100 μ m

4.3.1 Yield Studies

With much work going into the optimisation of the technique an important characteristic to measure within the a-Lith technique is yield of devices, which has not previously been carried out on a large scale. The creation of arrays of 100s of nanogap devices on one substrate is simple and is now only limited by the mask used for patterning the first metal. To explore the yield of the a-Lith procedure, a substrate with 400 individual circular devices, show in Figure 4.4A, was fabricated and tested for electrical isolation between the Al common electrode and the 400 individual Au circle electrodes.

The I-V plot of the nanogap electrodes (Figure 4.4B) show that, out of the 400 device measured, 12 were partially or fully shorted (indicated by the higher currents on the plot) showing a yield of 97%. The isolated devices are denoted by the low current I-V sweeps showing no pathway for the charge carriers to move through. In the case of these shorted devices (which were mainly found on the edge of the substrate), they were not caused by failure in the a-Lith procedure but either by defects caused by human error or the contact lithography step for patterning the Al; which is known to cause failings in patterning (see section 2.1.1). With improvement in these non-critical steps such as changing the Al patterning step and reduction in human contact with the substrate (both of which are needed if this technique is to be up-scaled and commercialised) the yield of a-Lith should be able to be increased to 100%.

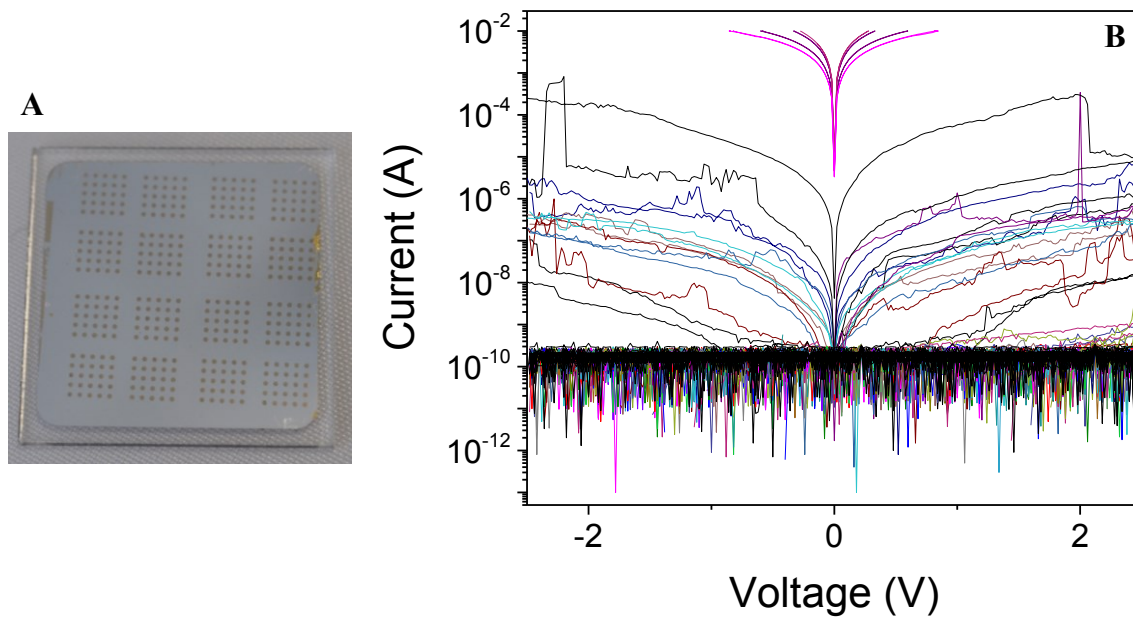


Figure 4.4: (A) Image of the 2mm x 2 mm a-Lith substrate of 400 Au electrodes surrounded by a common Al electrode used in the statistical analysis. (B) I-V characteristics of the 400 empty nanogap electrodes showing a 97% yield.

4.4 Process Optimisation

It has been proven that a-Lith is a very successful in-lab technique, however for it to be scaled-up and to keep device uniformity, other issues need to be explored and addressed including the uniformity of the gap. As shown in the previous section, the technique has high yield in terms of electrode isolation, however, the gap between the electrodes can fluctuate in size and have non-uniform shape with batch to batch variation in nanogap size. A typical SEM image of the nanogap (Figure 4.5) demonstrates that there are issues with uniformity in the gap size and shape which could lead to issues when creating devices that need a very small tolerance for error.

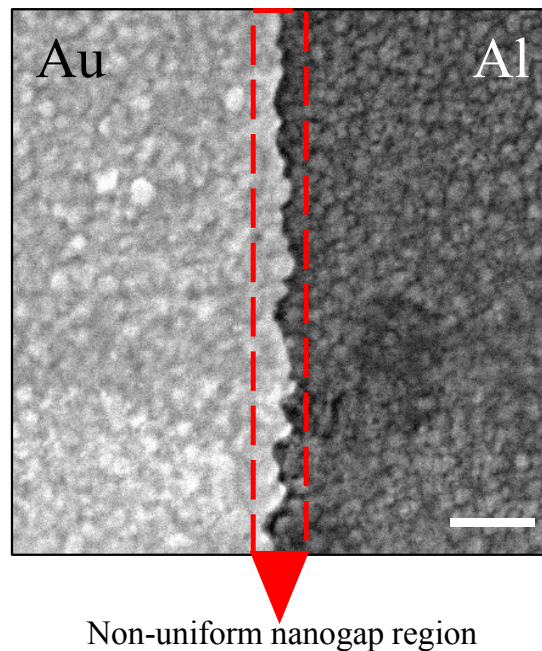


Figure 4.5: Typical SEM micrograph of nanogap created using adhesion lithography showing a lack of uniformity. Scale Bar: 200 nm.

Factors that will affect the nanogap regularity include the grain size of both metals and the roughness of the first metal, as this will vary the adhesive forces and cohesive forces that act upon the metals. This in turn, will affect the peeling step of the second metal and hence the nanogap formation. Typically, the devices have been created with a thickness of 40 nm, as it has shown to create very small nanogaps (~15 nm) and it is a suitable thickness for device electrodes. Changing the thickness of electrodes can improve device properties due to increased current and would be favourable for some device applications. This, however, could affect gap

formation as adhesive/cohesive forces play such a large part in the formation of the nanogap and so needs to be investigated.

4.4.1 Grain Size influence

It is expected that the ultimate resolution of the nanogap is the length of the SAM used but this will only be realised if the a-Lith process is optimised. The grain sizes of each metal are integral to the quality of the gap between the two metals. Studies into the effect of grain sizes on the roughness and adhesion of thin metal films indicate smaller grain sizes in thin films allow for greater adhesion to a substrate [144][145][146]. Grain sizes will also affect the fracture mechanics of a material as the grain boundaries are often the weak points of a film and metals will fracture along a grain boundary, a phenomenon known as intergranular cracking [147]. More information in the physics of adhesion can be found in section 2.2.11. To improve the regularity of the nanogap, a study into changing the grain size of both the deposited metals by varying the deposition rate of both the first and second metal is explored. Zinc oxide (ZnO) Schottky diodes have also been created to see the effect these changes have on device performance.

A common way to deposit metal thin films is thermal evaporation. As the deposition rate via thermal evaporation increases it is expected that the grain sizes of the metal thin film will decrease due to an increase in nucleation sites [148]. Reactions can occur with residual oxygen within the chamber that can reduce the grain size at lower deposition rates due to absorption into the layer, with high deposition rates absorbing less oxygen [149]. In this study however, the evaporator used was in a glovebox that had an oxygen level below 0.1 ppm which should help eliminate this effect.

2.1.1.1 Changes in the first metal

The first metal deposited in a-Lith is normally Al. In this study the metal deposition rate of Al has been varied at 0.01, 0.05, 0.07, 0.1, 0.15, 0.2, 0.5 and 1 nm/s to see the effect the change of grain size and roughness of M1 has on the nanogap created using a-Lith. To keep measurements as regulated as possible, the other stages of a-Lith including: SAM deposition and second metal (Au) evaporation were carried out simultaneously for each device. The thickness of the first metal was kept at $40\text{ nm} \pm 1\text{ nm}$. The evaporation of the Au was kept at 0.05nm/s and all samples were placed in the same evaporation. After a-Lith all the samples we

placed in a UV ozone to remove the SAM for 60s with all samples measured at as similar a time as possible.

Shown in Figure: 4.6 are topographic AFM micrographs of the different deposition rates. Here we can see a definite change in the grain sizes of the metal as the rate is increased from 0.01-1 nm/s, with grain sizes decreasing with increasing deposition rate. This suggests there was little oxygen present when the Al was evaporated, as the reported effects of increasing grain size with deposition rate are not seen. For the 0.01 nm/s rate, grain size is very varied with the largest grains 150 nm wide. For the quickest deposition rate (1 nm/s), the largest grain size falls to 70 nm with less variation in size. RMS roughness values and height histograms for each deposition rate are also shown in Figure 4.6 and a clear trend can be seen with a decrease in roughness as the deposition rate increases. This value decreases very sharply until 0.2nm/s deposition rate where the trend begins to level off, but still showing a slight reduction in film roughness as the deposition rate increases. The height histograms also indicate this, showing a far greater distribution in height for the slower deposition rates. This roughness and grain size change will not only affect the a-Lith nanogap, but could also affect the semiconductor layers processed on top of the electrodes for device creation. These samples were then taken through the standard a-Lith process (section 4.3) with AFM and SEM images captured to identify the influence of the change in grain size and roughness on the nanogap electrodes.

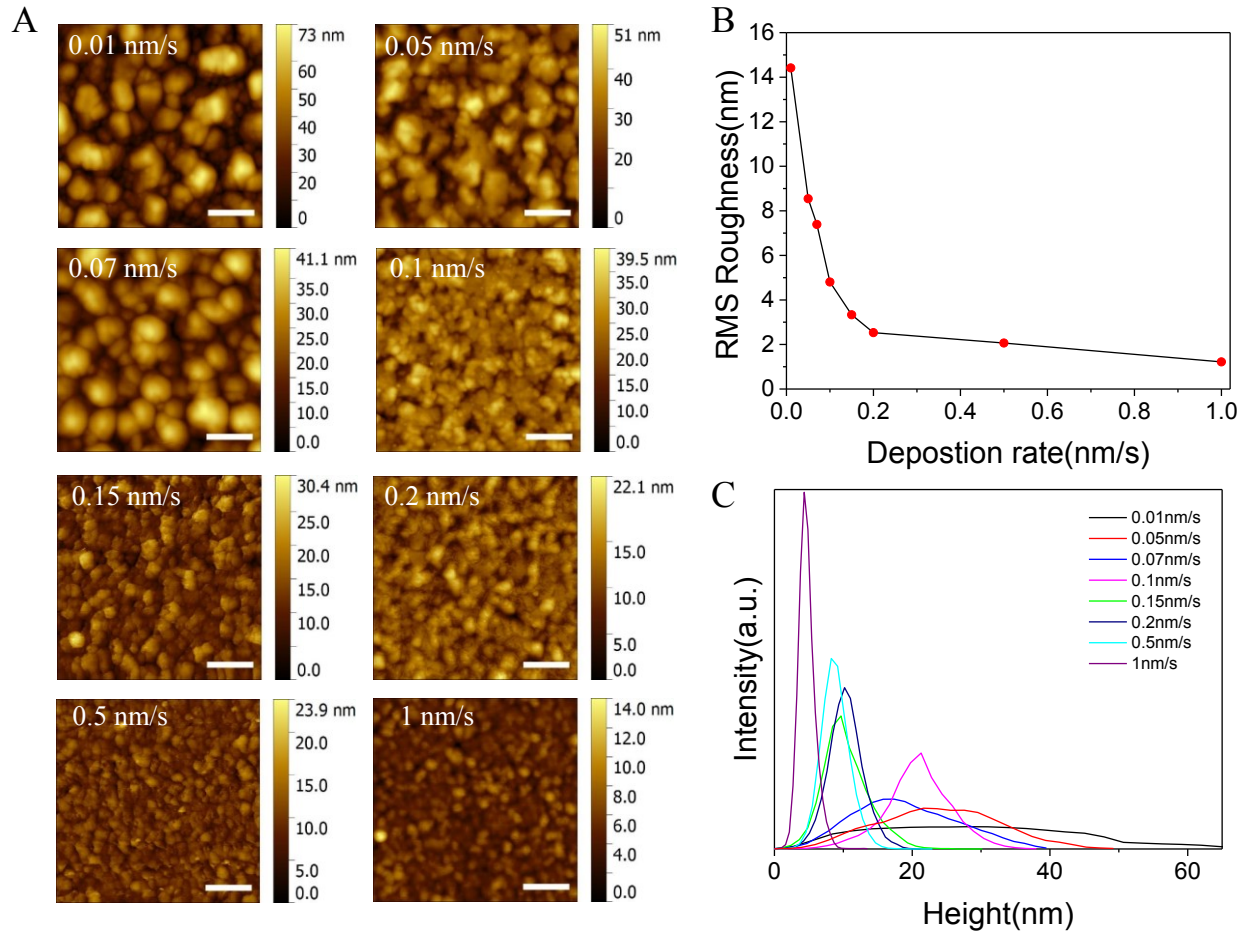


Figure 4.6: (A) AFM topography images of varying deposition rates of Al (B) RMS roughness and (C) height histograms plots for each deposition rate. Scale bar 200 nm.

AFM micrographs of the nanogap electrodes created using each Al deposition rate (Figure 4.7) show that almost all of the deposition rates were able to successfully create nanogap electrodes, however, for the lowest deposition rate (0.01 nm/s) the a-Lith has partially failed with the gold fracturing at approximately 1 μm away from the aluminium. This was actually one of the more successful electrodes for this deposition rate with some electrodes being completely damaged with the M2 almost entirely removed. This is most likely due to the high roughness of the aluminium film (which is nearly 2 times higher than the next deposition rate) causing non-uniformity of the Au film and reducing the adhesive forces between the Au and the substrate. The rest of the deposition rates were more successful when creating the nanogap, but as the grain sizes get smaller the nanogap appears more regular with the Au more able to follow the shape of the grains. This shows that the higher deposition rates allow for a more uniform gap size. The overall roughness of the nanogap electrodes is also reduced with increased deposition

rate. Line scans were taken with the AFM, but due to its relatively low lateral resolution (~ 30 nm), information about the nanogap (normally sub 30nm) was impossible to extrapolate.

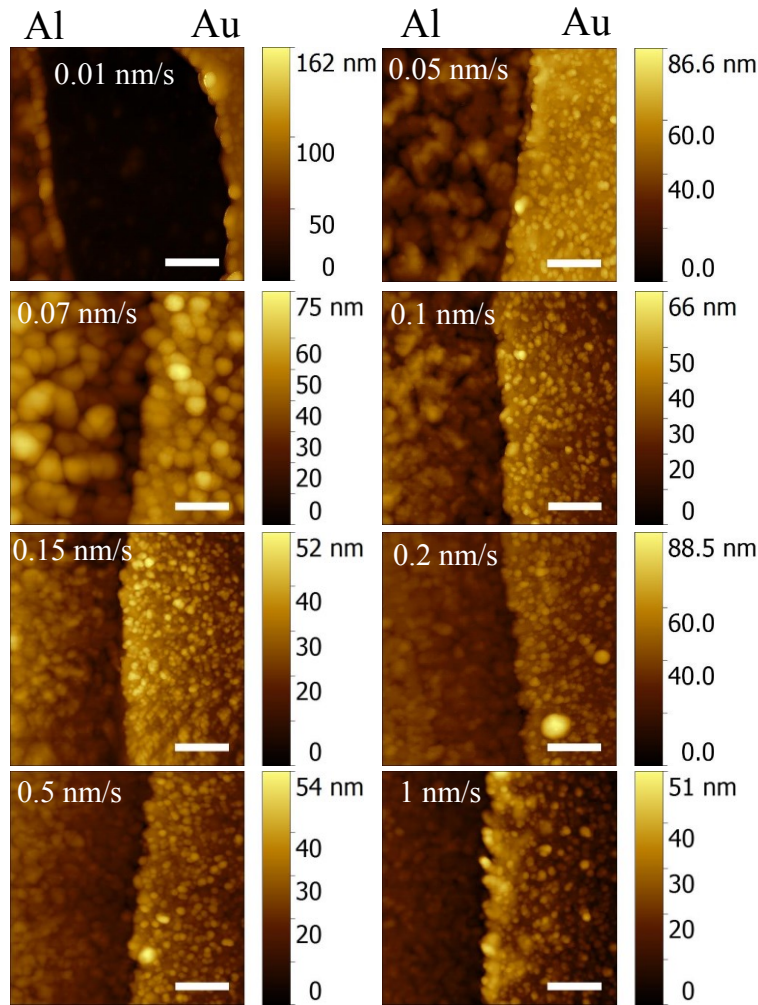


Figure 4.7: AFM topography images of the nanogap electrodes with varying Al deposition rates and a constant Au deposition rate of 0.05 nm/s. Scale Bar: 200nm.

To further characterise the nanogap, SEM images have also been taken (Figure 4.8) confirming the results from the AFM images and giving a little more detail to the nature of the nanogap interface due to its improved resolution. Again, it can be seen that the 0.01 nm/s deposition rate sample has failed with the Au film delaminating from the surface. For the other samples, as the deposition rate increases and so the grain size decreases the Au appears to more closely follow the Al boundary. The smaller grain sizes create a more uniform Al interface, allowing more consistent fracture force across the Au as it is removed from the Al. The large grain sizes causes a less uniform gap with some areas along the nanogap much wider than others.

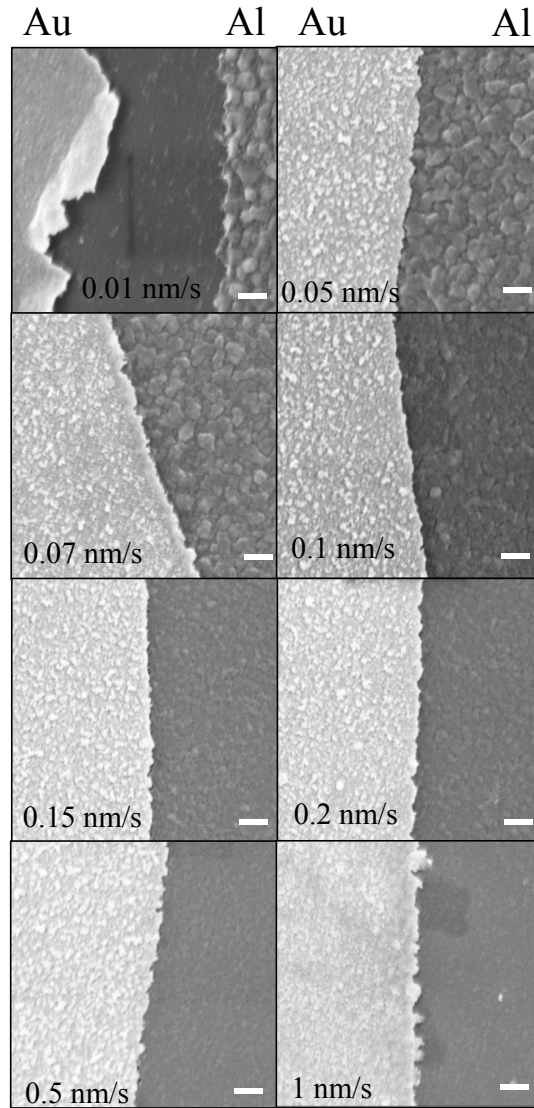


Figure 4.8: SEM micrographs of the nanogap electrodes with varying Al deposition rates and a constant Au deposition rate of 0.05 nm/s. Scale bar: 200nm.

Previous studies have indicated that grain size and roughness can affect the WF of a metal. With smaller grain sizes reducing the WF due to increased grain boundary lengths and increased irregular lattice distortion that will change the nature of electrons on the surface of the metal [150]–[152]. The increase of surface roughness also decreases the WF due to its effect on the dipole barrier of the surface [153]–[157]. Kelvin probe measurements were taken to identify the effect of the change in deposition rate has on the WF of the Al (Figure 4.9). This is a very surface sensitive technique that can be affected by surface contaminants. The measurement was taken in air after cleaning the substrates with a solvent wash and placing them in the UV ozone for 20 mins. The samples were then left in air for the same amount of

time and subsequently measured to give the most accurate results. Also as the technique is air sensitive the trend of the measurement is more interesting than the absolute value of the WF for each sample. Looking at the overall trend there is a decrease in WF with increasing deposition rate, though the 0.5 nm/s data is slightly anomalous. This could be because of the incredibly sensitive nature of the WF to surface morphology and perhaps there are other factors affecting the WF. Low WFs would be expected for samples with the smaller grain sizes and hence with increased deposition rate.

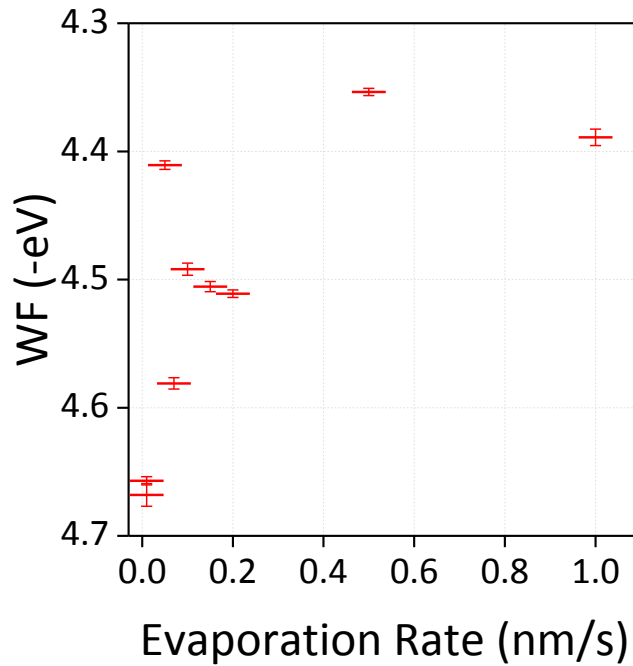


Figure 4.9: Kelvin probe measurements of Al WF for varying deposition rates.

To see if the change in nanogap shape/size, due to the deposition rate, would affect device performance, Schottky diodes were made using ZnO to create Schottky diodes using previously reported methods where ZnO hydrate ($\text{ZnO} \cdot x\text{H}_2\text{O}$, 97% Sigma Aldrich) was dissolved in ammonium hydroxide at a concentration of 10mg/ml and stirred for two hours [158][159]. The solution was then spin coated on to the a-Lith electrodes of varying Al deposition rate at 1500 rpm for 30 s and annealed at 180 °C for 1 hour, this deposition was repeated twice. The devices were measured in nitrogen with an Agilent source parameter analyser with 10 devices evaluated for each deposition rate. The semi-Log plots of the I-V characteristics are shown in Figure 4.10A. As expected for the ZnO diodes the 0.01 nm/s device had a far lower device performance due to the much larger gap between the two electrodes). The other devices have a small change in characteristics. The leakage currents which should change with gap width

are very variable with little difference in the range for each deposition rate. Shown in Figure 4.10B is the rectification ratio (RR) versus deposition rate with a linear fit. This was fitted discounting the 0.01 nm/s rate as the large gap size was due to a failure in the a-Lith process and not determined by the grain size. Here we can see a linear trend with the RR suggesting higher ratios at higher deposition rates. There is also less variability at the high deposition rates, suggesting that a change in deposition rate does effect device performance. The variation in devices is likely due to the disparity in the nanogaps at lower deposition rates. The improved performance of the higher deposition rates could be due to the decrease in WF in Al changing the barrier to conduction from the Al to the ZnO. Previously reports using this deposition method have shown the conduction band minimum of ZnO at 3.7 eV with a Fermi level of 4.3 eV [160]. The reduced WF of the Al would allow for better charge injection. Interestingly the 0.05 nm/s deposition rate also has increased RR following the trend in the WF data, suggesting it has affected device properties. It should be noted that ZnO is a solution processed material that can in itself have variations in performance due to inconsistencies in the thin film. This was however controlled as much as possible throughout the experiment via strict controls on amount of solution dropped onto the substrate and consistent deposition parameters.

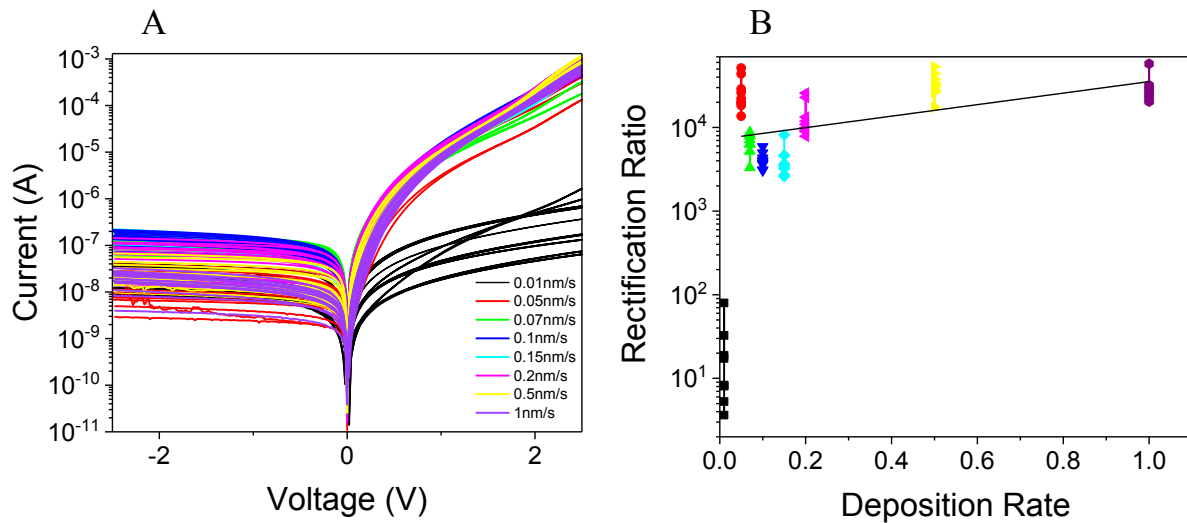


Figure 4.10: (A) Semi-Log plot of I-V characteristics for ZnO a-Lith diodes with different deposition rates for Al with 10 devices measured for each rate (B) Comparison of rectification ratios of devices for each Al deposition rate at ± 2.5 V.

2.1.1.2 Changes in the second metal

The change in the second metal of the a-Lith procedure is expected to have an effect on the formation of the nanogap because the critical fracture mechanics to create the gap happen in

this layer. It is expected that the fracture of the second metal will follow not on the grain boundary of the first metal, but will fracture at its own grain boundaries as this is the weakest part of the metal structure (this is further discussed in section 2.1.11).

To allow for variation in the gap to be attributed to deposition rate changes in the second metal, the first metal has been kept at a constant deposition rate of 0.1 nm/s with all substrates placed in the same evaporation. The patterning and SAM treatment were also kept consistent for each sample. The second metal (Au) was deposited using thermal evaporation at 0.01, 0.03, 0.05 and 0.1 nm/s deposition rates. An interlayer of 5 nm of Al was deposited before the Au to improve the adhesion of the Au to the glass substrate. This adhesion layer was kept at a constant deposition rate of 0.1 nm/s. The thickness of the second metal plus adhesion layer was kept at $40 \text{ nm} \pm 1.5 \text{ nm}$. AFM topography images of each of the different deposition rates (Figure 4.11) shows little change in the grain size and roughness with the lowest deposition rate (0.01 nm/s) smoother than the other three samples. The height distribution graph also confirms this. This lack of variation between the samples could be due to the 5 nm adhesion layer of Al that is evaporated just before the Au to improve substrate adhesion. Adhesion layers have will control the nucleation and growth of grains of Au [161] and as the Al was deposited at a similar rate for each sample the effects on Au grain sizes are likely to be similar.

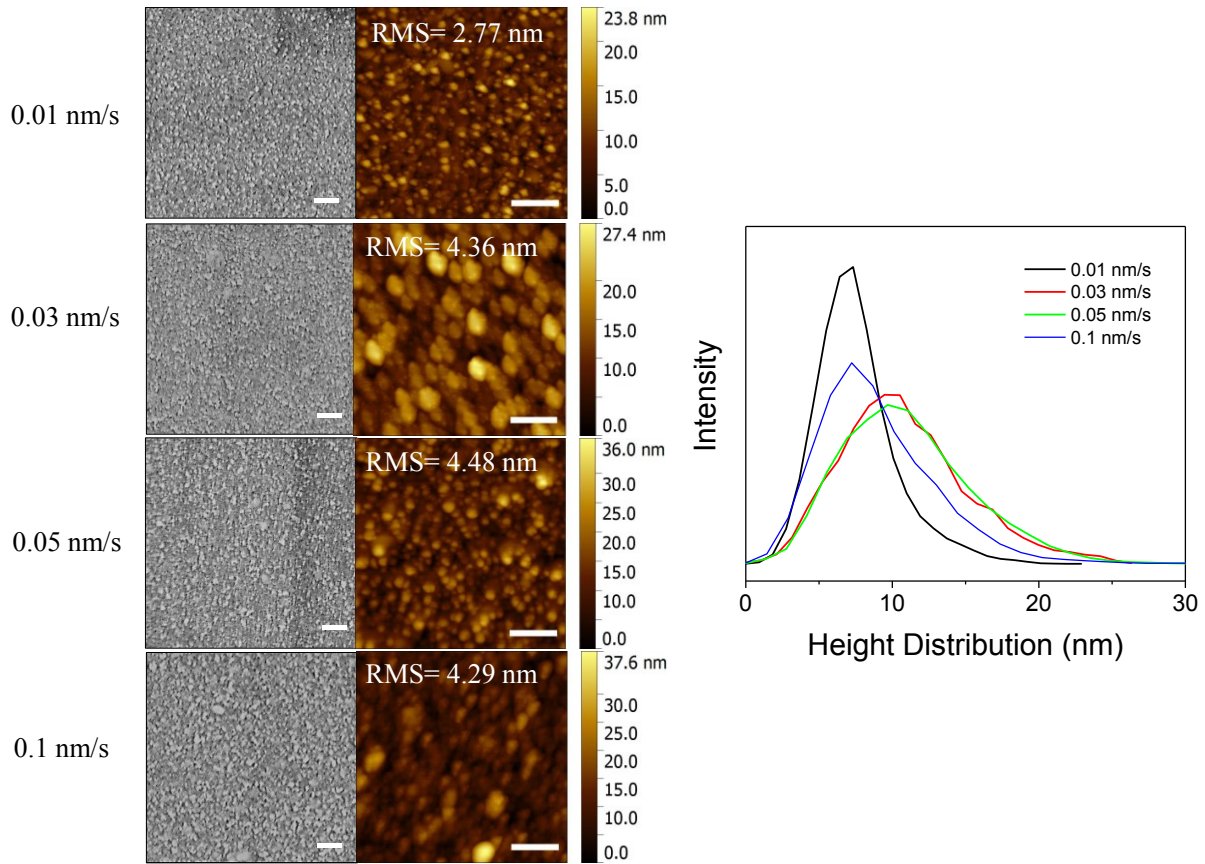


Figure 4.11: SEM and AFM topography images with associated height histograms of thin films of Au with varying deposition rates. Scale bars: 200 nm.

AFM images of the nanogap created for each deposition rate (Figure 4.12) also show similar uniformity in the nanogaps, with the Au following the defined Al interface. All samples show fairly uniform gaps but the resolution of the AFM tip (~ 30 nm) is unable to clearly define the size and variation in nanogaps. SEM images, which have higher resolution, were taken of the nanogaps (shown in Figure 4.13) and suggests that as the deposition rate increases the gold follows the grain boundary of the aluminium more easily and it appears to delaminate less. This suggests that the deposition rate of the second metal has affected the nanogap. This in turn could be due to the greater energy of the higher deposition rates, which will then cause better adhesion of the Au to the Al interfacial layer. This will mean that as the fracture of the metal occurs at the Au interface, the adhesive force of the Au to the substrate will be higher and so the fracture will not cause as much delamination of the gold. More quantitative analysis of gap size and shape could help to confirm this such as high resolution TEM, though this would only give a size of gap at one point along the nanogap so would not be able to quantify variation in the nanogap on one a-Lith electrode. If carried out for multiple instances along a gap it would become an extremely time consuming measurement.

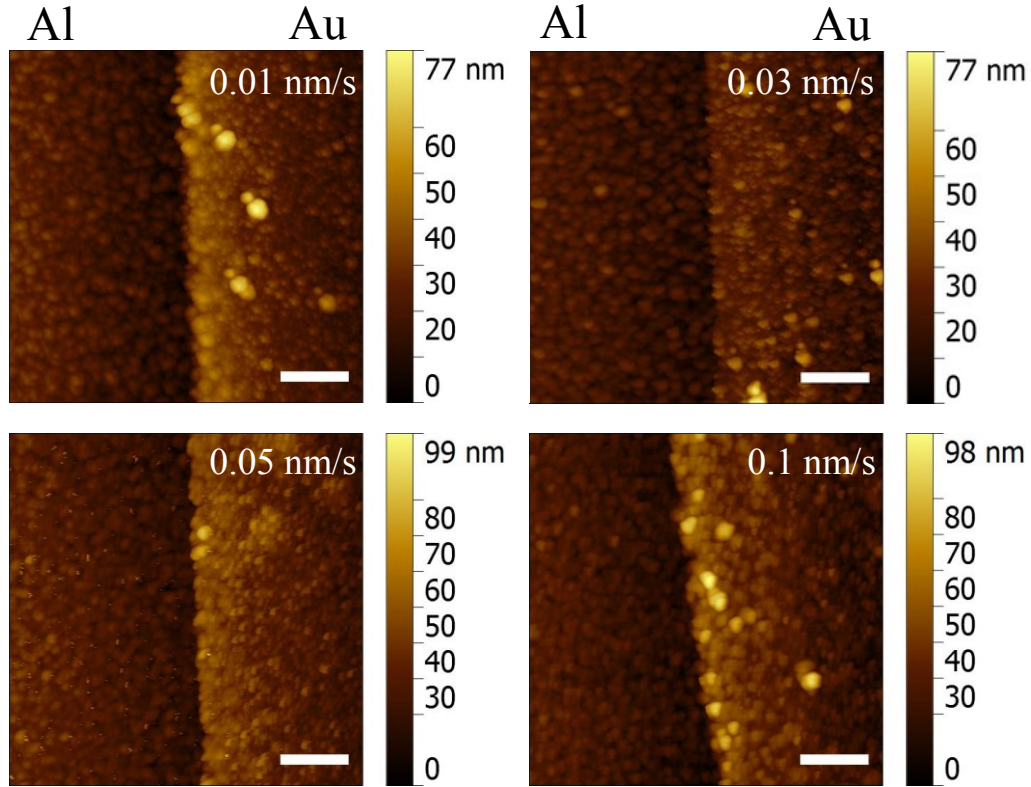


Figure 4.12: AFM topography images of the nanogap electrodes created using varying Au deposition rates with Al deposition rate kept at 0.1 nm/s for the 5 nm adhesion layer and Al electrode. Scale Bars: 200nm.

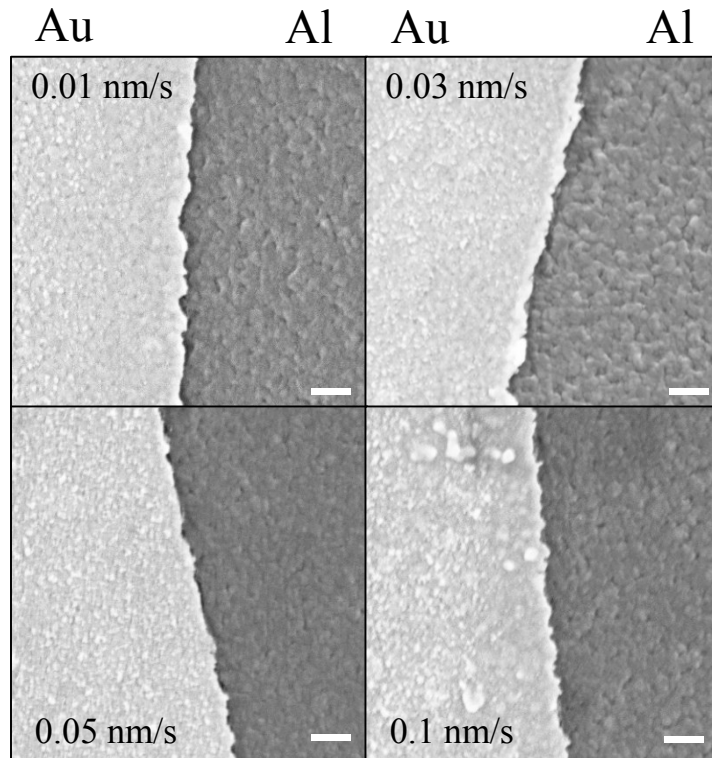


Figure 4.13: SEM micrographs of nanogap electrodes created using varying Au deposition rates with Al deposition rate kept at 0.1 nm/s for the 5 nm adhesion layer and Al electrode. Scale Bars: 200nm.

Kelvin Probe measurement were also carried out to show the effect of the deposition rate on the WF of the metal. As stated previously, this is a very surface sensitive technique where often absolute values are not taken, with the trend or change between the values seen as more significant/accurate. Figure 4.14 shows a clear linear trend of decreasing WF with increasing evaporation rate. As shown in the previous section, this decrease can be caused by a reduction in grain size and higher surface roughness. The AFM and SEM images show little grain size change, this could be due to an increase in roughness on the macro scale as the deposition rates increased. Kelvin probe is a macro scaled technique so the WF is measured across a large area of the thin film as compared to the nanogap area, which may have a higher roughness then the imaging techniques show.

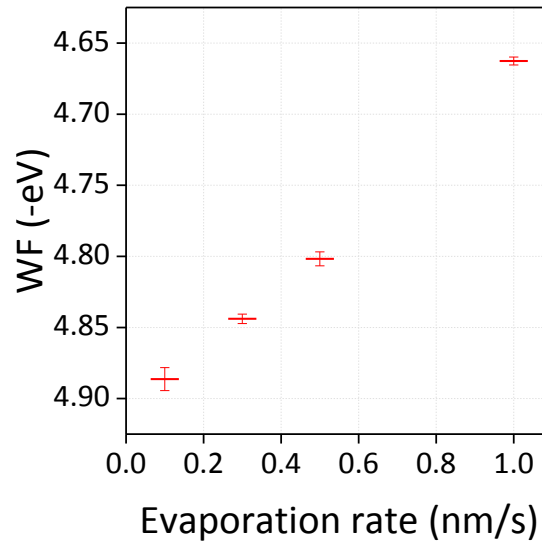


Figure 4.14: Kelvin probe measurement of the WF of Au at varying deposition rates.

Devices were then made using ZnO as the active material as in the previous section. The semi-log I-V plot (Figure 4.15A) shows the electrical characteristics of 15 devices for each deposition rate with uniformity appearing to increase with increasing deposition rate. The RR of each device for the separate deposition rates has been plotted (Figure 4.15B) and it can again be seen via the linear trend fitted that there is less variation in the higher deposition rates most likely due to the increased uniformity of the gap. The WF changes of the Au are also likely to affect the device performance, as it will change the Schottky barrier formed between the ZnO and the Au. Theory suggests that a decrease in Au WF should decrease the Schottky barrier between the Au and ZnO, which in turn causes a decrease turn on voltage. This however is not

seen in the devices as the turn on is at 0 V for all devices suggesting that other factors are more influential on device performance.

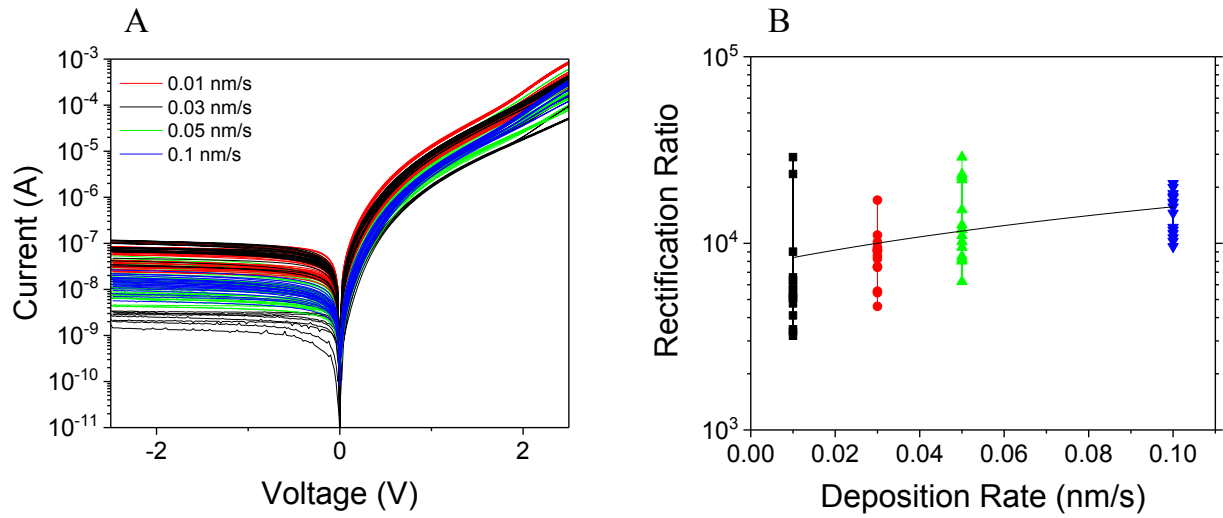


Figure 4.15: (A) I-V plot of ZnO a-Lith diodes with 15 devices for each different deposition rate of Au. (B) Comparison of rectification ratios at ± 2.5 V for each deposition rate.

4.4.2 Metal Thickness

Increasing thickness of the metal electrodes in planar diode devices is known to increase device performance due to increased electrode area, causing more current to be injected and on/off ratios to increase [162], [163]. This increase in performance is relevant for many different types of a-Lith produced devices but the effect of this thickness enhancement on the nanogap needs to be investigated. Increasing metal thickness in the a-Lith procedure is expected to enlarge the nanogaps as it will cause the cohesion and adhesion forces in the process to change. Previous reports have shown that adhesion energy decreases with film thickness, allowing easier delamination of the thin films from a substrate [145][164]. For a-Lith, as the M2 thickness is increased, cohesion forces will increase affecting the gap size. This means as M2 is fractured at the interface of M1, more force will therefore be needed to fracture it. As M1 gets thicker it is expected height change will affect how the fracture of the M2 occurs also affecting the formation of the nanogap. In this section height changes in both metals simultaneously and variations in just one metal are investigated.

2.1.1.3 Changes in both metals

First both M1 and M2 thickness were varied together. A-Lith substrates with 40, 60, 100 and 120 nm Al and Au electrodes were created by varying the deposition time of the thermal evaporator. For experimental control deposition rates were kept the same for each evaporation; 0.1 nm/s for Al and 0.05 nm/s for Au with all devices processed on the same day under the same conditions. AFM topography images of the nanogaps (Figure 4.16) show a large increase in the gap size as the thickness of the metals increases. Ten line scans, extrapolated from the topography images and placed at random across the nanogap, have been taken across each set of nanogap electrodes. From these line scans, an average gap size for each electrode thickness has been estimated. For the 40 nm thickness electrode a nanogap width of >30 nm (resolution of AFM) is seen. This is the normal device thickness used in the a-Lith process, and has been shown in multiple instances to create nanogaps ~15 nm in width. The 60 nm thickness has a nanogap width of 60nm, the 100 nm thickness a width of 80 nm and 120 nm thickness an average width of 90nm, confirming that as the thickness of the metals is increased, the average gap size increases.

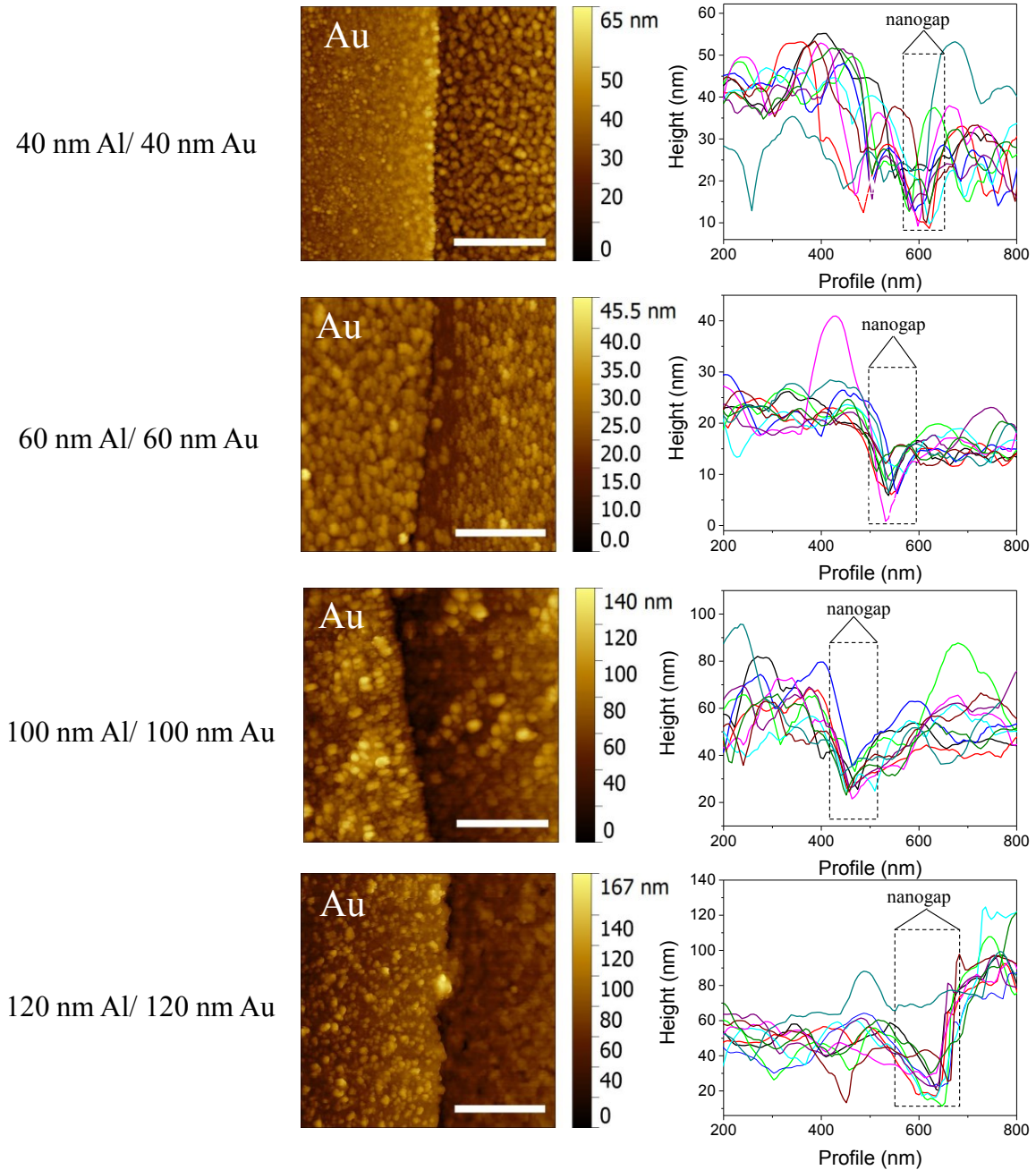


Figure 4.16: AFM topography images and line scans of Al/Au nanogap electrodes created via a-Lith with 40 nm, 60 nm, 100 nm and 120 nm electrode thickness. Scale bar 1 μ m.

To further analyse the nanogap electrodes, SEM micrographs of the different thicknesses have been taken (Figure 4.17) corroborating that there is a widening of the nanogap as the thickness of the metals is increased with more non-uniformity in the thicker devices. This non-uniformity is most likely due to the increased force used to fracture the Au from itself due to larger cohesion forces in thicker films. Fracture and adhesion, however, are complicated to describe using only one factor and other features will influence nanogap formation. Another

characteristic that may affect this are grain sizes of the metal which have been shown to increase with increasing thickness [165] and which has been shown in previous sections to affect nanogap formation. Controlling grain size via deposition rate but increasing thickness could be another experiment to further this study but is beyond the scope of this thesis.

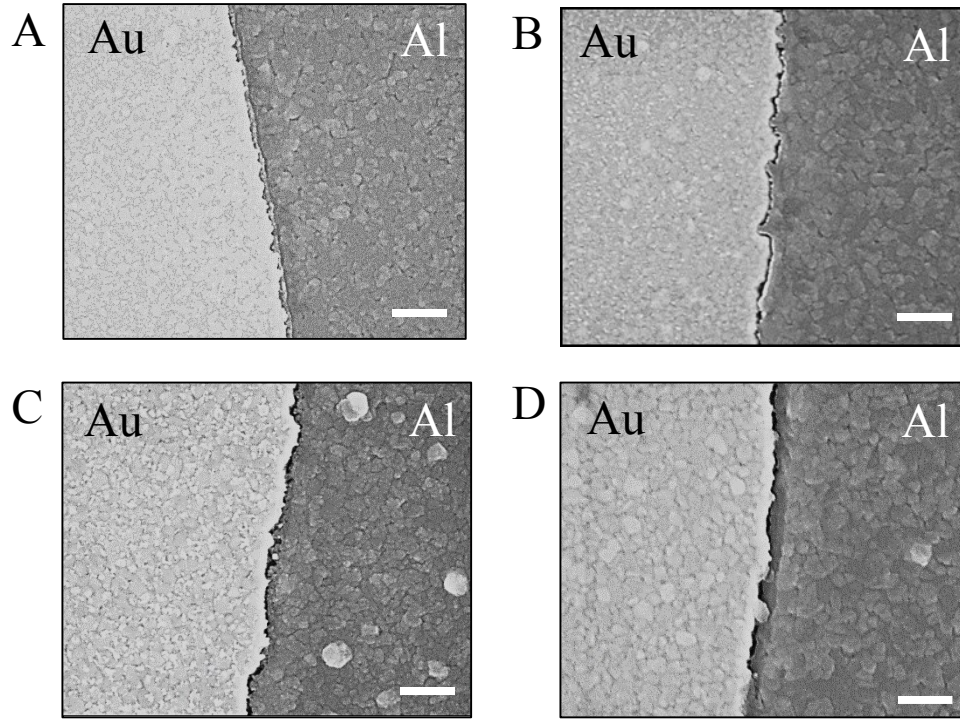


Figure 4.17: SEM micrographs of nanogap electrode created via a-Lith with (A) 40 nm, (B) 60 nm, (C) 100 nm and (D) 120 nm Al and Au thicknesses. Scale bars: 300 nm.

To see how this gap size change would affect device performance, devices were created from these varying thickness substrates. This was achieved by thermally evaporating C_{60} on top of the substrates and measuring the devices in nitrogen to allow for greater control over the thickness of the semiconducting layer for each electrode thickness. It would be expected that if the nanogap size stayed constant, as the thickness of the metals increased the current of diode devices would also increase linearly due to a larger area electrode for increased current injection from the electrodes. The semi-log and linear I-V plots of 5 devices for each thickness show (Figure 4.18A and B) there is, however, little change in current for the increased thickness devices. This suggests that the change in gap size is affecting the device current, with the thicker devices having a reduction in expected current due to the increased gap size. The reverse current, on average, is also not affected by the increasing electrode thickness. Something that must be taken into consideration with these measurements and the use of evaporated semiconducting materials is whether the material is filling the nanogap or simply sitting on top

of the electrodes, this could affect the device characteristics i.e. current maximum. To further explore this one could take multiple TEM images across the nanogap for each electrode height, to analysis the extent to which the evaporated material fills the nanogap.

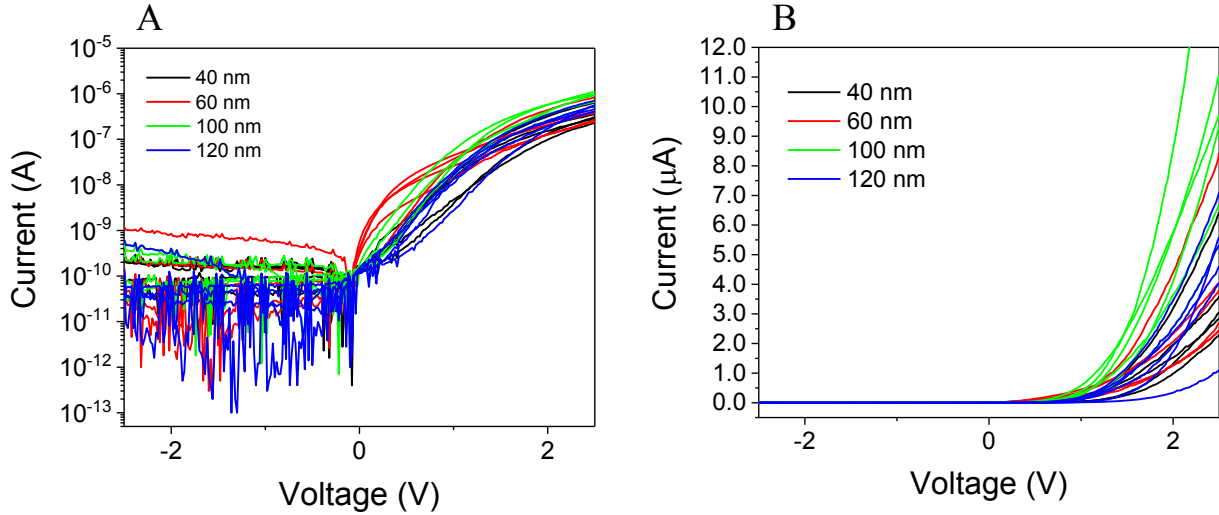


Figure 4.18: (A) Semi-log and (B) Linear plots of C₆₀ a-Lith diodes with 40nm, 60nm, 100nm and 120nm Al and Au thickness electrodes.

2.1.1.4 Changes in the first metal

To understand the a-Lith process more thoroughly height changes in just the first electrode have been carried out. Here the thickness of the second metal (Au) was kept constant at 40 nm whilst the first metal was varied at 40, 60, 100 and 120 nm. Again AFM scans were taken and 10 line scans have been extrapolated from the topography images (Figure 4.19). The average gap size for increasing thickness is >30nm (AFM resolution limit), 80nm, 90nm, 100nm respectively. The average gap size has increased for each metal thickness as compared to the samples where the thickness were kept the same for both metals. This suggests that as the thickness of the first metal increases, the second metal is placed under greater strain causing it to fracture under more force and creating larger nanogaps.

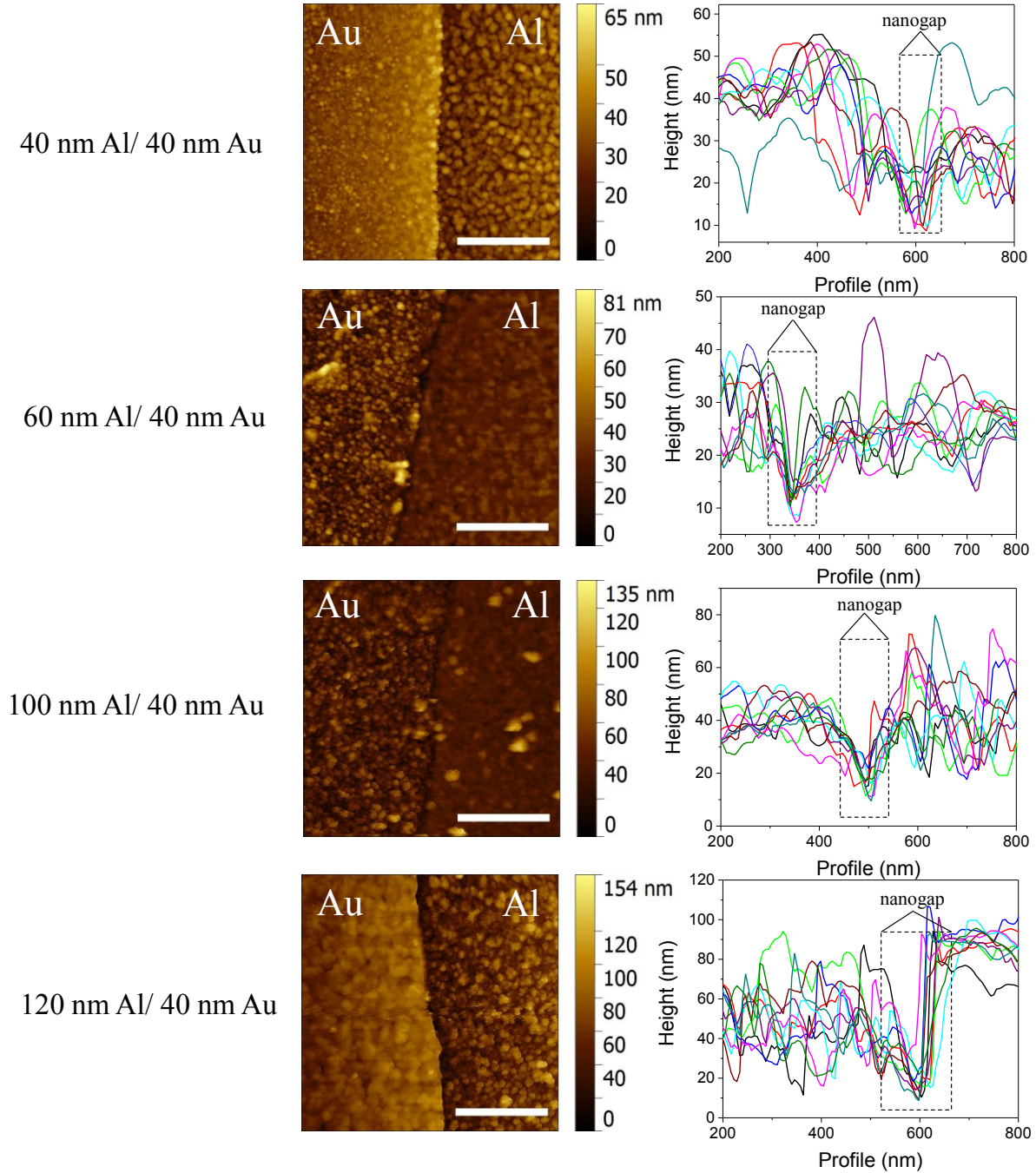


Figure 4.19: AFM topography images and 10 line scans of each nanogap electrode created via a-Lith with 40 nm, 60 nm, 100 nm and 120 nm Al thickness and the Au held at 40 nm thickness. Scale bar 1 μ m.

Again SEM micrographs of the different thickness electrodes were taken to further analysis the nanogap (Figure 4.20). They show a widening of the gap as the thickness of the metals is increased with the gaps larger even when compared to the a-Lith samples with matched thickness (section 4.3.2.1.) The thicker devices are also a lot less uniform, with the gap size varying greatly for the thicker Al devices. This is most likely due to the adhesion forces at the

interface decreasing for the Au, as the thickness is increased. The Au would also be under a lot more strain due to the increased thickness of the Al. Both of these factors will result in more of the Au fracturing off the surface of the substrate. The SEM images also suggest an increase in grain size as the Al thickness is increased.

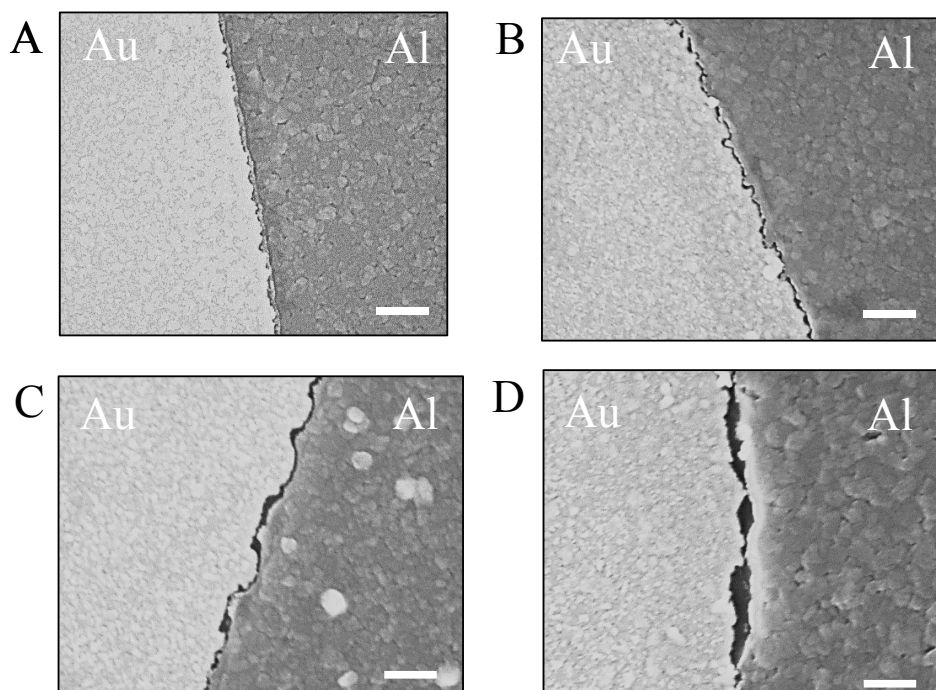


Figure 4.20: SEM micrographs of nanogap electrode created via a-Lith with (A) 40 nm, (B) 60 nm, (C) 100 nm and (D) 120 nm Al thickness and Au at a constant 40nm thickness. Scale bars: 300 nm.

2.1.1.5 Changes in the second metal

Here the thickness of the first metal (Al) was kept constant at 40 nm and the second metal (Au) varied at 40, 60, 100 and 120 nm by increasing the deposition time of the thermal evaporation. The deposition rates were kept constant at 0.1 nm/s. As the thickness of the second metal becomes greater than the first there is a failure in the a-Lith procedure. Figure 4.21A, the 60 nm Au sample, shows that the Au has mainly been removed but there is noticeable overlap of the Au on the Al at the interface between the two metals. . Even in the areas where the gold has removed from the Al surface clear overlap of the Au on the Al can be seen This increases for the 100nm Au thickness (Figure 4.21B) with more gold left on the surface and worsens again for the 120 nm Au thickness (figure 4.21C) where a lot of Au is left on the surface with little fracture at the Al/Au interface. This lack of Au removal is due to the strengthening of cohesion forces of the Au as the thickness is increased. The lack of a large enough step change at the Al

interface, may also decrease Au cohesion forces and increase Au stress at the metal interface, reducing the likelihood of Au thin film fracture. This study shows the importance of matching the thickness of the two metals for successful nanogap formation. If the thickness of the second metal deviates too high above the first, metal devices created using a-Lith will very likely be shorted.

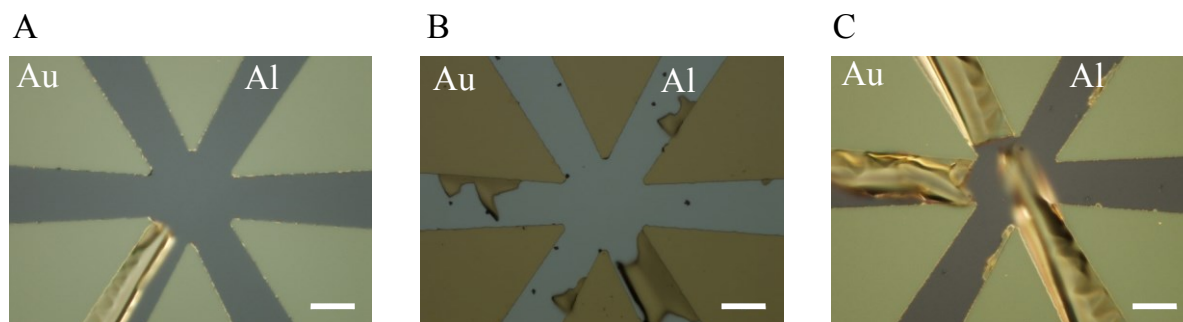


Figure 4.21: Optical micrographs of a-Lith electrodes with a thickness of 40 nm for the Al and (A) 60 nm (B) 100 nm and (C) 120 nm for Au. Scale bar: 20 μm .

4.5 Adhesion Lithography on Plastic

Creating asymmetric nanogap electrodes on traditional ridged substrates has become facile, it is however difficult to then repeat this process on plastic with the same success rate. This is due to the worsening of properties such as adhesion and wettability on plastic substrates for deposition of materials. PET is a polyester based plastic that has been used in industrial applications for decades, with PET metallised by Al used in the packaging and semiconductor industries with much investigation into the nature of thin film metal deposition onto the PET surface [166]. Previously literature has shown that annealing the PET films can increase the adhesion of metals onto the surface at temperatures greater than 100°C. This is possibly due to the recrystallization of the PET as it is heated past its glass transition temperature (T_g) of $\sim 81^\circ\text{C}$ [115], [167], [168]. Using an annealing step to increase the adhesion of the second metal in the a-Lith process was investigated to see if it could improve the quality and yield of nanogap electrodes on PET substrates.

Al (40 nm) was deposited on a PET substrate (DuPont Teijin Films), patterned using contact lithography and covered in a SAM in the same conditions as previously mentioned for glass substrates (section 4.3) The second metal (40 nm Au with a 5 nm Al adhesion layer) was then deposited onto the substrate. After this the a-Lith samples on plastic were annealed at different temperatures above or around the T_g . The different samples were annealed at 80, 100, 120, 140

and 160°C with one sample going through no annealing step for comparison. This annealing was carried out for 30mins in a N₂ atmosphere. Glue was then applied on top of the substrates, dried and then peeled off as is the standard a-Lith procedure. As the temperature is increased the a-Lith is more successful as displayed in the photographs presented in Figure 4.22. For the none annealed sample and the sample annealed at 80°C the a-Lith totally fails with the second metal being complete removed from both the Al and the substrate by the glue. The first metal (Al) is also slightly damage showing a reduced adhesion of the Al on PET as compared to glass. With the annealing temperature increased to 100°C there is partial success with the Au sticking to some areas of the substrate but in a non-uniform way with many defects and large gaps between the two metals. The first metal has again been damaged indicating there is still poor adhesion to the substrate. From 120°C the a-Lith electrodes have almost fully stuck to the surface with only a few defect seen. The annealing at 140°C improves on this with the Au remaining on all of the electrode spaces. This again is more successful at 160°C however, at this temperature the substrate starts to deform meaning for future tests 140°C seems to be the ideal temperature to use. This test was repeated on multiple substrates with repeated increase of adhesion at higher temperatures between the thin film metal layers and the PET substrate. Annealing of PET films is a successful way of improving the a-Lith success rate on flexible films and opens up many more device applications for the a-Lith procedure.

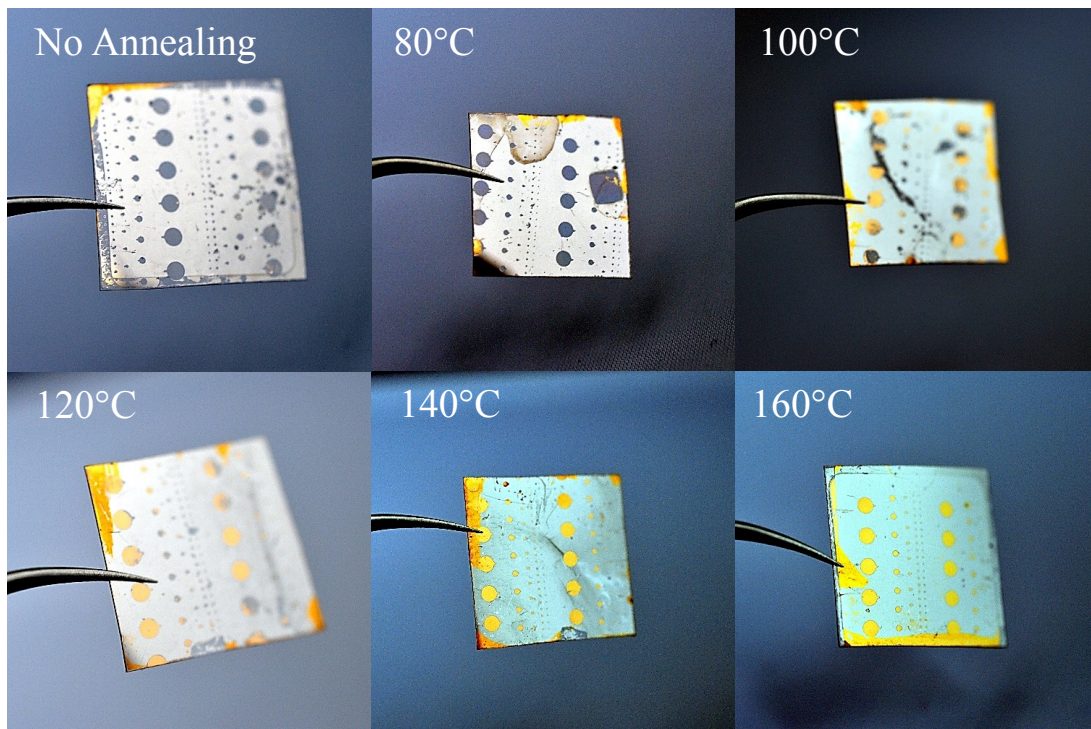


Figure 4.22: A-Lith on PET films of 25 mm x 25 mm with different annealing steps after the deposition of the second metal to see the effect of temperature on electrode formation.

4.6 Conclusions

This chapter presented further optimisation of the a-Lith technique with more control of the fabrication of the nanogap between the electrodes by controlling the deposition rate of the metals. Varying the deposition rate of the first metal (Al) from 0.01 nm/s to 1 nm/s showed that faster deposition rates decreased the Al grain sizes and reduced the roughness of the Al thin film by over 1 order of magnitude from 16 to 1 rms roughness. This also had the effect of decreasing WF (a reduction of ~ 0.3 eV) and increasing gap uniformity with increasing deposition rate. When Schottky devices were created using these nanogap electrodes, more variability was seen in devices made with a lower deposition rate. With the variation of deposition rate of the second metal (Au) from 0.01 nm/s to 0.1 nm/s, there was little change in grain size and roughness possibly due to the influence of the Al adhesion layer. The WF of the metal, however, decreased with increasing deposition rate. With a reduction of over 0.2 eV for the highest and lowest deposition rates. The uniformity of the gap was also affected which was increased with deposition rate. Again, when devices were created, those produced with the higher deposition rate had less variability when comparing RR. These changes are most likely due to increased thin film adhesion for higher deposition rates, causing higher quality nanogap formation.

The effect of change in thickness of the metals between 40 nm to 120 nm on the nanogap was also investigated. First both metals were varied simultaneously with the gap size increasing with increasing thickness. The gap size increased from ~ 15 nm for the 40 nm electrodes to ~ 90 nm for the 120 nm electrodes. This was further confirmed when diodes were made using the nanogap electrodes created and the current did not increase with increasing thickness which would be expected if the nanogap remained consistent. The first metal was then varied from 40 nm to 120 nm with the second metal kept at a constant 40 nm thickness. This caused the gaps to increase further in comparison to the matched thickness electrodes. This is due to increased stress and fracturing of the thin second metal across the thicker metal layers. Next the first metal was kept constant and the second metal was varied. Here, when the thickness of the second metal was greater than that of the first, the fracturing of the metal was not successful and the nanogaps were not properly formed. Residual Au remained on top of the Al and bridged the nanogap causing shorts across the electrodes.

Last the a-Lith process was optimised on PET films. There has been previous success with different plastic substrates but these results are inconsistent, with very low yield even just on a single substrate. To improve this, the PET was heated before the final peel stage, this allowed for greater adhesion between the second metal and substrate. From 120 °C the adhesion improved to create electrodes, 140 °C provided better adhesion with smaller gap sizes as did 160 °C but this higher temperature began to deform the PET. This preliminary investigation indicates that heating the PET substrate will allow for an increase in yield of nanogap electrodes created via a-Lith on flexible substrates.

Future work on optimisation of the a-Lith procedure should include using other metal deposition techniques (such as sputtering) to investigate if nanogap uniformity can be further improved. Exploring other patterning techniques for the first metal such as nanoimprint lithography would allow for necessary up-scaling of the technique. Future optimisation at larger thickness of the metals is also needed so variation in height does not cause disparity in gap size, this requires more in-depth study of the fracture mechanics and adhesion forces at the nanogap interface. Lastly more development of the technique on plastic substrates to increase yield and allow for repeatable device fabrication would open up a vast number of device applications.

Chapter 5

Nanogap Based Photodetectors

5.1 Introduction

Alternative fabrication techniques for photodetectors have been of interest since the advent of solution processed semiconductors. These allow for not only cheaper manufacturing technologies but also novel applications including the use of flexible substrates for conformable sensors. The development of new materials further permit wavelength specific devices without the need for expensive filters. Easy tuning of the band gap means photodetectors can be produced that can detect specific wavelengths across the UV-Vis-IR region of the electromagnetic spectrum (Figure 5.1).

Due to the unique simplicity of the technique, a-Lith can create large-areas of nanogap electrodes that allow for high performance devices. Early research presented on photodiodes using P3HT:PCBM blends shows the asymmetric electrodes acting as photodiodes not photoconductors; this allows for greater change in photocurrent due to reduced dark currents [105]. Additionally the low dimensionality of these electrodes should create high sensitivity devices. Fabrication of asymmetric nanogap electrodes in conjunction with high performance solution processed materials, means that the wavelength absorption of the device can be tuned

simply by depositing a specific material on top of the a-Lith electrodes, indicating the versatility of the technique to create photodiodes for extensive applications.

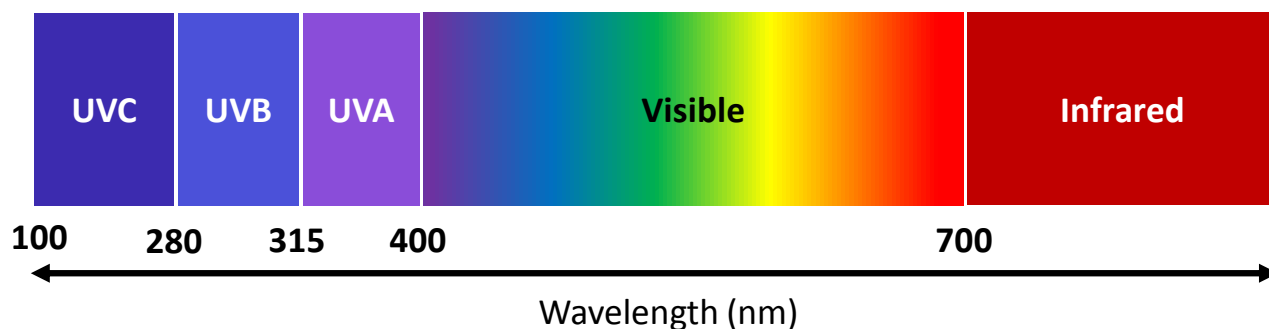


Figure 5.1: Schematic of UV-Vis-IR sections of the Electromagnetic spectrum.

This chapter presents numerous applications possible when applying a-Lith to the fabrication of photodetectors. Different groups of materials were explored for a variety of purposes including deep ultraviolet (DUV), ultraviolet (UV) and visible photodetectors. First, copper (I) thiocyanate (CuSCN), normally used as a hole transport layer, is used to create DUV photodetectors and compared to other high performance detectors. Solution-processed zinc oxide (ZnO) is then explored as a UV photodetector. Finally, high efficiency poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-co-3-fluorothieno[3,4-b]thiophene-2-carboxylate] (PTB7-Th) is investigated for visible light photodetectors as a Schottky photodiode and a donor in a bulk heterojunction structure with [6,6]-Phenyl-C71-butyric acid methyl ester (PC₇₁BM.).

5.2 A-Lith Deep Ultraviolet Photodetectors

This section explores solution-processed low temperature DUV photodiodes produced via adhesion lithography and the wide bandgap (WBG) DUV absorbing material CuSCN. The combination of this novel architecture with the attractive properties presented by this photoactive material results in low dark currents, high responsivity and extremely sensitive DUV photodetectors. More specifically, illumination of the fabricated devices with 280 nm, 390 nm and visible (400-700 nm) light LEDs demonstrates their visible-blind nature. Furthermore, variation of the device width from 1 cm to 10 cm, which is facilitated by this highly versatile technique, allows increased photocurrent in the photoconductive state (for the longer widths), whilst retaining the low dark current. These results pave the way to fabrication

of high performing flexible photodetector devices as both a-LiH and CuSCN processing are fully compatible with plastic substrates.

5.2.1 Background: Deep UV Photodiodes

Deep ultraviolet (DUV) photodetectors have many commercial applications, such as chemical and biological analysis and monitoring, optical communications and flame detection [169]. These often require visible-blind detectors showing high sensitivity as well as increased stability and reproducibility (visible blind detectors do not absorb light from the visible spectrum). Current research on DUV photodetectors is based mainly on inorganic materials, such as silicon carbide (SiC) [170][171], diamond [172][173], gallium nitride (GaN) [12] and gallium oxide (β -Ga₂O₃) [174]–[180]. To increase device performance a recent report also uses intermediate band structure semiconductor Bi_xSn_{1-x}O₂ to increase responsivity while decreasing dark current values. This does, however, decrease the visible-blind nature of the device [181]. Although these devices are characterised by high performance and are suitable to be applied in harsh environments, they often require laborious fabrication processes; which renders them impractical for lower cost applications. To address this challenge, some studies on organic materials, which are known for their ease of processing, have also been reported. For example, N,N-bis(naphthalen-1-yl)-N,N-bis(phenyl)benzidine (NPB) with bis(2-methyl-8-quinolinolato) (4-phenylphenolato) Al (BALq) [182] and 4,4',4''-tri-(2-methylphenyl phenylamino) triphenylamine (m-MTDATA) with 4,7-diphenyl-1,10-phenanthroline- (bathophenanthroline) (Bphen) [183] have been employed in organic photodetector (OPD) devices. These devices not only rely on thermal evaporation of the active layers but also exhibit moderate device performance. Fully or partially solution-processed devices, i.e. compatible with printing technologies, have been demonstrated based on sodium tantalate (NaTaO₃) [184], NaTaO₃ with 1,3,5-tri(m-pyrid-3-yl-phenyl) benzene (TmPyPB) [185] and graphene quantum dots [186], however their performance cannot compete with the non-printed devices. Table 5.1 summarises some performance characteristics of DUV photodiodes based on the above mentioned materials and the values obtained in this study.

Material	Deposition	Device type	Wavelength (nm)	Intensity (mW/cm ²)	Responsivity A/W	Voltage (V)	T _R	Ref
Silicon Carbide	Laser plasma	MSM	250	2	0.18	10	90 s	[171]
βGa ₂ O ₃ /diamond-	CVD	MSM	240	n/a		16	>0.3 s	[173]
GaN	CVD on GaN wafer	planar pin diode	280	n/a	0.15 at 0 V	0-92	1 μs	[13]
β-Ga ₂ O ₃ nanowires	CVD	MSM	254	0.07	377	10	1.20 ns	[175]
ZnO-Ga ₂ O ₃ core-shell microwires.	CVD and FIB	MSM with In and Ti/AU electrodes	254	1.67	3000	6	20 μs	[176]
β-Ga ₂ O ₃ /SiC	Thermal evaporation on SiC wafer	Sandwich	210-260	40	0.07-0.04	2	ms	[177]
β-Ga ₂ O ₃ /NSTO	sputtering	Sandwich	254	0.045	43	10	0.07s	[178]
Graphene/βGa ₂ O ₃	CVD on βGa ₂ O ₃ wafer	Sandwich	254	0.05	39.3	20	94.8 s	[179]
βGa ₂ O ₃	Thermal oxidation	Sandwich	254	2	0.0029	50	1 μs	[180]
Bi _x Sn _{1-x} O ₂	sputtering	MSM	280	0.0008	60	1	3 s	[181]
NPB and Balq	Thermal Evaporation	Sandwich	270	1.35	0.014	12	n/a	[182]
m-MTDATA and Bpen	Thermal evaporation	Sandwich	280	0.428	0.309	8	n/a	[183]
NaTaO ₃	Solution	MSM	260	0.135	0.0415	5	n/a	[184]
TmPyPB/Py-NaTaO ₃ NCs	Solution	Sandwich	280	5	0.02	3	0.22 s	[185]
Graphene Quantum Dots	Solution	MSM with Au and Ag electrodes	254	0.042	0.002	5	64 ms	[186]
CuSCN	Solution	MSM with Al and Au electrodes	280	0.220	79	2	1-50 s	Work from this thesis

Table 5.1: Comparison of DUV photodetectors in literature (Adapted with permission from Wyatt-Moon *et al.* [137] Copyright 2017 American Chemical Society).

Recently, there has been a push for developing flexible sensors for healthcare applications. An application of particular interest is a sunlight sensor that detects UV radiation. There are two bands of UV light that reach the Earth's surface and cause humans' damage: UVA (320-400nm) and UVB (280-320nm). Of these UVB is considered the more harmful, causing not only sunburn but also direct deoxyribose nucleic acid (DNA) damage and therefore potentially leads to cancer [187]. If consumers were able to monitor and reduce their UVB exposure it could help reduce this risk. Devices currently commercially available are based on photochemical cells, where a light catalysed chemical change indicates the extent of UV exposure [188]. These devices are disposable and single-use that are unable to distinguish

between the different UV bands. Although research into reusable electronic devices for this application has been around since the 1990s [189], there has been limited progress. Only in the last few years, has there have increased reports on flexible UV diodes for sunlight detection. Dang et al reported on zinc oxide (ZnO)-nanorod/graphene hybrid field effect transistors (FETs) showing high responsivity and mechanical robustness [190]. However ZnO absorbs strongly in the UVA band and makes no distinction between UVA and UVB which is critical for providing accurate information to the end user. Furthermore, this device was only tested at 365 nm, so its sensitivity to the UVB range is unknown. Another report shows a device based on zinc germanate (Zn_2GeO_4) and indium germanate ($\text{In}_2\text{Ge}_2\text{O}_7$) nanowire mats [191]. These devices also showed high stability under mechanical stress, but due to the use of chemical vapour deposition and the irregular nature of the nanowire mats, is not suitable for large-scale production.

5.2.2 A-Lith architecture in deep UV

From the photodetector device fabrication standpoint, one must take the essential attributes of the different possible architectures into consideration. A device structure commonly used in such optoelectronic applications is a vertical (sandwich) configuration of metal electrodes and active layer(s) (Figure 5.2A). This requires at least one electrode to be transparent to the DUV part of the spectrum, which is not trivial as most available substrates absorb DUV light. A more convenient architecture is the planar metal-semiconductor-metal (MSM) structure, as in this case nanostructured 2D materials can be employed [192], which allow for top illumination of the photodetector (Figure 5.2B). Devices created via a-Lith not only have the benefits of a planar (top-illuminated) structure, but also the use of different work function metals. Additionally the low dimensionality of the nanochannel separating the two electrodes is expected to increase the device performance (Figure 5.2C).

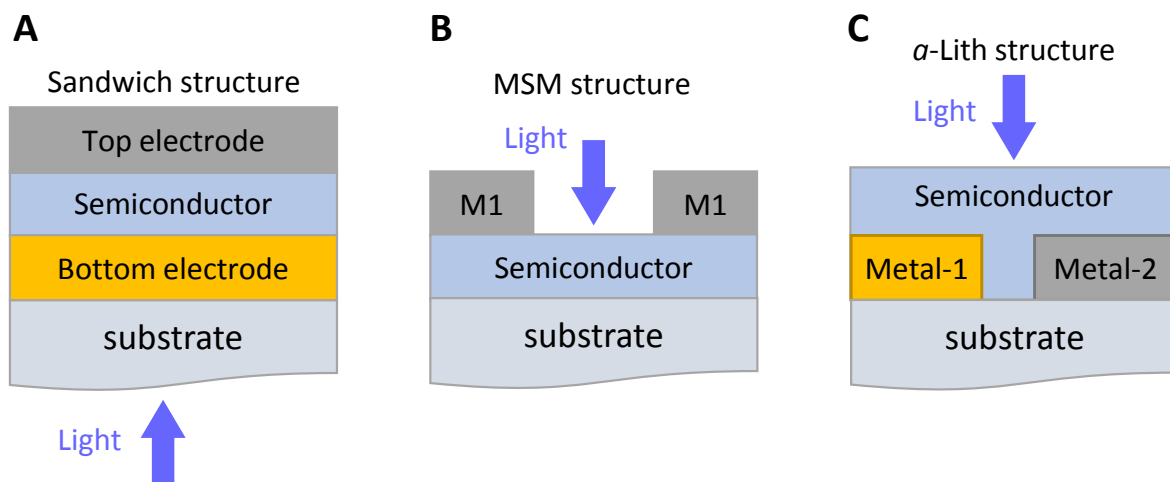


Figure 5.2: Device architectures of typical DUV photodetectors as compared to the adhesion lithography structure: **(A)** sandwich (vertical) structure with bottom illumination through the transparent electrode, **(B)** MSM planar structure, typically used with 2D materials, with symmetric contacts, and **(C)** a-Lith (planar) structure employing asymmetric contacts. (Reprinted with permission from Wyatt-Moon *et al.* [137] Copyright 2017 American Chemical Society).

5.2.3 Copper (I) Thiocyanate

To create UV band specific devices with high performance; that also fulfil the requirements for fabrication on flexible substrates, new materials and device concepts need to be introduced. A good candidate material that has been recently successfully employed in plastic electronics applications is copper (I) thiocyanate (CuSCN) [193]. CuSCN is a wide bandgap (WBG) intrinsic semiconductor material that only absorbs in the deep UV region and can be made p-type by creating an excess of thiocyanate ions [122]. It has recently been used as hole transport layer (HTL) improving the efficiency and stability of organic light emitting diodes (OLEDs) as well as organic and perovskite solar cells [194]–[197]. One of its main attributes is the ease of deposition, as it can be solution-processed from non-toxic solvents at low temperatures (below 110 °C). CuSCN has also been employed along with ZnO nanostructures to form pn heterojunctions for UVA photodetectors [198]–[200] but, to the best of the author’s knowledge, it has never been used as the photosensitive material itself. Moreover, a recent study showed that CuSCN based transistors and inverter circuits coped well under mechanical stress showing further proof of its potential for flexible electronic devices [201].

For the material characterisation and devices presented in this section CuSCN (purchased from Sigma Aldrich) was dissolved in diethyl sulfide (DES) at a concentration of 15 mg/ml and left to stir for 2 hours. The solution was then spin-coated at 2000 rpm for 60 s onto substrates in a dry nitrogen glovebox and subsequently annealed at 110 °C for 15 min. For the photodiodes, a-Lith Al/Au electrodes were placed in the UV-Ozone for 30 min prior to CuSCN deposition. Optoelectronic characterisation was performed using light-emitting diodes (LEDs) emitting at 280 nm at various optical power levels, and at 390 nm, 475 nm, 525 nm and 625 nm at an optical power density of 90 $\mu\text{W cm}^{-2}$. The LED current was controlled with a Keithley 2400 source meter. The spectra of the LEDs were characterised using an Ocean Optics spectrometer and the optical power was calibrated using an optical power meter (PM120V Thor Labs).

CuSCN was chosen as it is a wide bandgap DUV absorbing material. As shown in Figure 5.3A the absorption spectra has an onset of absorption at 315 nm with peaks at 300 and 240 nm. CuSCN was spin coated onto a quartz substrate with the absorption spectrum being calculated from the transmittance of the material with the substrate absorption subtracted. The absorption shows a good overlap with the UVB region of the spectrum, and almost no absorption at UVA, visible and NIR parts of the optical spectrum. These spectral characteristics suggest that CuSCN is an ideal candidate to be implemented in visible-blind photodetectors that operate in the DUV/UVB region.

Tauc plots from the data allow for an estimation of the optical bandgap of CuSCN (Figure 5.3B). Previous reports shows that the nature of the bandgap type is not yet determined and so both direct and indirect calculations were represented by the $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ plots respectively. This shows that CuSCN either has a direct bandgap of ~ 3.6 or an indirect bandgap of ~ 3.9 which is comparable to other results [202][203]. This method does not give a definite answer on the nature of the electronic structure of CuSCN but does demonstrate the wide bandgap characteristics of the material.

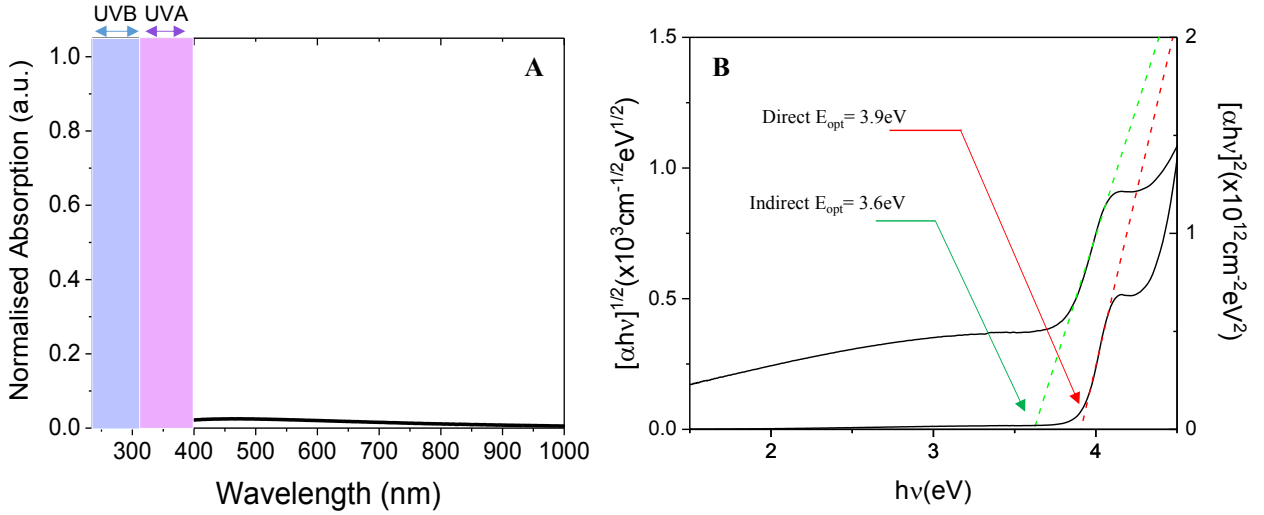


Figure 5.3: (A) UV-Vis absorption and (B) Tauc plots of CuSCN film.

5.2.4 Device structure

The selection of the metal electrodes for the DUV photodetector was based on the band diagram (in a flat band configuration) depicted in Figure 5.4. Taking these results and data for the Fermi level from the literature (5.0-5.1 eV) [199], an Ohmic contact would be expected at the Au/CuSCN interface and a Schottky contact should be formed with the Al electrode due to the large energetic barrier ($\sim 1 \text{ V}$) between CuSCN Fermi level and the Al electrode work function. This means that a Schottky contact is expected to form when employing this particular device structure, which is beneficial for this application as it is expected to lead to low dark currents and high rectification ratio. Note: This of course is assuming idealised values of the work function of the metals and is also assuming bulk like properties of the CuSCN without any quantisation of the energy levels caused by the confinement of the material within the nanogap. The choice of work function values from literature rather than from the previous chapter is due to the kelvin probe values taken in air on unclean samples whereas the devices were created on clean samples with the CuSCN spin coated in a nitrogen atmosphere.

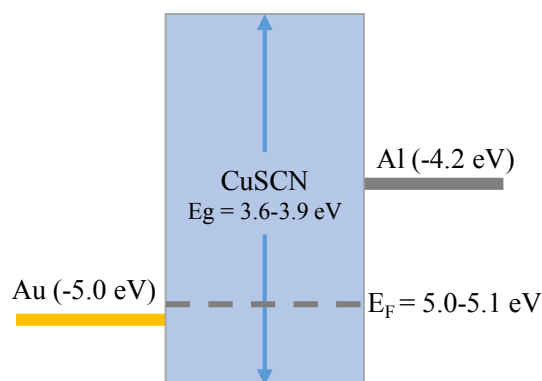


Figure 5.4: Band structure of CuSCN-based photodetectors.

AFM topography images of the CuSCN layers on top of the Al/Au nanogap electrodes (Figure 5.5) show that CuSCN is a nano-crystalline material with an average grain size of 40 nm; this should allow for good transport and charge transport in the a-Lith photodiode. This data only shows the grain structure of the material on top of the gap, within the gap it is perhaps different in structure with smaller grains as the gap will be on average 15 nm and the grain size on top is 40 nm. When spin coated on top of the nanogap electrodes as described above, the CuSCN film covers the electrodes with an indent in the CuSCN just being discerned on top of the nanogap as indicated by the 3D topography AFM micrograph. The layer, however, is continuous with an RMS surface roughness of 4.1 nm.

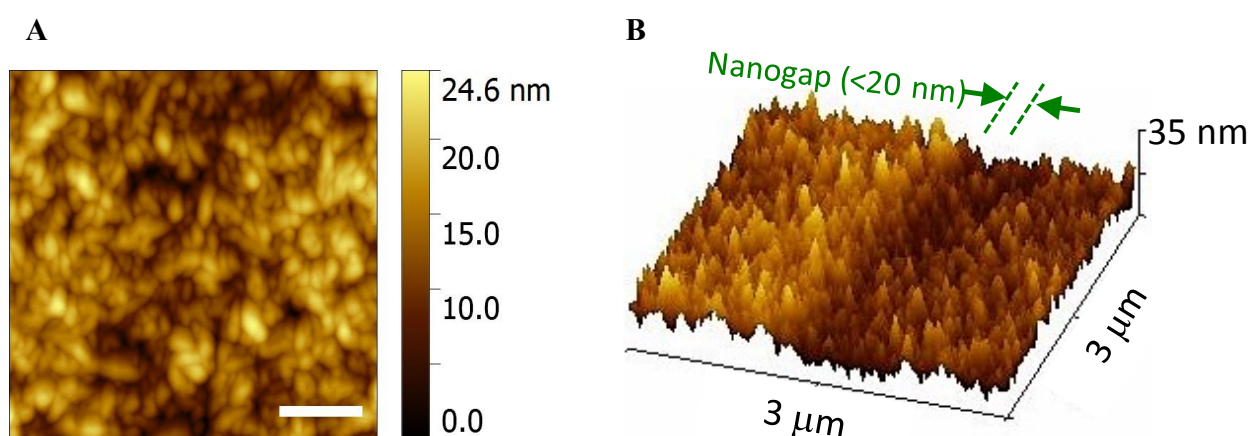


Figure 5.5: (A) 2D 1x1 μm and (B) 3D AFM 3x3 μm topography of CuSCN film spin-cast on top of the adhesion lithography fabricated electrodes. Scale bar: 200nm. (Adapted with permission from Wyatt-Moon *et al.* [137] Copyright 2017 American Chemical Society).

5.2.5 Diode Characterisation

The semi-log plot of the I-V characteristics of the CuSCN diode (Figure 5.6) demonstrates the rectifying nature of the diode exhibiting a turn on voltage of ~ 0.6 V and a high rectification ratio (RR) of near 10^4 at ± 2.5 V for a 1 cm width device. This can be attributed not only to the material properties, but also to the ultra-low dimensionality and the co-planar architecture of the metal electrodes, which help minimise the series resistance [138]. The turn on of the device is expected to be affected by the barrier formed at the Furthermore, the low reverse dark current of this diode, the value of which reaches the limits of the measurement setup, confirm the Schottky contact formation between Al and CuSCN. The Au/CuSCN contact allows current to flow under bias confirming its Ohmic nature. High performance can be achieved using this material due to the unique nature of a-Lith; no other research found uses CuSCN as the active material in diode or photodiode devices.

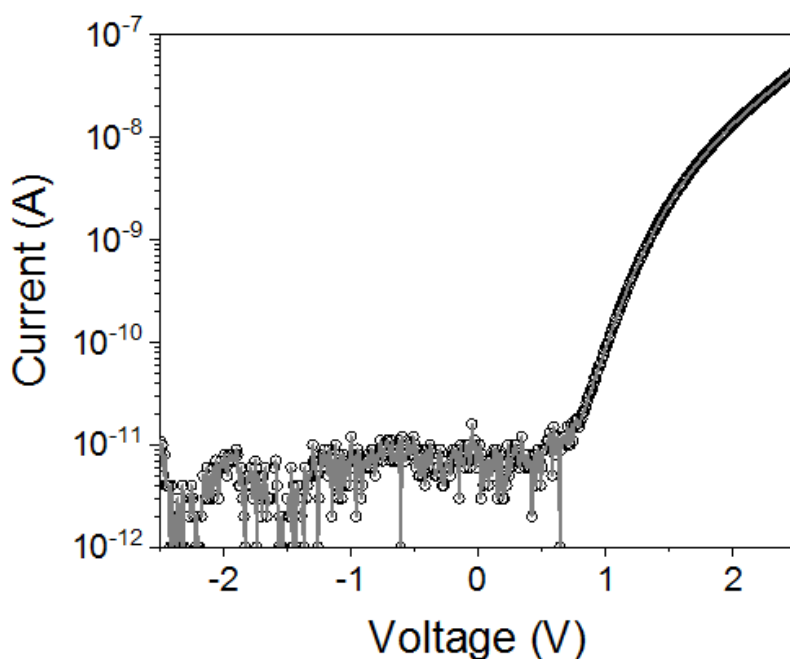


Figure 5.6: Semi-log I-V plot of CuSCN diode. (Adapted with permission from Wyatt-Moon *et al.* [137] Copyright 2017 American Chemical Society).

5.2.6 Photodiode Characterisation

To analyse the DUV photodiode characteristics, devices were illuminated with the 280 nm emitting LED at an optical power density of $220 \mu\text{Wcm}^{-2}$. Figure 5.7A shows that the current

at -2 V is increased over 3 orders of magnitude, as compared to the dark current. This high on-off ratio proves the high DUV photodetecting ability of these devices, with charge separation occurring even though this is a Schottky photodiode with only one active material. This is due to the nanoscale device width, allowing the depletion region of the device to fully cover the device area facilitating charge separation (see section 2.3.3.1 for more info). The device also increases in photocurrent in the forward direction, although this can be attributed to the length of time the device takes to return to ground state. The time response of the CuSCN photodiode is depicted in Figure 5.7A with the 280 nm LED switched on for 25 s to allow for saturation of the photodiode, before being allowed to relax to ground state. A rise time of 1 s can then be derived but the fall time is significantly slower with the initial drop in current taking ~30s. This response speed is not as high as other reported devices (see Table 1). This slow speed accounts for the shape of the I-V characteristics and is most likely caused by defects within the active material. The response could also be due to ionic transport within CuSCN, as ions are usually associated with slow response speeds and large device hysteresis.

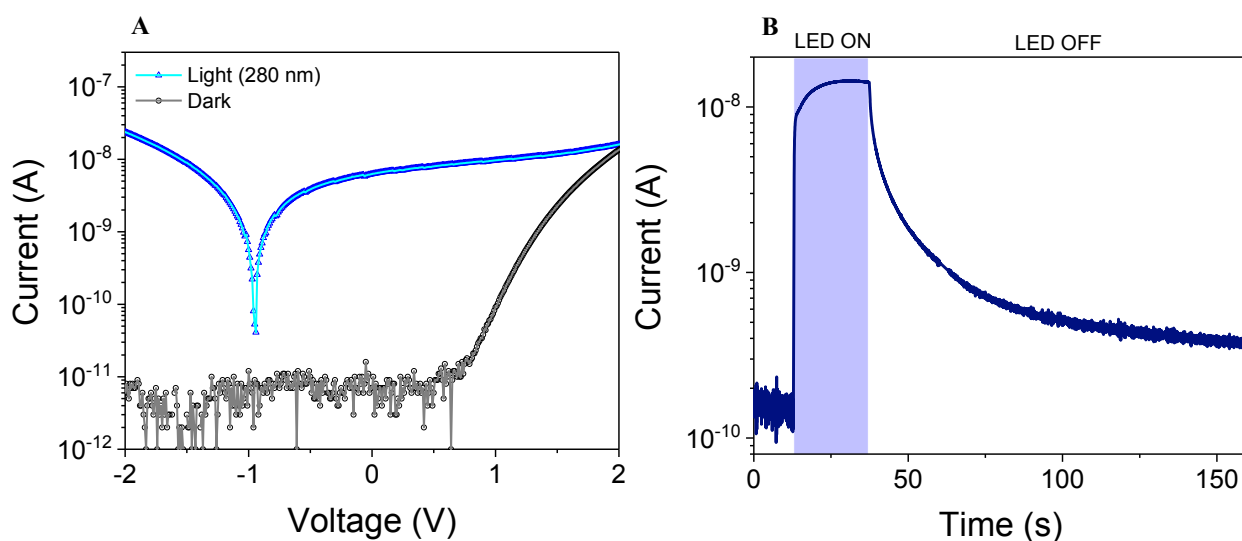


Figure 5.7: (A) Semi-log I-V plot of CuSCN photodiode in the dark and under illumination at 280 nm with optical power density of $220 \mu\text{W cm}^{-2}$. (B) Time response of CuSCN photodiode after illumination for 25 sec under same conditions as in (A) and biased at -2 V. (Adapted with permission from Wyatt-Moon *et al.* [137] Copyright 2017 American Chemical Society).

To further characterise the a-Lith photodiodes, the values of two commonly employed figures of merit, namely responsivity (R) and photosensitivity (PS), were calculated. The calculation of these parameters is fully described in section 2.3.3, with R dependent on device area, calculated by taking the product of electrode separation, estimated at ~ 15 nm, and the device

width (w) (here $w = 1$ cm). The devices presented in Figure 5.7A have an $R = 79$ A/W and $PS = 719$. These values are very high compared to existing devices and, to the best of our knowledge, have only been surpassed by two other reported devices that were fabricated using comparatively complicated techniques such as chemical vapour deposition (CVD) [176], and CVD with focused ion beam milling (FIB) [177] (see also Table 5.1). One of the main reasons for the high responsivity is likely the small illumination area and low dark currents due to the unique nanogap electrodes created by a-Lith.

Figure 5.8 shows the photocurrent at -2 V bias under 280 nm illumination at various optical power densities. The log-log plot shows a square root dependence of the current on the optical power. This is mostly likely due to trapping, recombination and electron-hole generation within the semiconductor [175][204]. This data also shows the extreme photosensitivity of the a-Lith photodiode even at a low optical power density of $0.2 \mu\text{W cm}^{-2}$ (with a value for PS of ~ 7) where light can be detected with over an order of magnitude difference to the dark current. This extreme sensitivity to low power light is attributed the low dimensionality of the a-Lith structures allowing for even the smallest change to be detected.

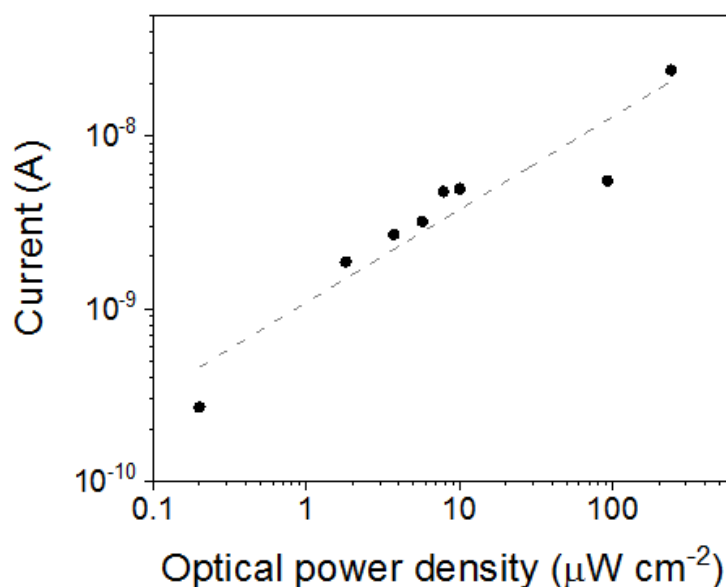


Figure 5.8: Photodiode current at different optical power density levels for illumination at 280 nm with the diode biased at -2 V. (Adapted with permission from Wyatt-Moon *et al.* [137] Copyright 2017 American Chemical Society).

Subsequently, to confirm the wavelength specific sensitivity, the photodiode was illuminated with LEDs emitting at different wavelengths but at the same optical power of $90 \mu\text{W cm}^{-2}$.

When placed under illumination from the wavelengths in the visible region (470 nm, 522 nm, and 630 nm), the diode characteristics remained unchanged and were identical to the dark I-V curve omitting measurement equipment variation (Figure 5.9A). This confirms that these photodiodes are visible-blind, as expected upon employing the WBG semiconductor CuSCN as photoactive material. Under 390 nm illumination, however, there is a slight change in the I-V characteristic, with the responsivity increasing an order of magnitude as compared to the device under visible light illumination. CuSCN has been reported to have a transmittance of 86% at 390 nm compared to $> 90\%$ for wavelengths above 450 nm [203]. The optical absorption at this wavelength could be dramatically enhanced when light passes through a nanogap between two metals filled with a light absorbing semiconducting material due to resonant excitation of the fundamental field-symmetric surface plasmon-polariton (SPP) mode supported by the metal slit (nanogap) [205][206]. Thus, a conceivable explanation for the photoresponse at 390nm could be that the SPP effect caused by the Au/Al interdigitated nanogap structure enhances the absorption of photons with a wavelength of 390 nm, followed by an indirect transfer of carriers from the photoexcited bands of the metal to the conduction band of the semiconductor. Direct creation/injection of charge carriers in the CuSCN cannot, however, be ruled out [207]. Further detailed spectroscopic characterisation is needed to substantiate this.

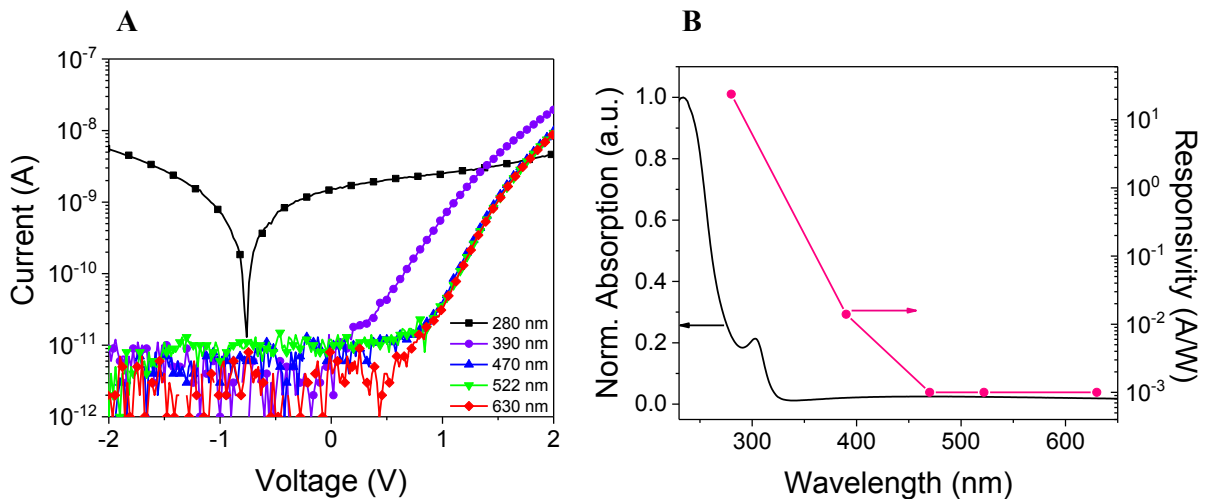


Figure 5.9: (A) Semi-log I-V plot of CuSCN photodiode under different illumination wavelengths: 280 nm, 390nm, 470 nm, 522 nm, and 630 nm at the same optical power density ($90 \mu\text{W cm}^{-2}$). (B) UV-Vis absorption spectrum and spectral responsivity at $90 \mu\text{W cm}^{-2}$ with the diode biased at -2V, confirming the visible-blind nature of CuSCN-based photodetectors. (Adapted with permission from Wyatt-Moon *et al.* [137] Copyright 2017 American Chemical Society).

5.2.7 Scaling the Size of CuSCN Photodiodes

An attractive feature of a-Lith is the wide range of customisation possible, in terms of size and shape, whilst maintaining a sub 15 nm nanogap between electrodes. This was applied to further increase the photodiode performance. Photodiodes with asymmetric Au/Al interdigitated electrodes of varying size (and thus overall diode size) were created to allow for the greatest photoelectric effect in the respective photodiodes. The inset of Figure 5.10 depicts the optical micrographs of the electrodes used, including devices of different electrode width, varying dependent on the pitch separation and the total perimeter of each structure.

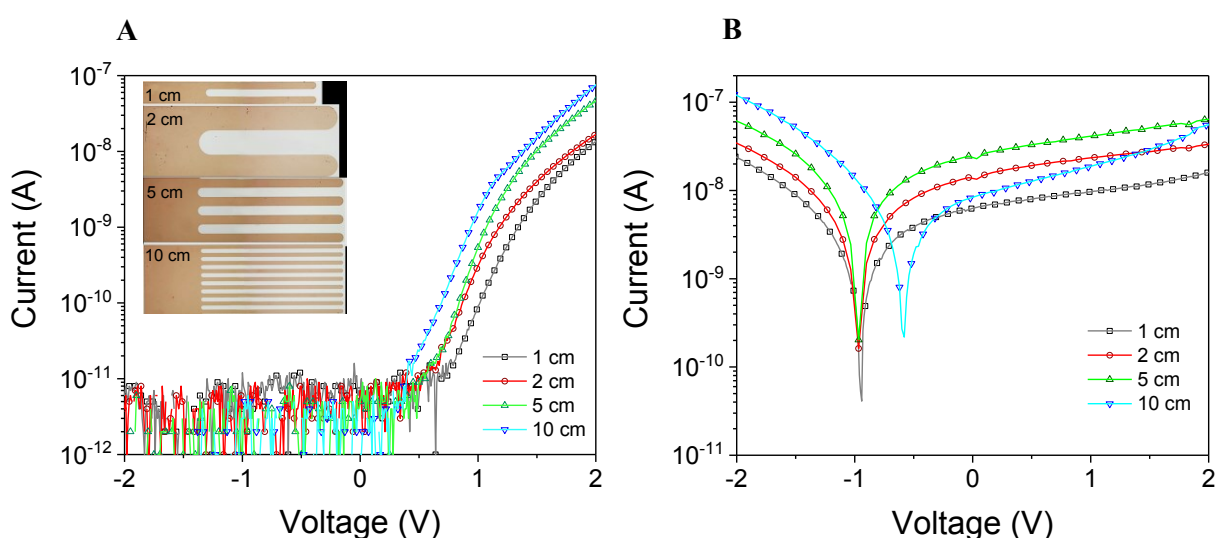


Figure 5.10: Semi-log I-V plots of varying width CuSCN photodiodes: (A) in the dark and (B) under illumination at 280 nm with optical power density of $220 \mu\text{W cm}^{-2}$. Inset: Optical micrographs of the varying width coplanar Al/Au interdigitated electrodes used in this study. (Adapted with permission from Wyatt-Moon *et al.* [137] Copyright 2017 American Chemical Society).

Figure 5.10A shows the I-V characteristics in the dark of four different width diodes (1, 2, 5 and 10 cm). As the device width increases, so does the current in the forward direction as expected, owing to the greater opportunity for charge carriers to flow. The reverse current remains stable (low) for all widths, however, due to the high quality Schottky contact that is formed between Al and CuSCN, preventing leakage current. When the devices are irradiated with the UV-LED emitting at 280 nm, the photocurrent is additionally increased due to the same effect. In the photoconductive state (-2 V) there is an increase of 10 times the photocurrent, between the 1 cm and 10 cm width devices (Figure 5.10B). There is a change in

current of over 4 orders of magnitude from dark to illumination in the 10 cm device. This equates to PS of the largest device of 4400 which is 6 times larger than the 1 cm device. R of this device is 49 A/W at -2 V which is lower than the 1 cm device due to R being dependent on device area. The R and S values for all the device widths are shown in Table 5.2 This demonstrates that by increasing the diode width, better PS can be obtained due to the ability of a-Lith to allow stable dark current values even with increasing device areas. The R values, however, decrease so a compromise between the two is needed to achieve the best device parameters.

Device width (cm)	Responsivity A/W	Photosensitivity
1	79	719
2	58	1060
5	41	1878
10	49	4434

Table 5.2: Responsivity and Photosensitivity data for different device widths.

5.3 A-Lith ZnO UV Photodetectors

To demonstrate the performance of a-Lith in other photodiode applications, solution processed ZnO was deposited onto a-Lith electrodes to create UV photodiodes. ZnO is a wide band gap material that is low cost with good chemical stability making it suitable for large area electronic fabrication. The devices were illuminated with 390nm LEDs at 7 mWcm⁻² optical power density. The resultant devices were sensitive, with low dark currents, showing the versatility of a-Lith in fabrication of high performing photodetectors for UV sensitive applications.

5.3.1 Background: ZnO Photodiodes

Zinc Oxide has been used for many years as an active material for ultra violet photodetectors due to its fairly wide band gap (WBG) (~3.2 eV). Using WBG materials that are “visible-blind” like ZnO means that, unlike current commercial technologies, filters are no longer needed to allow the correct wavelength to be detected [169]. Depending on the deposition method chosen,

ZnO can also be a very simple material to process, allowing high quality devices to be created but using much cheaper fabrication methods, with the additionally beneficial possibility of compatibility with polymer substrates due to low temperature processing. [158]. Due to all of these factors there has been much work carried out on creating high performance ZnO photodiodes. Most devices have used more expensive fabrication techniques such as sputtering and CVD to create a crystalline and defect free ZnO films or to grow nanowire devices [208]–[210]. These devices are either MSM devices employing the same material for the electrodes or sandwich devices that are usually p-n junctions. Many of the devices have fast rise times with increased fall times due to a photochemical effect causing reabsorption of oxygen on the ZnO surface [211]–[213].

5.3.2 Device Structure

ZnO has previously been used on a-Lith electrodes to create solution processed high frequency Schottky diodes, exploiting the high mobility of ZnO in conjunction with the low dimensionality and asymmetric nature of the electrodes possible with a-Lith [129], [138]. These devices had a high rectification ratio and benefit from extremely low dark currents due to the Schottky barrier created between the ZnO active material and Au electrodes, showing potential for use in photodiode applications.

To create the photodiodes a ZnO solution was created by dissolving ZnO hydrate ($\text{ZnO} \cdot x\text{H}_2\text{O}$, 97% Sigma Aldrich) was dissolved in ammonium hydroxide at a concentration of 10 mg/ml and stirred for two hours (as in previous sections) The solution was then spin coated directly onto a-Lith nanogap electrodes of Au and Al at 1500 rpm for 30s and annealed at 180°C for 30 mins. This was then repeated one more time with this process carried out in air (device schematic is shown in Figure 5.11A). The energy levels of the materials (Figure 5.11B) show an expected favourable injection from the Al contact showing Ohmic injection, with the Au electrode acting as a blocking Schottky contact. Again the work function values were taken from literature due to a UV ozone treatment of the electrodes prior to deposition and not taken from the previous chapter. ZnO films produced using this fabrication technique have been shown to create crystalline films between the two a-Lith nanogap electrodes [129]. The UV-Vis absorption spectrum of the ZnO was taken by spin coating the ZnO solution on cleaned quartz and annealing in the same manner as described above. The transmittance of the thin film was measured and converted to absorption as detailed in section 3.3.4. Shown in Figure 5.11C,

the absorption spectrum indicates its “visible-blind” nature and shows an absorption peak near 220 nm which is the detection limit of the UV-Vis spectrometer used to measure this absorption spectrum. The material has an onset of absorption at 420 nm showing that the ZnO photodiodes should be able to absorb both the UVA and UVB region of the electromagnetic spectrum.

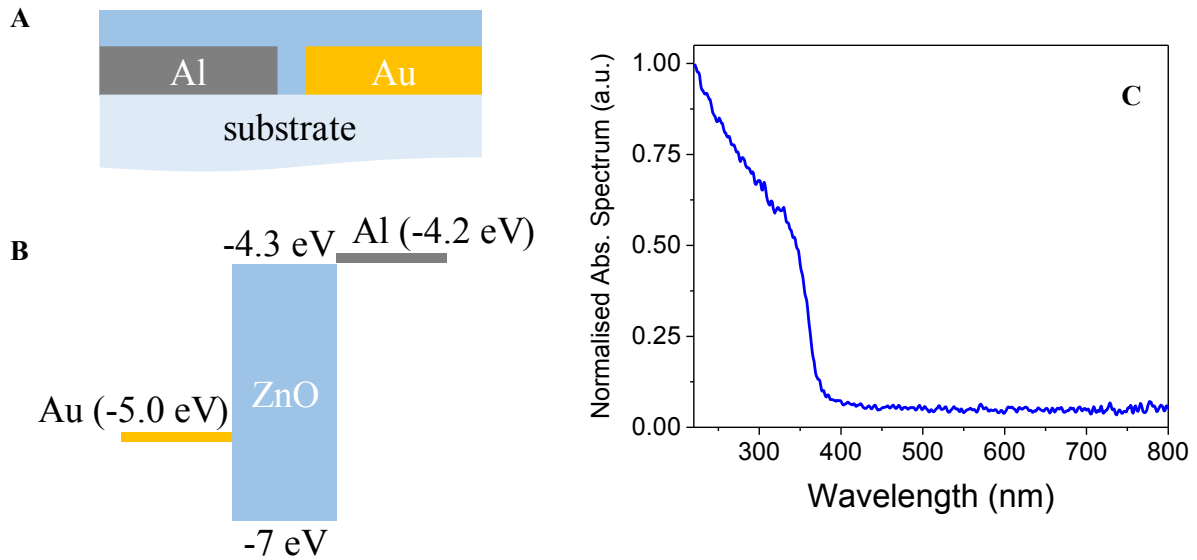


Figure 5.11: (A) Device schematic and (B) Band structure for ZnO Photodetector (C) Absorption spectrum of ZnO film on quartz.

5.3.3 Photodiode Characterisation

Figure 5.12A shows the normal dark current and illumination characteristics of the ZnO diode. Under dark conditions the rectification ratio of the diode is 10^4 at ± 2 V with a turn on voltage of ≈ 0.5 V. ZnO photodiodes were subsequently illuminated by 390 nm light at 7 mW cm^{-2} optical power density. When saturated in UV light for 30 mins the device reverse current increases by over 2 orders of magnitude. Whilst this is a large current increase, after 10 and then 20 mins in dark conditions it shows little reduction. This is most likely due to a mechanism that causes increased photocurrent, alongside electron hole separation. ZnO photodiodes are often dominated by a photochemical effect, caused by oxygen being adsorbed onto the surface of the ZnO [199]. When the diode is illuminated with UV light, oxygen ions are formed and combine with holes which subsequently desorb from the surface. The remaining electrons collect at the anode, causing a decrease in depletion width within the device [213], [214]. When the device is again under dark conditions the oxygen is reabsorbed onto the

surface; this is a very slow process hence the considerably low reduction in current after 20 mins in the dark. This is further demonstrated in Figure 5.12B where the light has been pulsed on and off. In the on-state the current increases fairly rapidly, but in the off-state the device has no time to reabsorb the oxygen so there is little or no decrease in current, allowing for cumulative increase in current over time.

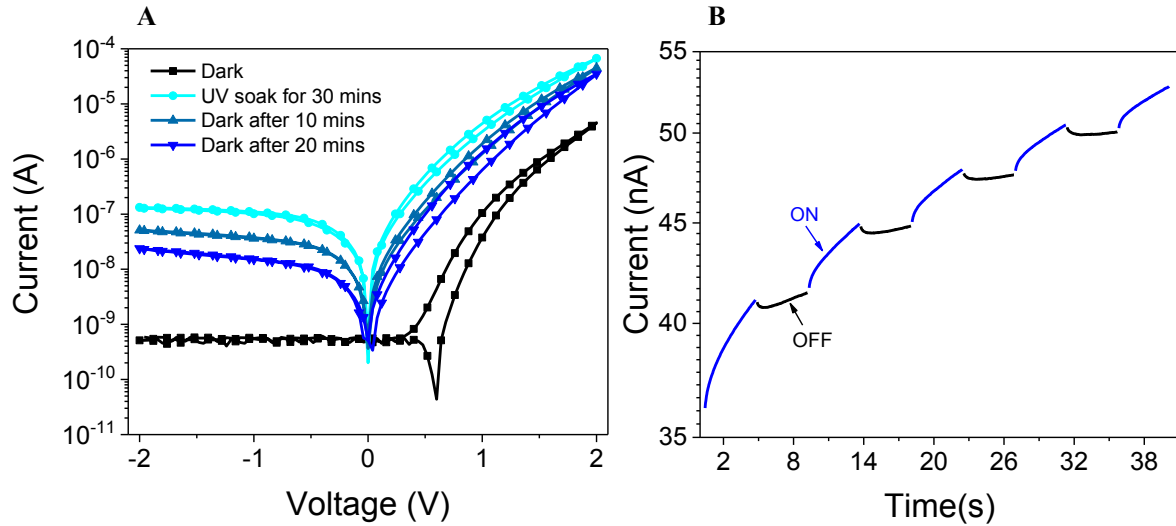


Figure 5.12: (A) Semi-log plot of I-V dark and under 390nm illumination at 7 mWcm^{-2} optical power density (B) Pulsed measurements at -2 V.

With all of the features we can see that the ZnO photodiode could be valuable in continuous monitoring applications as it takes a long time for the device to saturate under UV conditions, it is however not suited to rapid UV photodetection. There has been research to reduce the slow speed reaction of ZnO including adding other materials such as Au nanoparticles [215], [216] and Mg [217] or creating p-n diodes with the ZnO effectively capping it to reduce the photochemical effects of absorbed oxygen and allowing for better hole regeneration [218][199]. This however can be problematic for a-Lith based electrodes due to their small size, as it could cause bridging between the nanoparticles and electrodes resulting in increased dark current. The small scale of the gap between the electrodes also makes the alternative of pn junction diodes, hard to form within the nanogap.

5.4 A-Lith Visible Photodetectors

This section explores the use of a-Lith to create visible photodetectors using solution processed organic materials. The high performance polymer was used to fabricate both PTB7-Th heterojunction devices with PCBM and as single layer devices. Both were processed without the need for annealing, allowing for future applications on flexible substrates. These novel a-Lith devices have been compared to state-of-the-art technologies in terms of response time, responsivity, detectivity and photosensitivity.

5.4.1 Background Visible Photodiodes

Visible photodiodes are used in a vast number of applications including image sensing and colour detection [219][220]. Typically Si or other standard inorganic materials are used commercially, they are however unsuitable for new types of large area fabrication techniques such as printing as they are not suitable for solution processing. Si also absorbs in the IR region, requiring specialist filters for visible image sensing [220]. With the advent of new semiconducting materials, photodetectors can be easier to process using non-conventional fabrication techniques with active layers that can be modified for specific applications whilst also being physically flexible. For visible photodetectors these new materials normally fall into two categories: organic and perovskite with some research also focused on more novel 1D and 2D materials.

Due to the recent success of metal halide semiconducting perovskite materials in photovoltaic applications, there is increasing investigation into the materials as active layers in photodetector devices [221]. This group of materials are normally designed to absorb the entire visible spectrum and so are used in wide band applications. Photodetectors showing high detectivity and fast response times have been created, though there are issues with high dark currents reducing responsivity [222]–[225]. Unlike organic photodetectors, interlayers are not often able to optimise charge extraction, instead they are used to reduce dark current. Most perovskite metal halide photodetectors are created using a sandwich structure with two different WF metals for the anode and cathode due to the difficulty of fabricating asymmetric electrodes laterally. The use of metal halide perovskites in conjunction with a-Lith nanogaps, has been investigated for photodetector applications, due to their excellent light absorbing properties, though they are not presented in this thesis.

Much work has been carried out on polymer based photodiodes because of their ease of fabrication. Due to the poor charge carrier generation and transport the use of single material organic photodetectors is not normally viable thus bulk heterojunction structures are used. This relies on a donor and acceptor material, used to make carrier generation and separation more efficient. Standard high efficiency materials include donors such as poly-3-hexylthiophene (P3HT), poly[N-9-heptadecanyl-2,7 carbazole-alt-5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)] (PCDTBT) and poly(5,7-bis(4-decanyl-2-thienyl)-thieno(3,4-b)diathiazole-thiophene-2,5) (PDDTT) with acceptors normally comprising of a fullerene derivatives such as [6,6]- phenyl-C61-butyric acid methyl ester (PC₆₁BM), PC₇₁BM and C₆₀. [226]–[234]. Issues arise from these heterojunction structures, as the junction thickness has to be on the order of 100 nm due to poor mobility materials which then causes high leakage currents. This issue can be avoided by using planar electrodes with small separations as they allow for small active areas without increasing leakage currents.

5.4.2 PTB7-Th:PCBM Photodiodes

PTB7-Th:PCBM is a heterojunction that has been studied for photovoltaic applications as it can produce high efficiency devices [235]–[237]. Developed in 2013 PTB7-Th (chemical structure shown in Figure 5.13) is highly planar due to the side chains allowing for increased packing (increasing device performance) and greater absorption of longer wavelengths as compared to its sister polymer PTB7 [235]. The photovoltaic devices previously reported using PTB7-Th are bulk heterojunction structures using fullerene acceptors. A photodetector has also been created using PTB7-Th with P3HT as a second donor polymer. This was done to increase the spectral range of the device as PTB7-Th is known to be an NIR absorber. Although this device was shown to have high external quantum efficiency (EQE) [238], little work has been done on using this material in photodetector applications,

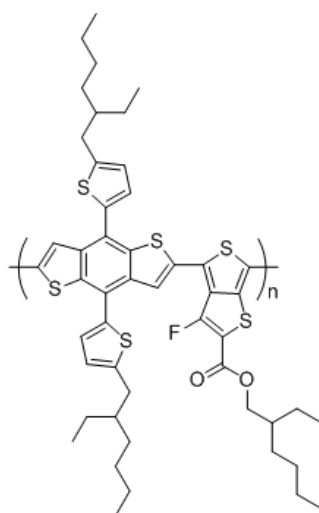


Figure 5.13: Chemical structure of PTB7-Th.

5.4.2.1 Device Structure

In this work a solution of PTB7-Th:PCBM in 1,2-Dichlorobenzene (DCB) at 10:15mg/ml was spin coated on top of a-Lith electrodes made from Au and Al at 2000 rpm for 60s with no annealing step. This lack of an annealing step is due to previous studies showing a degradation in photocurrent with a rise in dark current at higher temperatures caused by an increase in the domain size of the donor and acceptor sections [239]. This can be seen as an advantage as it allows the bulk heterojunction to be compatible with polymer substrates and makes it more appealing for large area fabrication as it removes one process step. Figure 5.14A shows the device schematic for a-Lith photodiodes featuring the heterojunction on top of the electrodes. The creation of this intermixed heterojunction may cause issues with short circuiting increasing reverse currents if the material composition is not well controlled. From the flat band diagram (Figure 5.14B) it is expected that when charge generation occurs it will take place at the interface between the two materials as it is the smallest energetic barrier to the creation of excitons, though it may also occur in the individual materials. The excitons should readily separate into individual charge carriers and be collected at the respective electrodes: the holes are transported from the donor (PTB7-Th) to the gold electrode and the electrons move from the PCBM to the Al due to favourable energy level alignments. The opposite charge carriers will be blocked due to the sizeable energetic barriers of the materials to opposite carriers, with a barrier of over 1 eV in the PTB7-Th for electrons and about 0.5 eV in the PCBM for holes. A reverse bias can however be used to help extract free charge carriers from the heterojunction by causing a further energetic barrier to the opposite carrier, whilst creating favourable drift

towards the complementary electrode of the charge carriers. The energy level for both materials were taken from previously reported data [238] [240]. The work function of the metals were also taken from literature (rather than chapter 4) for the same reason as the previous photodiode devices. Again as the material is solution process it's expected that the material will fill the gap as well as sitting on top of the electrodes. Bulk properties have been used to design this device but one cannot discount the fact that there may be quantisation of energy levels within the nanogap affecting device performance.

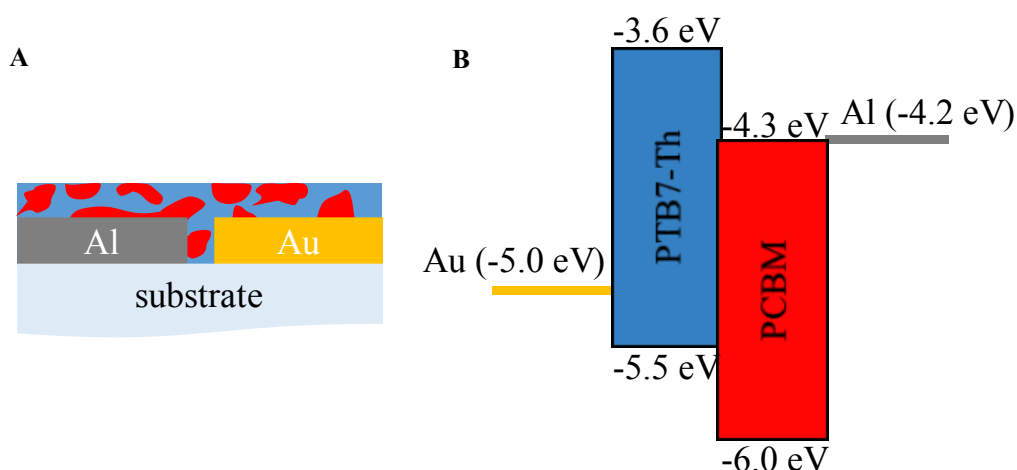


Figure 5.14: (A) Device schematic and (B) Band structure for PTB7-Th:PCBM photodetector.

Absorption spectra of the thin films of the individual materials (PTB7-Th and PCBM) and the heterojunction are shown in Figure 5.15. Thin films of the materials were created by dissolving the materials in DCB and spin coating them on cleaned quartz. The transmittance of the thin films was measured and converted to absorption as detailed in Section 3.3.4. PTB7-Th has peak absorption in the red/near-IR range at 710 nm with a shoulder at 640 nm. The PC₇₁BM absorbing well in the near UV/blue region of the electromagnetic spectrum with a peaks at 320, 380 and 475 nm. These two materials blended together provide an absorption coverage across the whole visible region, with peaks influenced by the individual materials- appearing at 710 nm and 320 nm. In areas where one material shows a reduction in absorption, the other absorbs, hence allowing the two materials to complement each other, highlighting the favourable nature of this combination for photovoltaic and photodiode applications.

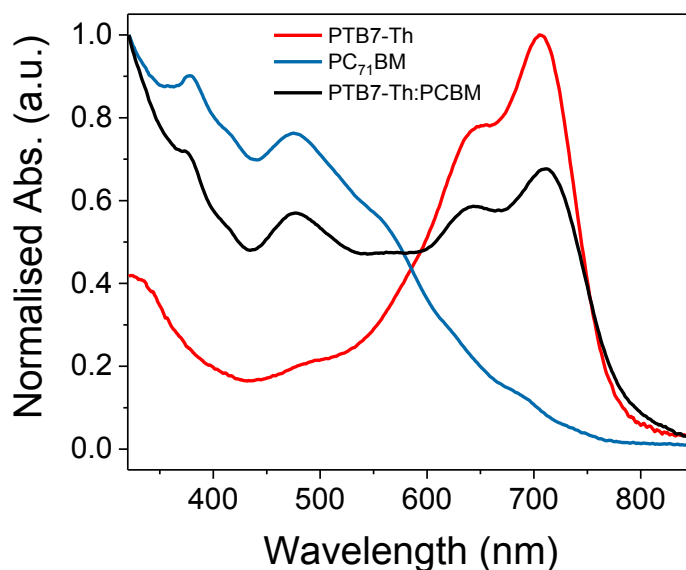


Figure 5.15: Normalised absorption spectrum of PTB7-Th, PCBM and PTB7-Th:PCBM 1:1.5 thin films on quartz.

5.4.2.2 Photodiode Characterisation

Semi-log plots of a typical device in dark (Figure 5.16) show the rectifying nature of the device. Both electrons and holes contribute to the diode current with the Au electrode injecting favourably into the PTB7-Th and the Al electrode injecting into the PCBM. The dark current is notably low for this device, on the order of 10^{-10} , demonstrating the method as highly effective in producing an organic heterojunction device. This dark current also indicates a lack of shorts from the PCBM. The turn on voltage for the diode is around 0.25 V for the forward scan suggesting a barrier to injection from the Au electrode. The rectification ratio (RR) is around 10^2 at ± 1 V.

The device was illuminated at 3 different wavelengths (470, 522 and 630 nm) with the same incident optical power $50 \mu\text{W cm}^{-2}$ (Figure 5.16). The response for each of these wavelengths is near identical, indicating that the heterojunction device is evenly responsive for the visible spectrum. At this low optical power ($50 \mu\text{W cm}^{-2}$) the photocurrent ratio is still around 10^2 at -1 V indicating substantial charge carrier separation between the materials.

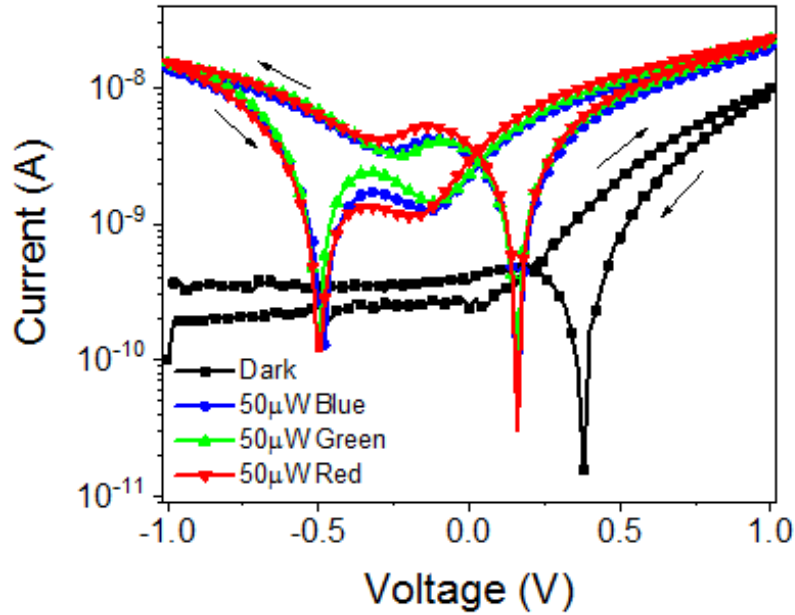


Figure 5.16: Semi-log I-V plot of PTB7-Th:PCBM photodiode under different illumination wavelengths: 470 nm, 522 nm, 630 nm at the same optical power density ($50 \mu\text{W cm}^{-2}$).

To test the sensitivity of the PTB7-Th:PCBM device it was placed under 630 nm illumination with varying optical power (Figure 5.17). Increasing optical power from 2 to $500 \mu\text{W cm}^{-2}$ led to a linear increase in the photocurrent. At $2 \mu\text{W cm}^{-2}$ the photocurrent is so low it is barely discernable from noise levels, with a current of 20 nA at $500 \mu\text{W cm}^{-2}$. Due to the low dimensionality of the devices, at high power, R has a value of 33 A/W and a detectivity (D) of 6×10^{13} Jones (when assuming only shot noise see Section 2.3.2) at -1 V. This is comparable to other state-of-the-art devices. These R and D values are a benefit of the a-Lith electrodes which allow for low dimensionality and therefore improve photocurrent whilst being asymmetric, creating low dark currents. Whilst these are low dark current values they are not as low as Schottky devices created using a-Lith hence producing a PS of only 49 at -1 V.

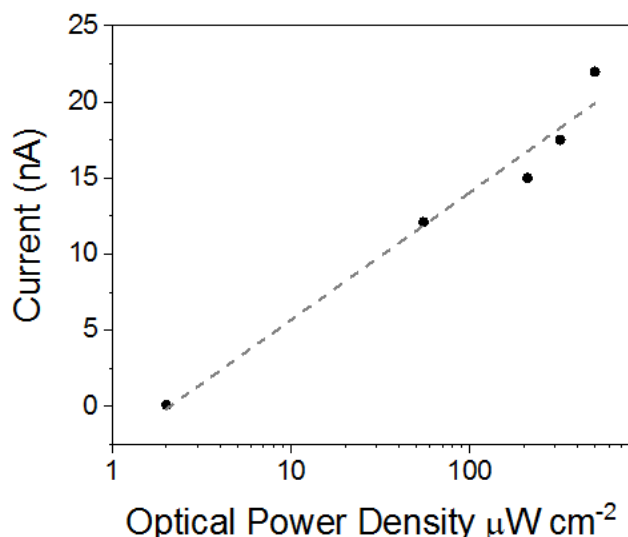


Figure 5.17: Photocurrent at different optical power density levels for illumination at 630 nm with the diode biased at -1 V and linear fit to the experimental data to help guide the eye.

Time response data was measured using a function generator to pulse a commercial LED, with the photodiode response measured via an oscilloscope (further details in Section 3.3.8). As shown in Figure 5.18A, the time response for the PTB7-Th:PCBM photodiodes is comparably quick when looked at in comparison to other heterojunction structures with planar nanogap electrodes [241][242]. The rise time of ~ 1.2 ms and decay time of ~ 1.5 ms was determined by the time taken to reach 10% and 90% of the signal as is standard for time response calculations (Figures 5.18 B-C). These times although fairly fast are not the highest seen for this material which suggests the charge transport is being limited by the device architecture rather than the carrier mobilities. Whilst most standard devices use HTL/ETL to improve charge extraction this is more complicated to achieve in a planar nanogap structure though the use of SAMs to modify charge extraction barriers could help improve this.

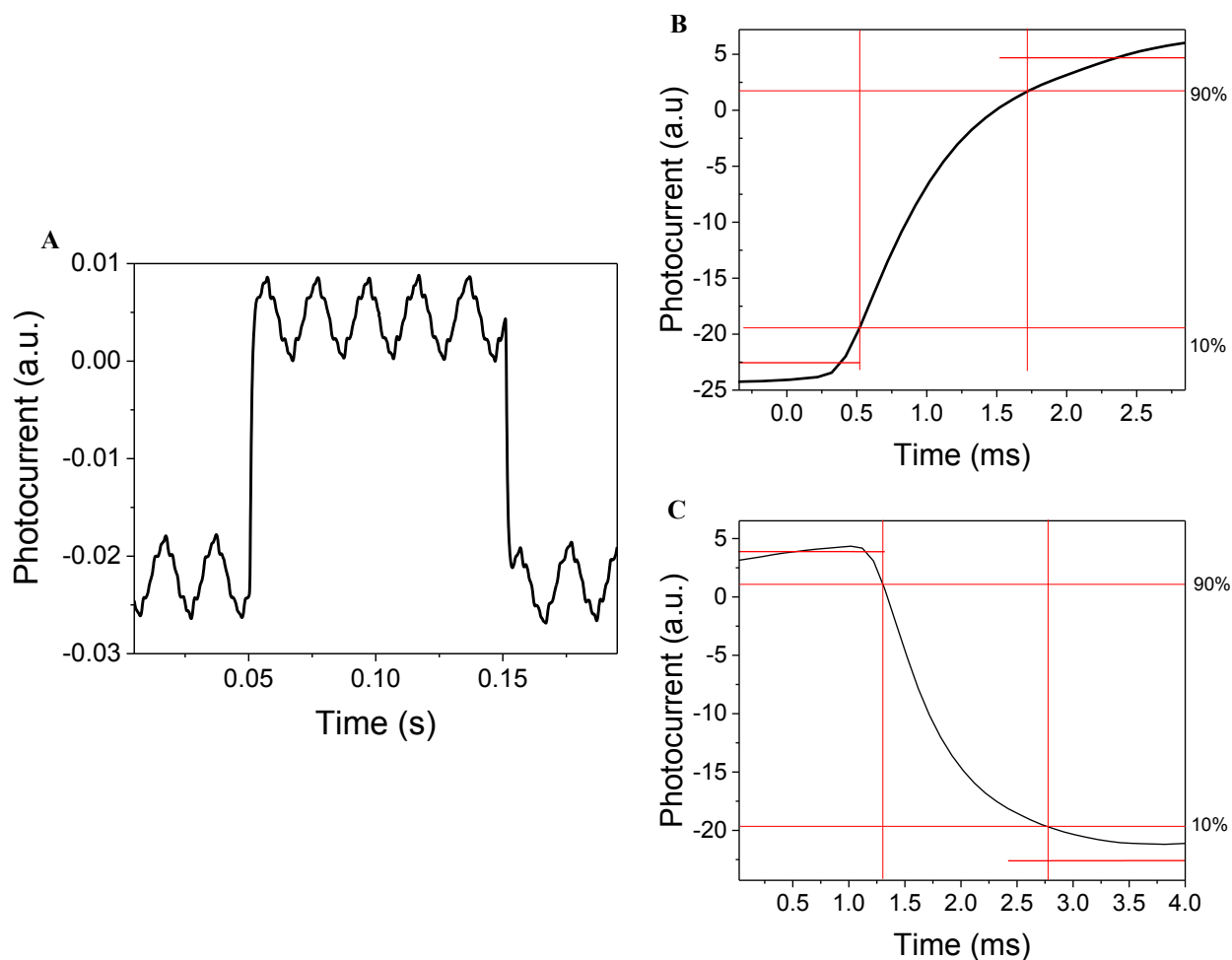


Figure 5.18: (A) Response of PTB7-Th:PCBM photodiode and calculation of the (B) rise and (C) fall times.

5.4.3 PTB7-Th Photodiodes

As mentioned in the previous section, organic photodiodes are normally heterojunctions because of poor charge separation in single material devices. Due to the asymmetric nature and small separation of the electrodes created via a-Lith, this charge separation can be improved. This method relies on decreasing recombination probability, with the application of a sufficiently large voltage capable of separating the charges. Whilst a few previous studies have shown nanogap electrodes and a single polymer as the active layer, when symmetric contacts were used the leakage in the reverse dark current was very high and little change was seen in the photocurrent [241]. When asymmetric contacts were used this led to better charge extraction and improved photocurrent as well as a reduction in the dark current [242].

5.4.3.1 Device structure

The device structure used in the polymer Schottky diodes was similar to the heterojunction structure but with the PCBM omitted (Figure 5.19A). PTB7-Th was dissolved in DCB at 10mg/ml and stirred for 24 hours. The resultant solution was then spin coated on top of a-Lith electrodes at 2000 rpm for 60s. The polymer is expected to have p-type injection from the Au electrode due to the extent of Fermi level alignment (Figure 5.19B), whilst the Al will act as a blocking electrode. Again, the work function of the metals were taken from literature instead of Chapter 4 for the same reason as the previous photodiode devices.

The absorption spectrum of a thin film of PTB7-Th on quartz is presented in Figure 5.19C and shows a peak at 710 nm with absorption seen throughout the visible, Near IR and Near UV electromagnetic spectrums.

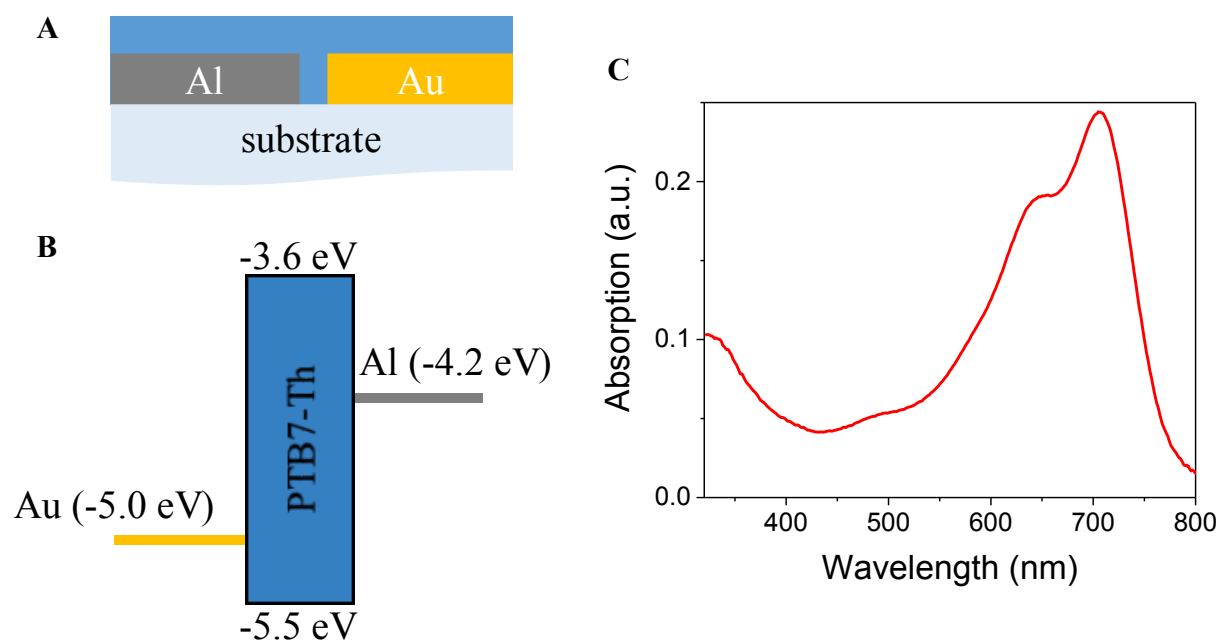


Figure 5.19: (A) Device schematic and (B) Band structure for PTB7-Th Photodetector. (C) Absorption of PTB7-Th thin film on quartz.

5.4.3.2 Photodiode Characterisation

The I-V plot in Figure 5.20A shows the diode characteristics in dark conditions and under illumination. The device shows a rectification ratio of 10^4 at ± 2.5 V and a turn on of 1.3 V in dark, due to the asymmetric electrodes. This turn on voltage is much higher than that of the bulk heterojunction structure which was 0.25 V this is most likely due to the structure of the

bulk heterojunction with added PCBM previously shown to increasing crystallinity of the film and polymer aiding charge transport [243].

When placed under 630 nm light at $500 \mu\text{W cm}^{-2}$ optical power intensity, the diode shows very little current change, unless higher voltages are used. Figure 5.20B shows the on/off switching of the device at -2 V under these illumination conditions. The dark current is very low around 10^{-12} and is near the detection limit of our system. This is two orders of magnitude lower than the heterojunction device due to the improved blocking contact between the Al and the PTB7-Th. The on current is nearly 2 orders of magnitude higher than the dark current.

Due to the Schottky nature of the diode, it would be expected that the response time would be very quick. To quantify this, measurements were attempted through a current amplifier and oscilloscope, however due to the very low currents the noise filter was unable to correctly distinguish between the true signal from the photodiode and the noise created through the measurement system (Figure 5.20C). The source parameter analyser cannot be used to take correct response times even though the signal is clear due to an innate measurement delay on the order of ms within the machine itself.

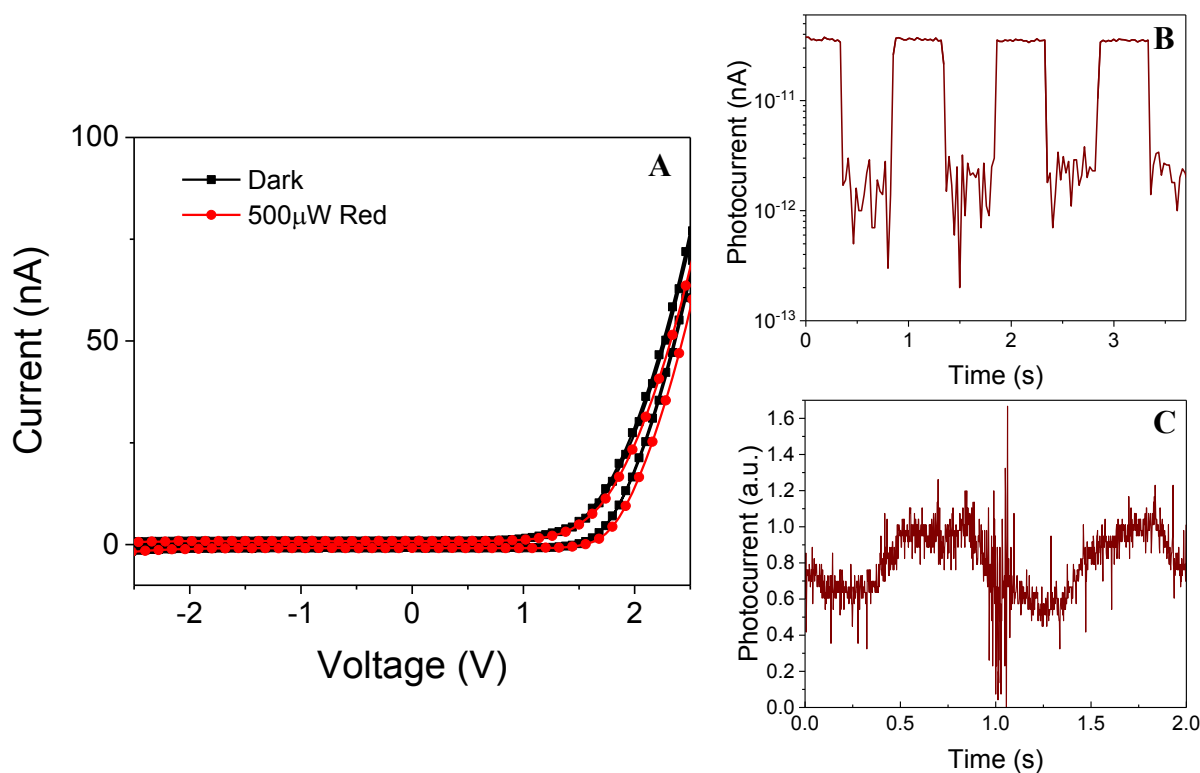


Figure 5.20: (A) I-V characteristics of PTB7-th Schottky diode in dark and under $500 \mu\text{W cm}^{-2}$ red light illumination and Time response (B) from source parameter analyser and (C) from oscilloscope at -2 V under $500 \mu\text{W cm}^{-2}$ red light illumination.

5.5 Conclusions

Deep UV photodiodes were fabricated using a-Lith to create asymmetric metal electrodes separated by a $\sim 15\text{nm}$ nanogap and using, the solution-processable DUV absorber, CuSCN as the active material. The novel architecture of these devices and appropriate material selection resulted in a high responsivity (79 A/W) and photosensitivity (718) devices without the need for a transparent contact and complicated fabrication techniques or elaborate materials processing. Scaling the device widths allowed for further improvement of device characteristics therefore proving the versatility of the a-Lith technique towards device performance optimisation.

Ultraviolet devices were also fabricated by spin coating ZnO onto a-Lith electrodes. These devices perform well as diodes and had a high photocurrent however the rise and fall times were incredibly slow on the order of 10 mins. This was due to the photochemical reactions taking place on the surface of the ZnO limiting the applications of these device to continuous monitoring.

Visible photodiodes were created using PTB7-Th: PC₇₁BM bulk heterojunction films and PTB7-Th-based Schottky diode configurations. The heterojunctions structures showed an even absorption over the visible wavelengths with high responsivity and fairly quick response times $\sim 1.3\text{ ms}$. The Schottky diodes showed less responsivity due to poor charge separation. The results indicate fast response times, with a more sensitive and lower noise system required to measure this. The dark currents were also 2 orders of magnitude lower than the heterojunction configuration due to the Schottky barrier between the Al and the polymer.

Overall this chapter has shown the versatility of the a-Lith technique to create various types of photodiodes that can absorb in many different areas of the electromagnetic spectrum just by

varying the active material. These devices have all shown to be high performing in one way or another. To date no research has been able to achieve these results with such a simple fabrication technique, clearly demonstrating the potential of a-Lith for photodetector applications.

Future work could include adding surface modification layers to the electrodes to allow for better charge separation and to improve device performance in terms of responsivity and detectivity. Transferring the devices onto plastic and testing device stability in air (possibly using some form of encapsulation) would allow for more applications to be realised as well as robust testing in harsh conditions such as higher and lower temperature environments with increased humidity. Additional work on different areas of the electromagnetic spectrum such as IR using other state of the art materials would be interesting as a-Lith could produce very sensitive IR photodiodes.

Chapter 6

Nanogap based Organic Light Emitting Diodes

6.1 Introduction

Research into organic light emitting diode (OLED) applications began in the late 80s and early 90s with seminal papers by C. W Tang and S. A. VanSlyke [126], and J. Burroughes et al [25]. Research is now focused on improving the efficiency of devices by not only improving the active material but also the device architecture using hole/electron transport/blocking layers to increase charge carrier injection. These advancements have led to the commercialisation of these technologies in applications such as high resolution displays and solid state lighting [244].

The use of nanoscale light emitting devices is seen as advantageous for applications in a variety of fields including high resolution displays, bioelectronics, high resolution imaging and nanolithography [245]–[249]. For these applications not only will many devices need to be fabricated at one time but all of these devices will also have to be uniform in nature, especially if realised in industrial applications. The use of organics in nano-LEDs is seen as an advantage

due to easy fabrication routes as compared to inorganic devices that require far more complicated fabrication techniques [247], [250].

This chapter describes the use of a-Lith with electroluminescent polymers to create nano polymer light emitting diodes (n-PLED). First devices are fabricated using the state of the art electroluminescent polymers; poly(9,9-dioctylfluorene-alt-bithiophene) (F8T2) poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) and poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and are subsequently characterised. F8T2 is then used as the standout material to explore the light emission, response and stability of the n-PLEDS. Also investigated is the impact of high fields on the n-PLEDs. Devices are also fabricated and characterised on PET films showing the first ever n-PLED created on plastic (to the author's knowledge). Diode characteristics before light emission are also explored due to the small geometry creating high performance polymer nano diodes with SAMs investigated as electrode modifiers to help improve the device characteristics.

6.2 Background Nano Light Emitting Diodes

Polymer based nano LEDs (n-PLEDs) have been investigated since 1995 when Granström *et al.* saw the advantage of using polymers to easily reduce the size and shape of an LED whilst allowing easy production of n-PLEDs [246]. In this study microfiltration membranes were used to pattern the poly(3,4-ethylene-dioxythiophene) (PEDOT) anode with thin films of the active material and Al-Ca cathode deposited on top, with the shape and size of the PEDOT defining the dimensions of the devices. The electroluminescence from these devices was captured through the cathode material, significantly decreasing the light intensity. Also device lifetime was reduced due to heat expansion of the PEDOT. Later studies use insulating layers to pattern either the electrode or polymer via fabrication techniques such as EBL to improve the reproducibility of devices, making them unsuitable for large area fabrication [251] [252].

From an operational standpoint, miniaturised polymer LEDs are advantageous to larger area ones, as higher current densities can be sustained thanks to efficient dissipation of Joule heating, as reduction in device size allows the heat from the device to be rapidly transferred to the substrate [253]–[255]. These small device active areas withstand high current densities due to better thermal management, which allows for greater electroluminescence. The suppression of OLED roll-off characteristics has been observed to be improved by reducing the device area to less than 200 nm [256]. Here it was shown that devices reduced in size but still larger than

200 nm were able to reduce singlet-heat annihilation (SHA) due to the reduced Joule heating, Further reduction it roll-off was seen below 200 nm due to suppression of singlet–polaron annihilation (SPA) as excitons are more easily able to escape the current flow region because it is similar to exciton diffusion length [257]. There has also been an improvement of organic materials that have demonstrated low threshold amplified spontaneous emission (ASE) in light-emitting polymer films [258]. These results are leading the realisation of electrically pumped organic lasers [259], with state of the art research trying to utilise these properties with novel device architecture. [260]. These technologies are however all relying on complicated fabrication techniques to create the desired high resolution nanostructures. The simplicity of a-Lith in creating nanogap electrodes combined with electroluminescent materials will allow the creation of such devices using large-area low cost manufacture.

The asymmetric nature of the a-Lith electrodes, which is difficult to obtain with other common nanopatterning techniques (Section 2.1), permits electroluminescent nanodevices to be created via simply depositing a single layer of active material on top of the electrode structures using low temperature and inexpensive deposition techniques. Further to this, the planar nature of the electrodes means that loss mechanisms are reduced as the light emission does not have to pass through one of the electrodes (a transparent metal oxide in standard devices) to escape the device [261].

6.3 Various Polymers for Light Emitting Diodes

When deposited on top of Al/Au a-Lith electrodes (Section 4.3) most electroluminescent polymers will have favourable injection of holes from the Au electrode, due to good alignment between the HOMO of the polymer and the work function of Au (Figure 6.1 (B)). However the Al will have a larger barrier to electron injection which will most likely cause a mismatch in charge carrier densities resulting in reduction in radiative emission at lower voltages. To investigate this and show the versatility of the a-Lith technique different wavelength emitters were used to create n-PLED devices. The materials chosen were: F8T2 from Cambridge Display technologies (CDT), F8BT and MDMO-PPV, both provided by Sigma Aldrich.

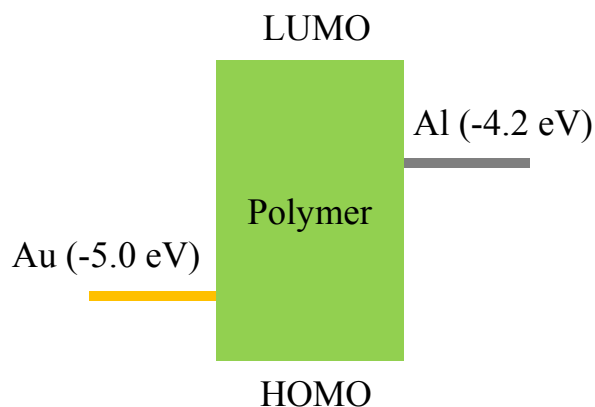


Figure 6.1: Band structure for polymer based n-PLED.

F8T2 shown in Figure 6.2A and F8BT (Figure 6.2B) are both polyfluorene copolymers with the additional units changing the band gaps of the materials and so the emission wavelength. This group of materials has produced many highly efficient electroluminescent polymers. F8T2 is a fairly ambipolar material with hole mobilities of $5 \times 10^{-3} \text{ cmV}^{-1}\text{s}^{-1}$ (attributed to the bi-thiophene within the block co-polymer) and electron mobilities of $6 \times 10^{-3} \text{ cmV}^{-1}\text{s}^{-1}$ with mobilities increasing as more order is added to the polymer thin film [262]. The HOMO and LUMO of F8T2 are 5.5 and 3.1 respectively from this we would expect favourable injection of holes from the Au electrode with a slight barrier $\sim 0.5 \text{ eV}$. There is a larger barrier to injection from the Al cathode due to the $\sim 1.1 \text{ eV}$ barrier inhibiting electron injection, causing a mismatch in charge injection. F8T2 is a green emitter which typically has emission peaks at 511 nm and 545 nm [263]. F8BT is a material that emits yellow-green light with an emission peak around 545 nm. It has hole mobilities of $4 \times 10^{-3} \text{ cmV}^{-1}\text{s}^{-1}$ and electron mobilities of $5 \times 10^{-3} \text{ cmV}^{-1}\text{s}^{-1}$ [264]. The HOMO and LUMO levels lie at 5.9 eV and 3.3 eV indicating it will have worse hole injection from the Au electrode but slightly better injection from the Al electrode as compared to F8T2 [265]. MDMO-PPV (Figure 6.2C) is from the phenylene vinylene group of polymers which is the most studied group for LEDs beginning with the first reported PLED [75]. It is a red emitting material due to the placement of the dimethyloctyloxy side group [266]. The HOMO is 5.4 eV and the LUMO is 3.2 eV suggesting it will have similar injection barriers to F8T2. The mobilities in this PPV based material however are low; around 10^{-4} - $10^{-5} \text{ cmV}^{-1}\text{s}^{-1}$ and so for devices with good injection MDMO-PPV will produce lower performance devices than the polyfluorene materials [267].

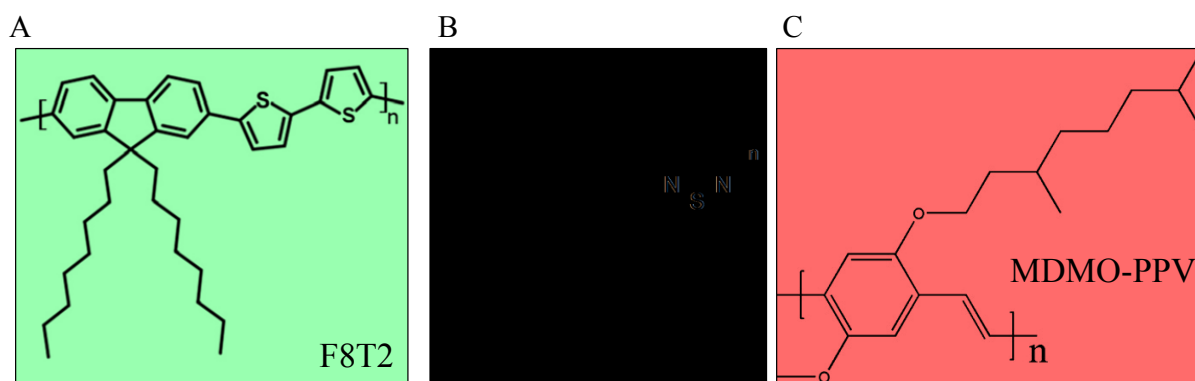


Figure 6.2: Chemical structures of (A) poly(9,9-dioctylfluorene-alt-bithiophene) (F8T2), (B) poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT), and (C) poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MDMO-PPV).

To create the nano-LEDs the polymers were each dissolved separately in tetrahydrofuran (THF) at a concentration of 5-10 mg/ml, spin-coated at 2000 rpm on to the a-Lith substrate (Figure 6.2A) and annealed at 70 °C for 10 min inside a N₂ filled glovebox. This annealing step was to remove any remaining solvent and not designed to change the material properties or morphology of the polymers. The electrodes were placed in a UV-Ozone for 30 mins prior to polymer deposition to remove contaminates and improve carrier injection via modification of the electrode WFs. The electrodes used were square Au electrodes with a width of 4 nm surrounded by a common Al electrode both with a thickness of 40 nm (Figure 6.2C (i)). The devices therefore, have high aspect ratios of around 200,000; defined as the ratio between the electrode width and the nanogap (here taken as 20 nm) and a device active area of 160 μm²; defined as the electrode thickness multiplied by the width of the nanogap.

Each device behaves like a diode at low voltage operation (0–3 V) with turn on voltages between 0-1 V with holes as the majority carrier indicated by the I-V plots in Figure 6.2B. All devices exhibit p-type behaviour due to the favourable injection from the Au electrode for each material. F8T2 and F8BT have similar diode characteristics whereas the MDMO-PPV devices have a higher turn-on voltage and lower current lower. This is due to the higher mobilities of the polyfluorene materials. The device characteristics of the diodes at low operating voltage are discussed in section 6.10 with F8T2 used as the example.

At ≈4 V the characteristics start to change and are no longer diode shaped this is due to the nanoscale separation of the electrodes causing extremely high fields across the electrodes (on

the order of GV m^{-1}). Very high current then passes through the device (on the order of mA) and it is in this high current region when light emission occurs.

Light emission is seen between 6.5-10 V with the I-V curve for each n-PLED exhibiting similar device characteristics. This light emission is due to charge carriers being balanced enough to form excitons and decay radiatively. The I-V characteristics are very similar to other n-PLED devices which suggests the I-V shape is also due to the nanogap electrodes [246]. The current for the F8T2 device and the light emitted is slightly brighter as seen in the optical micrographs of light emission from F8T2, F8BT and MDMO-PPV devices at 10V. These were obtained through a CCD camera and are shown in Figure 6.2C (ii)-(iv). The fully lit LEDs confirm the capability of a-Lith to create various n-PLEDs emitting a range of colours simple by changing the material deposited on the electrodes.

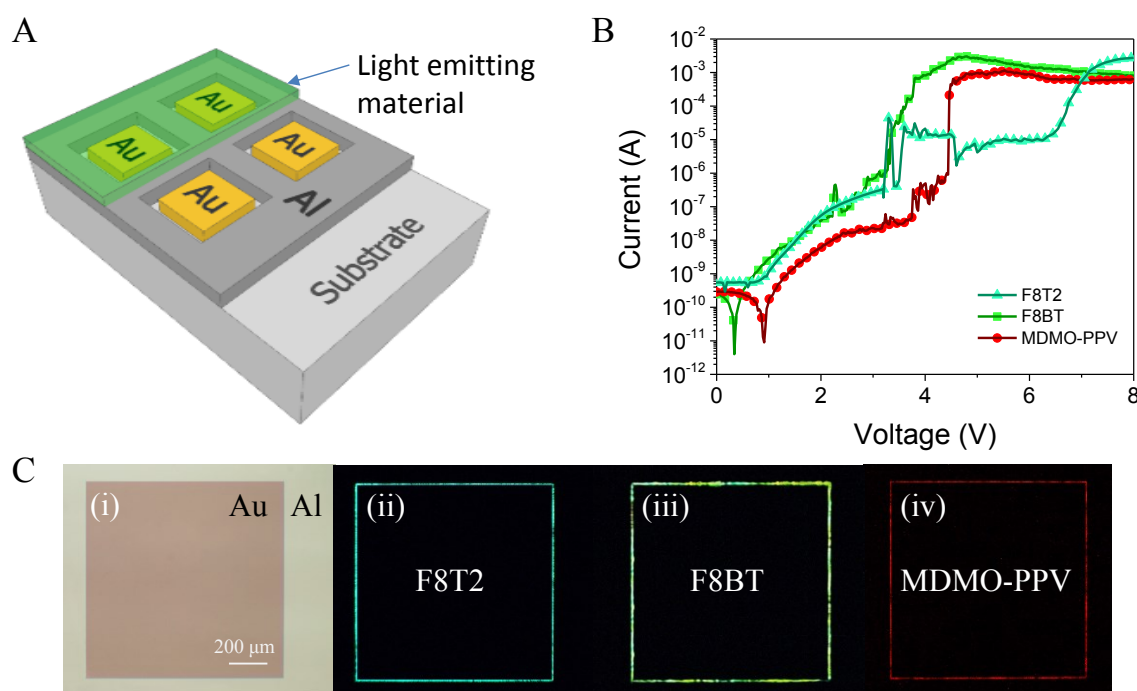


Figure 6.3: (A) 3D schematic of n-PLED devices (B) Semi Log plot of I-V characteristics of n-PLEDs for each polymer device (C) Optical micrographs of (i) square nanogap electrodes used for the n-PLEDs and electroluminescence emitted from the (ii) F8T2 (iii) F8BT and (iv) MDMO-PPV n-PLEDs.

From the optical microscope images, the area of emission appears to be larger than the nanogap size. The geometry of the a-Lith (given a 15 nm nanogap) would correspond to a top view emitting area of $\sim 80 \mu\text{m}^2$, but light appears to be emitted from a much broader region, this

could be due to the resolution limit of the microscope optics[251][252]. We cannot however, disregard the fact that due to spin-coating of the polymer solution on top of the whole substrate, current flow is not entirely confined within the nanogap channel volume. Illustrated in a 3D schematic (Figure 6.4), due to the small size of the gap exciton formation is able to occur not only in between the two electrodes but also slightly further into and above the metal electrodes causing a broader emission region. The high electric field strength induced in the nanochannel (in the order of GV m^{-1} during light emission conditions) increases the injection rate of charge carriers from the electrodes, not only in the lateral but also in the vertical direction, and thus the electron-hole recombination and exciton formation events happen at a larger volume than the one specified by the two electrodes and the nanogap channel. Stronger fields may also promote the extension of the exciton diffusion path length and lifetime further away from the nanogap area, permitting singlet decay and light emission to occur from a wider region. Similar experimental observations as well as simulations that have been carried out with sub-micron stripe-shaped inorganic LEDs revealed a wider current spreading for higher injection currents [268].

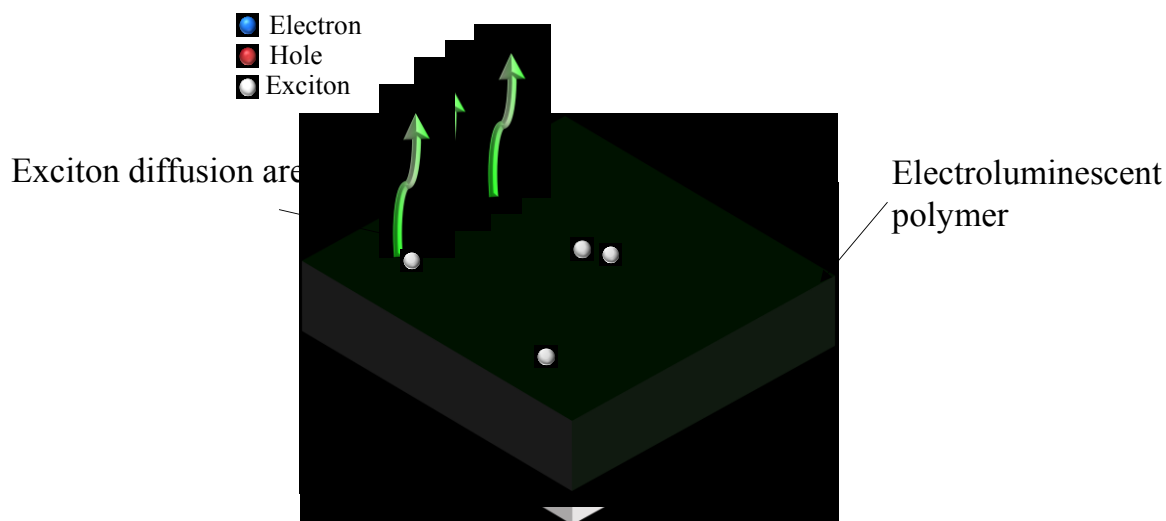


Figure 6.4: Schematic illustration of the exciton formation in the area inside and above the coplanar electrodes.

This set of experiments shows the versatility of the a-Lith technique to create a full colour gamut of n-PLEDs just through spin-coating a different single layer of polymer. Throughout the next sections the discussion will focus on F8T2 as a representative polymer to fully

characterise device and luminescent properties of the a-Lith n-PLED due to its favourable electroluminescence.

6.4 Characterisation of Light Emitted

The analysis of light emitted from the n-PLED is in itself not trivial, as most standard electroluminescence measurement setups are not designed for device structure such as those created by a-Lith OLEDs. In addition they do not offer the sensitivity to detect the emitted light. To fully characterise the light emission from these a-Lith made devices under biasing, a specific set-up was created where a photodiode (S1133 Hamamatsu) was placed above the LED and captured any light emitted. The lab was placed in darkness to remove any background noise on the optical signal. The photodiode response shows that light emission occurs when the device is biased between 6.5-10 V (Figure 6.5). The photodiode shows a device turn on ≈ 6.5 V however the exact determination of the n-PLED turn-on voltage may be limited by the specific detectivity of the photodetector used under the measurement conditions (the dark current, I_D , measured in our experimental setup was in the range of 100 pA, which is 10 times higher than the nominal $I_D = 10$ pA given by the manufacturer). From the LED I-V characteristics it can be seen that the current needed for light emission is very high, suggesting an imbalance of charge carriers most likely due to the relatively efficient injection of holes from the Au electrode and large barrier to injection for electrons at the Al electrode. The fact that light emission can occur, even with this mismatch, is likely due to the small separation of electrodes which is similar to the exciton diffusion length, reducing the occurrences of nonradiative decay due to exciton quenching at the metal.

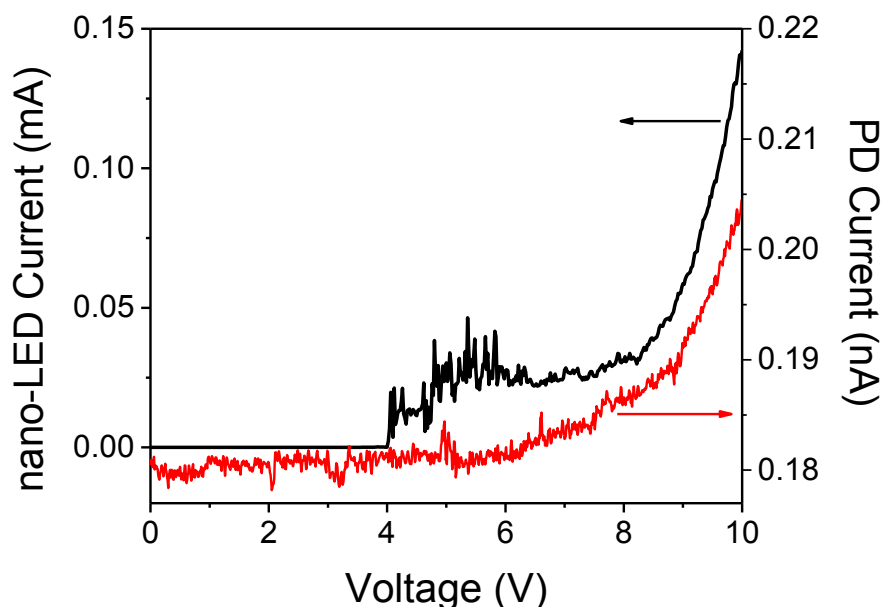


Figure 6.5: I-V characteristics of F8T2 nano-LED and current output of the photodiode used to monitor the emitted light.

Characterisation the photoluminescence (PL) and electroluminescence (EL) of the n-PLEDs was again not possible using conventional LED setups. Instead the devices were taken to the National Physical Laboratory (NPL) where a scanning spectroscopy was employed to measure the PL and EL across the nanogap devices. The PL spectra around the nanogap area of coplanar Au/Al electrodes were recorded using confocal Raman PL spectroscopy with 200 nm lateral resolution employing a 405 nm excitation source. EL spectra were recorded using the same setup through electrically biasing the n-PLED instead of using an excitation source. The PL of a reference thin film of F8T2 spin coated onto a cleaned quartz substrate was measured using a FluoroMax-3 spectrometer. The PL of the reference F8T2 has a maximum peak at 511 nm, a secondary peak at 544 nm and a slight shoulder at around 586 nm; all features comparable to previously reported work [263]. The PL signal measured from the nano-gap device, however, shows a clear shift in these peaks to 513, 549 and 590 nm, respectively. A decreased intensity in the first peak and increased intensities for the two other peaks, is also observed. The slight red shift are likely due to the confinement of the polymer inside the narrow nanogap channel, acting as a template for the variation of the polymer chain orientation. More specifically, increased self-absorption in the limited space may be responsible for the shift of the highest PL intensity from the 0-0 to 0-1 vibronic transition [269]. The red shift can also be attributed to an increase of effective conjugation length due to chain planarisation, favouring intrachain against

interchain energy transfer. The latter would result in the higher energy excitons migrating into the lower energy states along the same chain, inducing the observed spectral red-shift [270]. The EL spectrum closely follows the shape of the nanogap derived PL, with the main emission peak at 547 nm and shoulders at 512 nm and 592 nm. It should be noted here that electroluminescence is by definition emitted through the spatially constrained area of the recombination zone, whereas photoluminescence is usually an averaged emission from the whole excitation volume. The similarity between the EL and PL spectra measured at the nanogap area reveal a similar light emission mechanism dominating these structures despite the different excitation source.

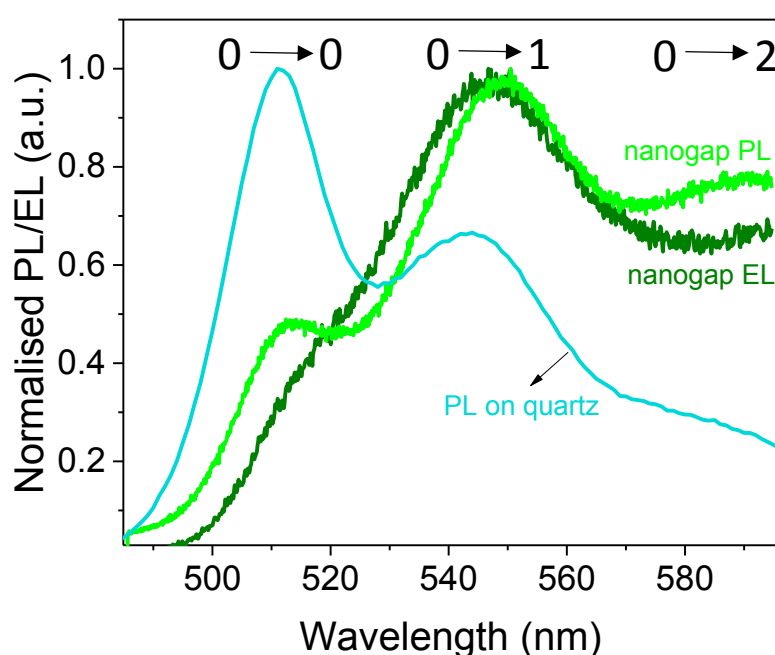


Figure 6.6: PL spectrum of F8T2 film on quartz and PL and EL spectra of F8T2 n-PLEDs recorded at the nanogap region. The respective vibrational transitions assigned to each peak are also shown.

6.5 Changes in Device Width

To increase the light emission from the n-PLEDs, the effect of increasing the device width was explored. Widths of 1, 2, 5, 10 and 20 cm were created simply by changing the mask used to pattern the first metal and adding in a second patterning step to isolate the electrodes from each other, this procedure is described in more detail in chapter 5. The diode characterisation of these devices at low voltage (Figure 6.7A) shows that as the width of the device is lengthened the current is increased. Additionally it is shown that all devices are diodes with little

leakage current. The devices all exhibit single carrier p-type behaviour due to the favourable injection from the Au electrode into the HOMO of F8T2. Here, similarly to previous sections, the nature of the devices changes as the voltage increases past 3 V with each device losing its diode like characteristics. This takes the form of a sharp increase in current and then a slight decrease in current as the light emission begins before the current then increases again (Figure 2B). Again the light is characterized by change in photodiode current (Figure 6.7C). This current is seen to intensify with increased width as would be expected as a longer width device will produce more light due to an increased emission region. Figure 6.7D shows the change in n-PLED and PD current with regards to width at a bias of 10 V. Both trends are fairly linear with variation in the n-PLED attributed to the high fields causing instability across the nanogap. The PD current is more linear indicating that even without stable currents the light emission remains fairly stable.

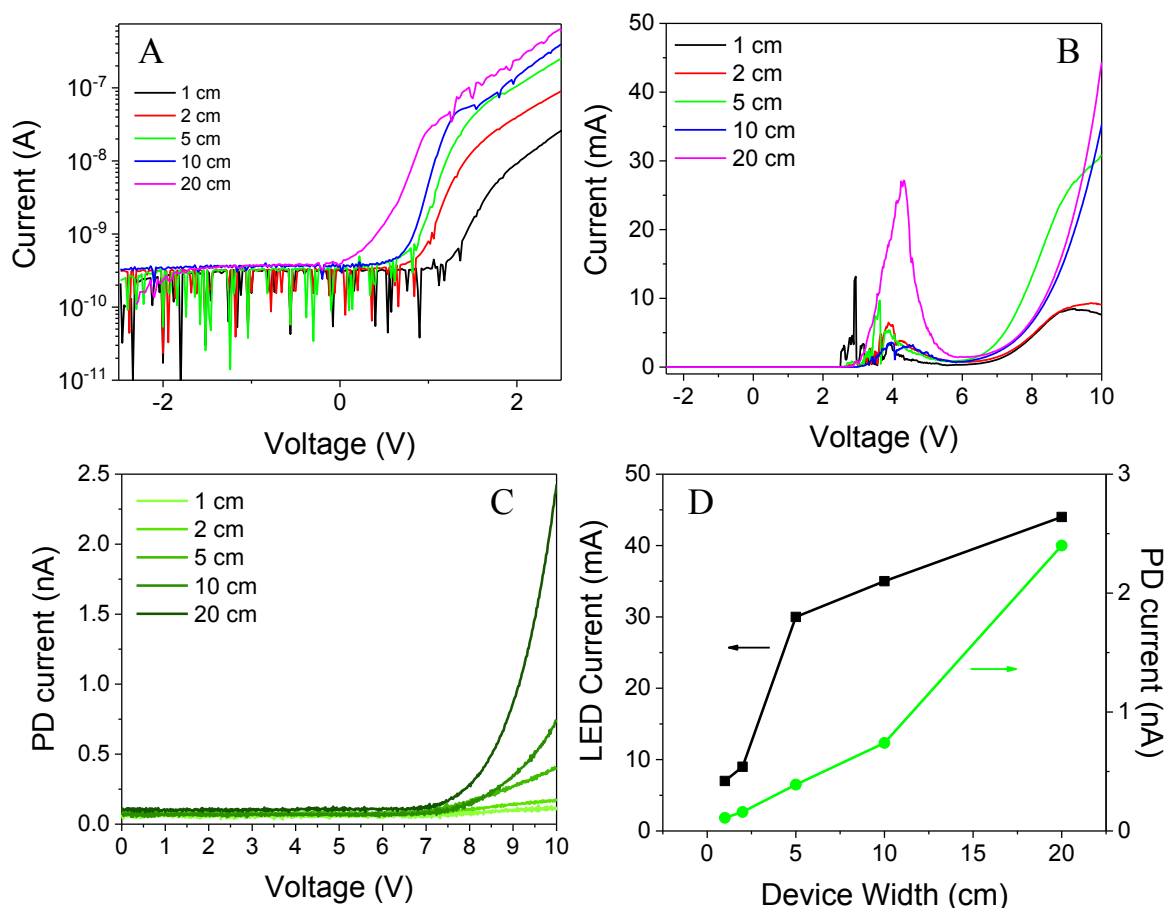


Figure 6.7: (A) Semi log plot of F8T2 OLEDs in diode regime (B) I-V characteristics of nano-LEDs fabricated with different widths interdigitated electrodes. (C) Photodiode response of the light emitted from the different width nano-LEDs. (D) Device width vs LED and PD current.

Figure 6.6 shows the illumination of each of the different width devices and shape of the electrodes. The micrographs are on the same scale which also shows that, by changing the device architecture and minimising the width of the interdigitated fingers of the electrodes whilst increasing the width of the device, the light per unit area can be greatly increased. It also indicates the ability of a-Lith to create devices with nanogap separation even with incredibly long widths.

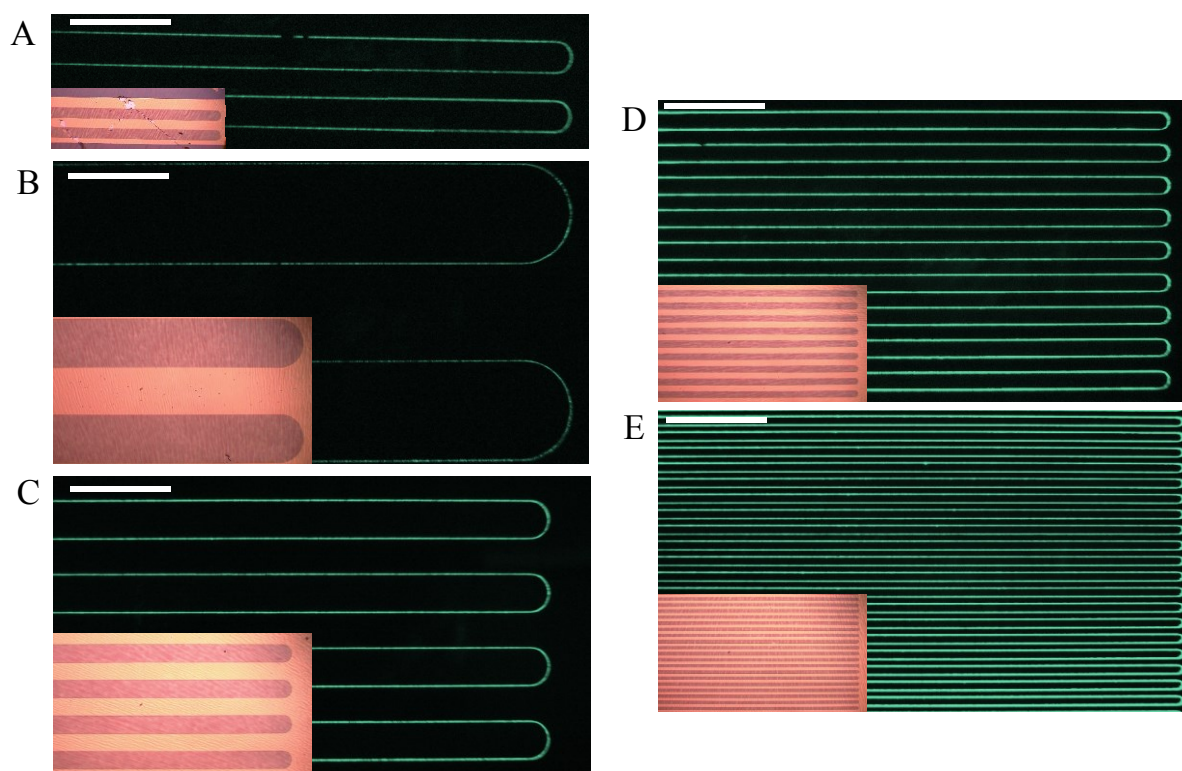


Figure 6.8: Optical micrographs showing illumination of each diode width at 10V (A) 1 cm (B) 2 cm (C) 5 cm (D) 10 cm (E) 20 cm Scale bar: 500 μ m. Inset: optical micrograph of electrode shape used for illumination.

6.6 Dynamic Response of n-PLEDs

Due to the small gap between the electrodes of the devices it would be expected that a-Lith n-PLEDs would be very fast switching devices. Charge carriers can be injected into the device and rapidly meet their counterparts to radiatively decay due to the small active area, thus allowing for fast switching of the light emission. To investigate this, a function generator was used to pulse a device on (10 V) and off at a 1 Hz frequency with a photodiode placed on top

of the device, biased at -2 V and its response amplified through a current amplifier and measured using an oscilloscope. The rise and fall times were calculated by taking 10 % and 90 % of the maximum value of the pulse and finding the response time between these two values Figure 6.9. This is standard practice when measuring response times. Both the rise and fall times for the n-PLED are 210 μ s. This value is low enough for the device to be used within display technology as millisecond response is sufficient in this field. Also the light response is able to be held for 0.5 s at maximum illumination with no current drop-off indicating these devices could be stable when operated in a pulsing mode.

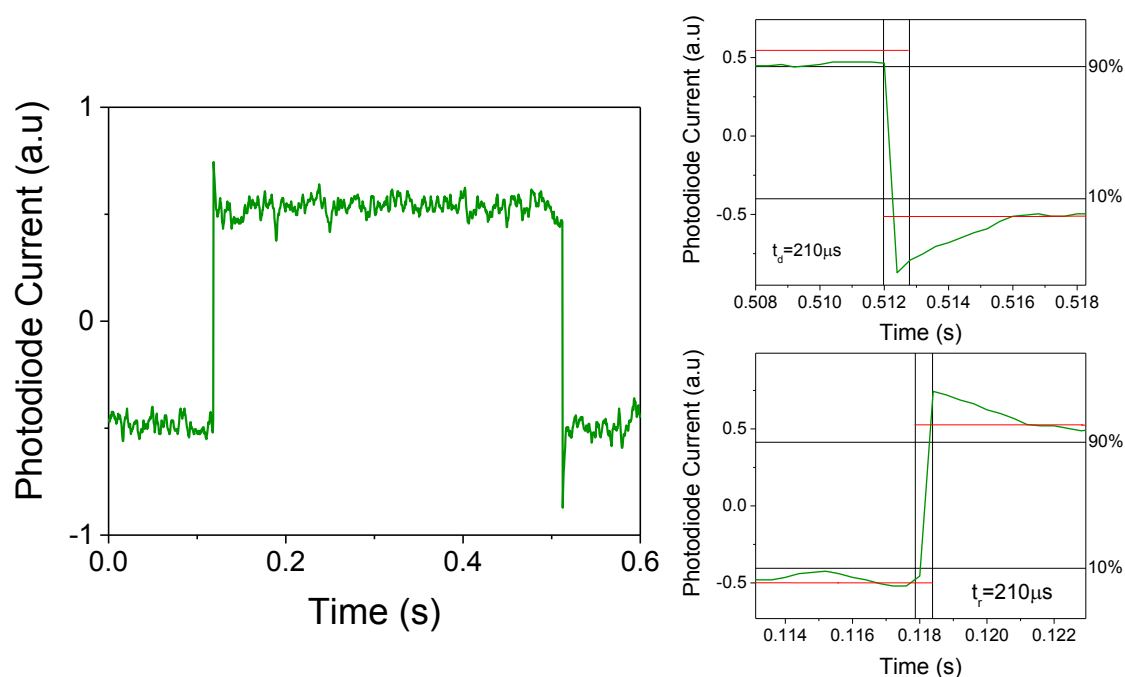


Figure 6.9: Speed of light emission. Device was pulsed from 0-10 V and the light emission was captured by a photodiode via an oscilloscope.

6.7 Pulsing of Devices

Due to the high field needed for light emission stability of devices can be an issue due to breakdown of the electrodes. To investigate this constant current mode at 12 V was compared to a pulsed setup where the LED was pulsed on and off with a 1 Hz square wave, illustrated in Figure 6.10A. A photodiode was used to capture to light output from the device. The constant voltage device starts with a stable current but after 5 s this current then increases and dramatically decreases (Figure 6.10B) reducing to a similar value. In terms of light emission (Figure 6.10C), the photodiode current follows the shape of the LED current and after ~22s the

light has stopped emitting, showing that the device has a very short lifetime most likely due to the high fields causing damage to the electrodes (see next section for more detail). The pulsed device has fairly stable current and the photodiode current follows with only a small reduction in light emission showing that pulsing these devices will increase device life time, even at high fields.

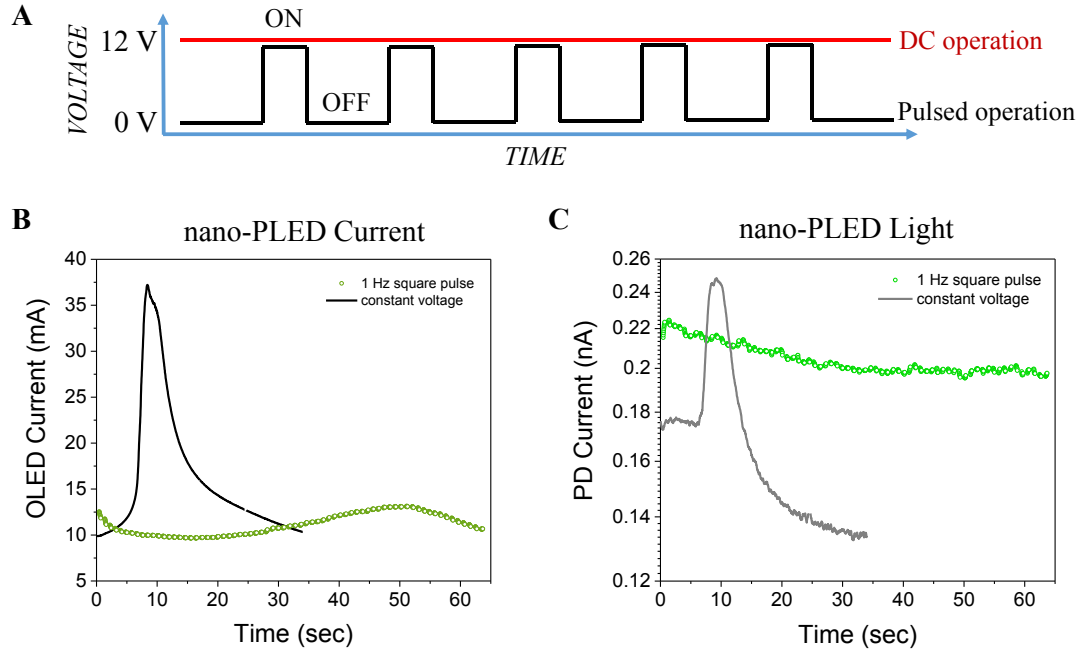


Figure 6.10: (A) Schematic of two modes of operation for the nano-LED device. (B) I-t plot of Nano-LED current at a constant 12 V and pulsed operation. (C) Photodiode response to the light emitted from the nano-LED under constant 12 V and pulsed operation.

6.8 Effect of Electric Field on the Nano-Gaps

To understand the effect of the high electrical field applied across the nanogap electrodes, optical and SEM micrographs of the nanogap were taken before and after device operation. When first created the nanogap has an average size ~ 15 nm if a device is biased at low voltages, < 3 V (though this value is material dependent), the gap is able to keep its shape and dimension. As the nanogap is biased at higher voltages > 3 V this changes and you can see this in the voltage sweep as the I-V characteristics are no longer diode like. This is the case for all devices created by a-Lith to date (with breakdown material dependent) but most applications including Schottky diodes and photodiodes are operated at a low voltage so do not have high fields distorting the shape of the electrodes. An application that has used this to its advantage is memristors which utilises the deformation in shape at high fields to change the state of the

electrodes from a low resistive state to a high resistive state [130]. This has shown to be reversible over 50 cycles. The a-Lith n-PLEDS also have to be operated at high voltages to allow for light emission, however degradation of the electrodes can cause irreversible breakdown. The following subsections will explore the effect of high fields on the n-PLEDs.

6.8.1 Nanogap Before Light Emission

When the n-PLED devices are swept between ± 3 V, diode characteristics are seen with injection from the Au into F8T2. The SEM micrograph of the device (Figure 6.11) shows no deformation of the nanogap with the second deposited metal (Au) following the shape of the first deposited metal (Al). After these low fields the shape of the nanogap has not deviated from its initial form/shape.

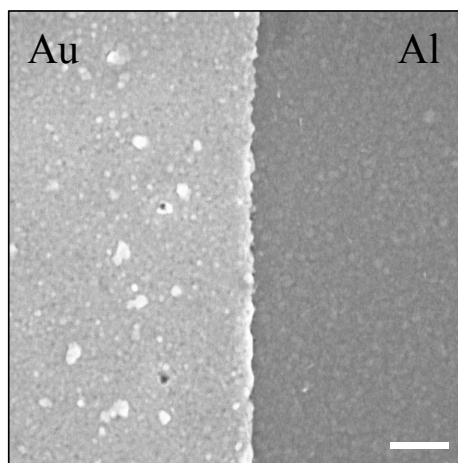


Figure 6.11: SEM of a-Lith electrode with F8T2 prior to application of high voltage. Scale Bar: 300 nm.

6.8.2 Nanogap After Light Emission

An optical micrograph and SEM image were taken just after light emission was observed from an n-PLED (Figure 6.12). From the optical micrograph little appears to have changed apart from the top corner of the electrode where there may be slight damage. The SEM image shows that there is substantial damage at the nanogap interface with both the electrode and polymer being damaged/melted. It appears that the high field has caused a high temperature that has damaged the electrodes. This damage does not extend to the bulk of either of the electrodes, most probably because the electric field is smaller further away from the nanogap. The device will continue to work under these conditions with light being emitted however if the device is

placed under more stress (high voltages over a long period) the electrodes will breakdown and the device will fail.

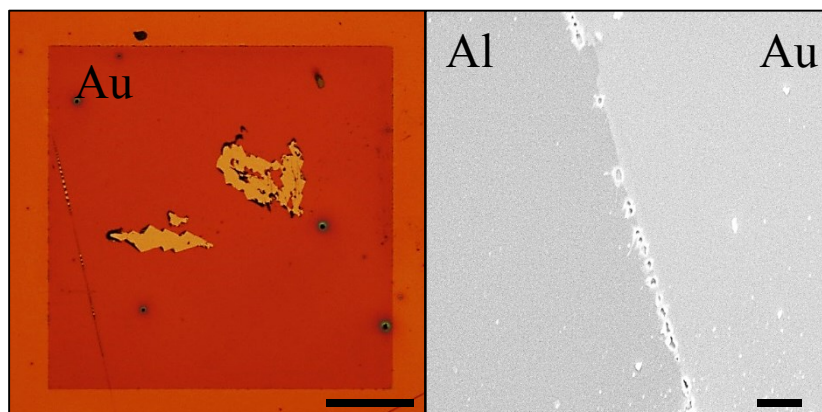


Figure 6.12: Optical micrograph and SEM of nanogap with F8T2 after light emission. Scale bars 200 μ m and 2 μ m respectively.

6.8.3 Nanogap After Full Breakdown

When the device is put under too high a voltage, usually above 17 V the nanogap is severely damaged. As shown in the optical micrograph in Figure 6.13 the damage can be seen across the whole nanogap area and the SEM images shows high damage along the nanogap with most of the nanogap destroyed. This device will no longer work as an OLED and shows no conduction even at higher voltages, due to the electrode damage.

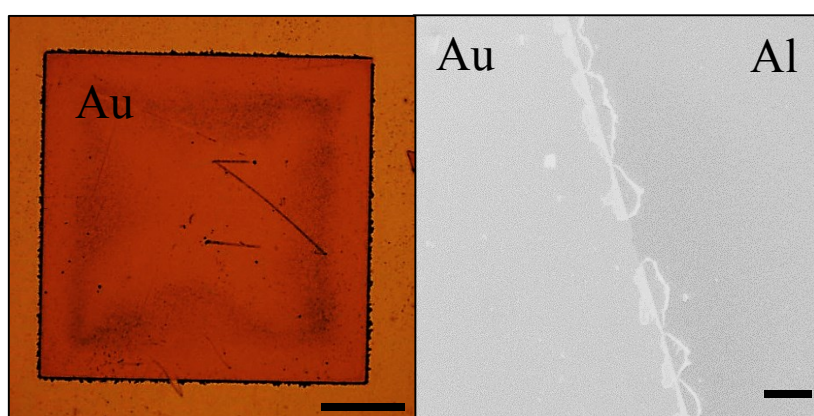


Figure 6.13: Optical micrograph and SEM of nanogap after breakdown. Scale bars 200 μ m and 50 μ m respectively.

6.8.4 Emission from the Nanogap

There is an additional fourth state that the electrodes can fall into. At higher fields usually around 12 V, instead of completely breaking down, high current light emission takes place independent of the emissive material used (Figure 6.14). This light emission is seen in the n-PLED but is not due to the material as this light emission has been seen in multiple materials and even within the empty nanogap. This light can be held at a constant voltage for over 20 mins. The optical micrograph of the electrodes shows slight damage to the electrodes, with less damage than the full breakdown of the electrodes, but more damage than after light emission. The SEM micrographs show an unusual state, where both electrodes have become damaged due to high field, but instead of completely melting away the two electrodes have become intermixed causing filaments that cause light emission via a currently unknown mechanism. The light emission may be the result of thermionic emission or a plasma-like discharge process. A more detailed study is needed to confirm the origin of this light emission, but is beyond the scope of this thesis.

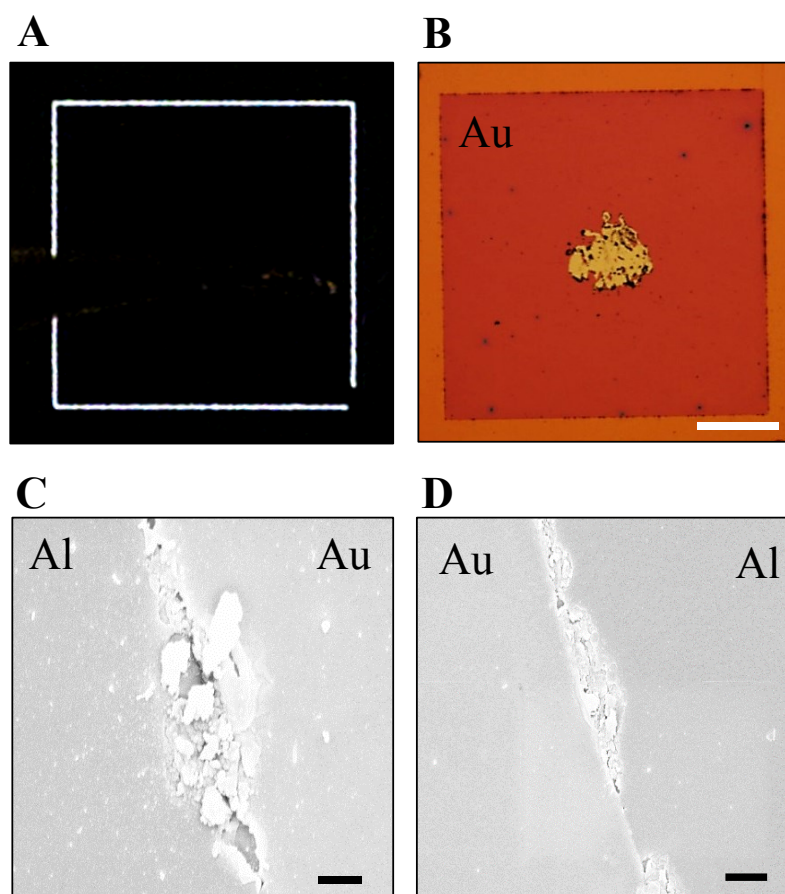


Figure 6.14: Optical micrographs of (A) white light emission from the nanogap and (B) effect of this emission on the nanogap electrodes. Scale bar: 200 μm and (C and D) SEMs of the nanogap after the light emission. Scale bars: 1 μm and 2 μm respectively.

6.9 N-PLEDs on Plastic Substrates

To produce n-PLED devices on plastic, the a-Lith procedure was carried out on ultra-smooth polyethylene terephthalate (PET) films (purchased from DuPont) in the same manner as previous substrates with an added annealing step of 140° C for 30 mins before the peel step to increase adhesion of the second metal (more detail in section 4.5). Figure 6.15A shows the a-Lith structures created on PET and Figure 6.15B shows the device in measurement setup. The interdigitated fingers are Au and they are surrounded by a common Al electrode. The light emission occurred at 6.5-10V, as with the glass substrates, with the optical micrograph of the light emission taken at 10 V (Figure 6.15C). Here the light emission is continuous and consistent with the results shown on glass, showing the flexibility of a-Lith to create nano-devices on a variety of different substrates. The bending of the substrate was on the macro scale and appears to have had little effect on the nanoscale devices as light emission is still seen under substrate stress. To the best of the author's knowledge this is the first example of a flexible n-PLED created on plastic.

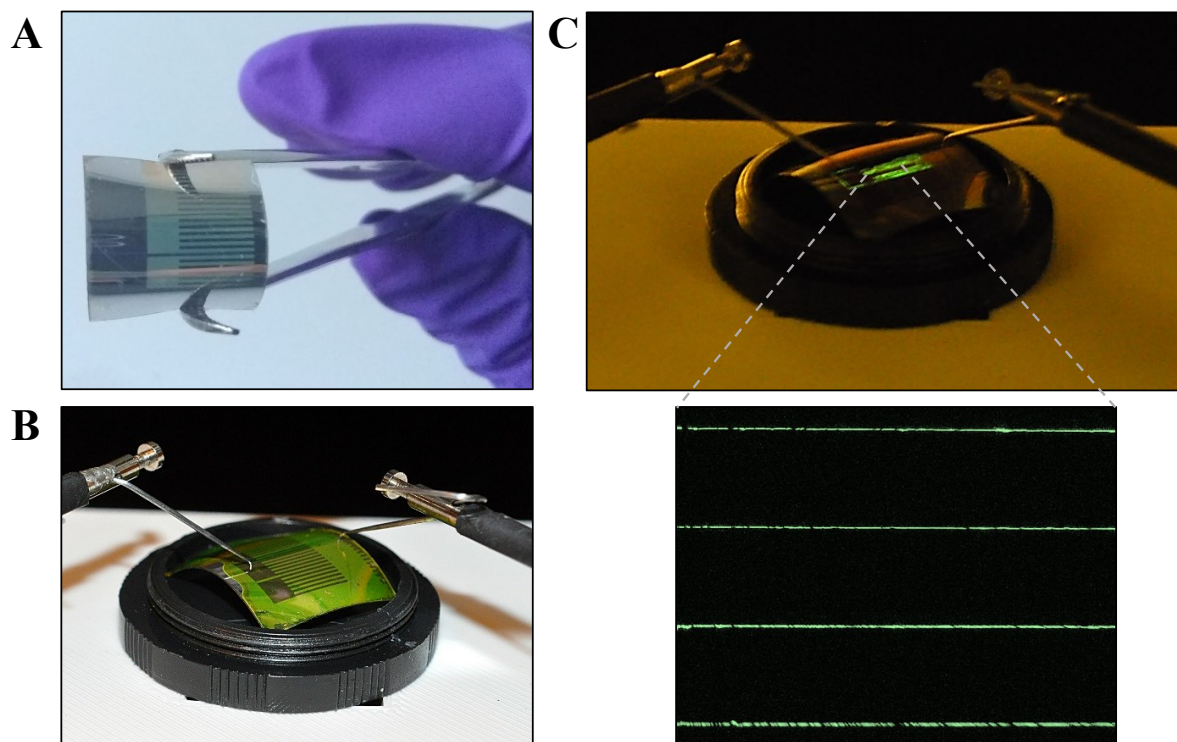


Figure 6.15: Photographs of plastic n-PLED samples: (A) a-Lith fabricated Al/Au nanogap structures on PET substrate. (B) F8T2 light emitting polymer spin coated on top of this substrate placed in the n-PLED measurement setup. (C) Light emission from the F8T2 n-PLED device under flexing conditions and respective optical micrograph of the emitted light from the nanogap region. Substrate 20mmx20mm.

6.10 Low-Voltage Diode Characterisation

Due to the small dimension of the a-Lith electrodes, high quality polymer diodes can be created. Investigating the characteristics of these diodes at low voltage, before they breakdown or emit is interesting. Presented in the next section is device characterisation of the F8T2 diode in the < 3 V operating regime where the nanogap is yet undamaged.

Nanogap diodes are very interesting as a test bed for materials and are used for fast switching applications. In principle, a-Lith made diodes allow for reduced switching speeds due to the low dimensionality and reduced RC constants. Additionally, their planar architecture helps to avoid electrical shorts between the electrodes; a major issue in conventional sandwich structures which lead to increases in leakage current. Furthermore, due to the nanogap nature of the active device area, high performance can be achieved even when low-mobility materials, such as disordered organic semiconductors, are employed.

Devices based on F8T2 are expected to behave as diodes due to the presence of a significant energy barrier between the LUMO of F8T2 and Al (Schottky contact) as well as the significantly lower injection barrier for holes injected from the Au electrode to the HOMO level (Ohmic contact). Figure 6.15 shows typical I-V characteristics for a F8T2-based nanogap diode. The device structure is similar to that used for n-PLED applications. However, here no light emission is observed from the nanogap due to the unipolar nature of the devices and the assumed lack of radiative carrier recombination. In the reverse bias region the off currents are very low and close to the limits of our measurement setup. The devices prepared on the square electrodes mentioned previously have a rectification ratio of $\approx 10^4$ at 3 V with a device turn on of ≈ 0.7 V. The low current seen below 0.7 V is due to the difference in the two electrode WFs which creates an intrinsic barrier to hole injection in the polymer. When the bias exceeds 0.7 V, charge carriers can overcome the barrier and the device switches on. The dramatic increase in current between 0.7 and 1.7 V is due to the potential barrier present between the Au and F8T2 that reduces upon application of the required bias. This rate of increase then decreases, beyond which the current is dependent on the transport properties of the polymer material itself. The barrier to injection due to the electrode WF mismatch can be reduced by modification of its WF.

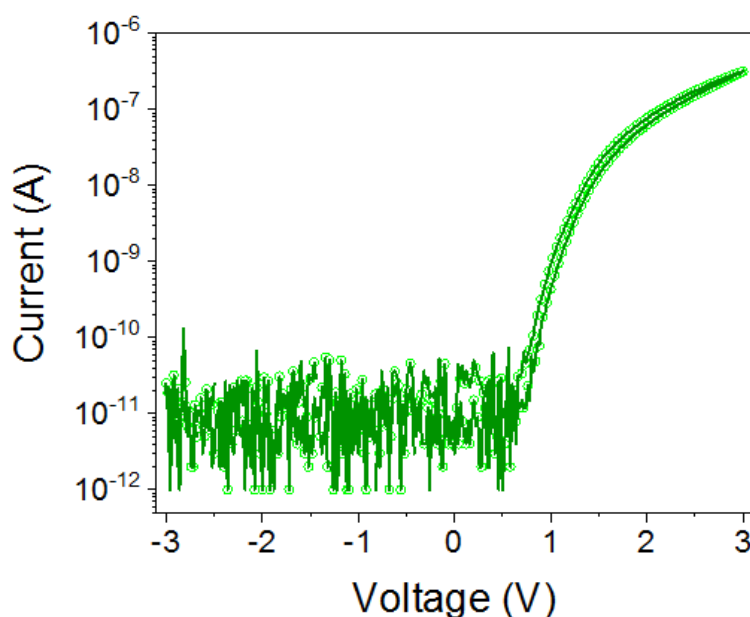


Figure 6.16: Semi-Log plot of I-V characteristics for F8T2 diode.

6.10.1 Electrode Workfunction Modification

To improve diode characteristics, often hole or electron transport layers will be used, reducing the charge injection barrier [265]. For planar structures this can be an issue as the layers are normally deposited as thin films and so a layer of the material would appear on both electrodes (Figure 6.17A) which can reduce device performance. Using a SAM that can selectively attach to one of the electrodes (Figure 6.17B) removes this problem and allows for modification of individual electrodes [99]. SAMs have been used in many previous instances to change the injection properties of electrodes [271]–[275]. This occurs because of the dipole moment of a SAM affecting the WF of a material. SAMs can also affect the morphology of a material which can then affect charge transport.

Thiol based SAMs are used because sulphur binds to Au covalently via the sulfhydryl group in thiols [276]. These thiols can be functionalised with specific molecules to affect the work function of a metal. The materials chosen in this study are pentafluorobenzenethiol (PFBT) and 4- (dimethylamino)benzenethiol (DABT). The structures of both are shown in the inset of Figure 6.18. These two thiol based SAMs should affect the Au electrodes in very different ways. PFBT, which has been used extensively to improve charge injection into p-type materials, would be expected to improve hole injection into the device by shifting the work function of Au to higher values and hence making the Au/F8T2 contact more Ohmic

[272][277]. DABT should degrade the Ohmic character of the Au contact by reducing the work function of the electrode, increasing the turn-on voltage of the device [271]. For this reason DABT has been shown to improve the performance of n-type devices when Au electrodes are used [278].

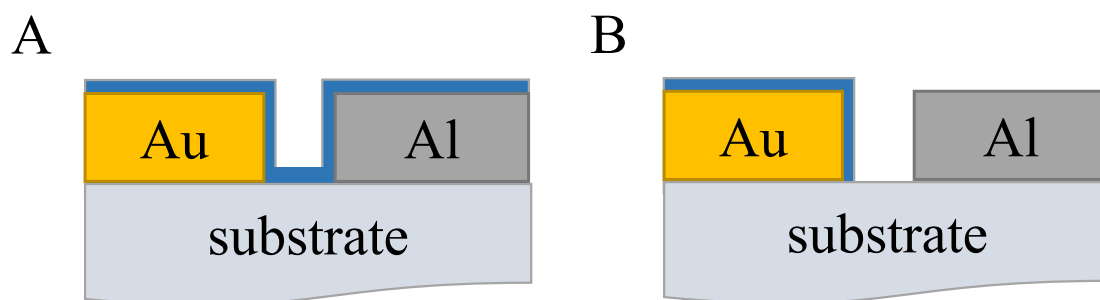


Figure 6.17: Schematic illustration of coplanar device depicting (A) a commonly solution-processed interfacial layer and (B) selective SAM-functionalization of electrodes.

To create the modified electrodes, first PFBT (Sigma Aldrich) was diluted in 2-isopropanol and DABT dissolved in acetonitrile at 1 mg/ml. The solutions were left to stir for 2 hours and then a-Lith Al/Au electrodes were immersed in the solutions for 30 mins. The samples were then rinsed with the respective solvent to remove any excess SAM. The electrodes were placed in a UV ozone for 5 mins prior to immersion along with a reference sample. F8T2 was then spin coated on the samples as previously described. The reference sample was left in air for 15 mins prior to spin coating to reduce the effect the UV ozone had on the device performance, so the devices could be more comparable to the SAM treated devices. This varies from previous samples which were spin coated straight after removal from the UV Ozone.

The effect of the SAMs on the Au electrode was investigated via kelvin probe measurements. DABT was shown to reduce the WF of Au to 4.4 eV, whereas PFBT increases it to 5.5 eV. The homo level of F8T2 is near 5.4 eV suggesting that the DABT will increase the metal/semiconductor barrier whilst PFBT will reduce this barrier increasing charge injection.

The semi-log I-V plot of the devices with different electrode treatment (Figure 6.18) shows a striking difference in the diode performance. The reference sample has a turn on voltage of 1 V and a current of 0.1 μA at 3 V. The PFBT diode shows a reduction in the turn-on voltage to 0.75 V and an increase in the forward current to 0.15 μA at 3 V proving that the PFBT has made injection from the Au electrode more Ohmic. The DABT device has an increased turn-on of ~ 1.25 V with a reduction in current of over an order of magnitude, indicating that this

SAM has indeed made the Au/F8T2 current injection worse. The results reveal the vast difference the SAM treatment of the injecting electrodes can have on device performance, even in the nano-scale dimensions.

It should be noted that the reference device has a higher turn-on and lower current than that of the UV Ozone treated devices in the previous section showing the large effect this has on the devices. Exposure to UV Ozone deepens the WF of the Au electrode by removing surface contaminants allowing for more favourable injection into the HOMO level of the polymer. The reason that UV ozone is not favourable for device fabrication is because its effects reduce over time with the Au WF returning to shallower values. Modification layers prove far more stable and so are more useful for real world applications.

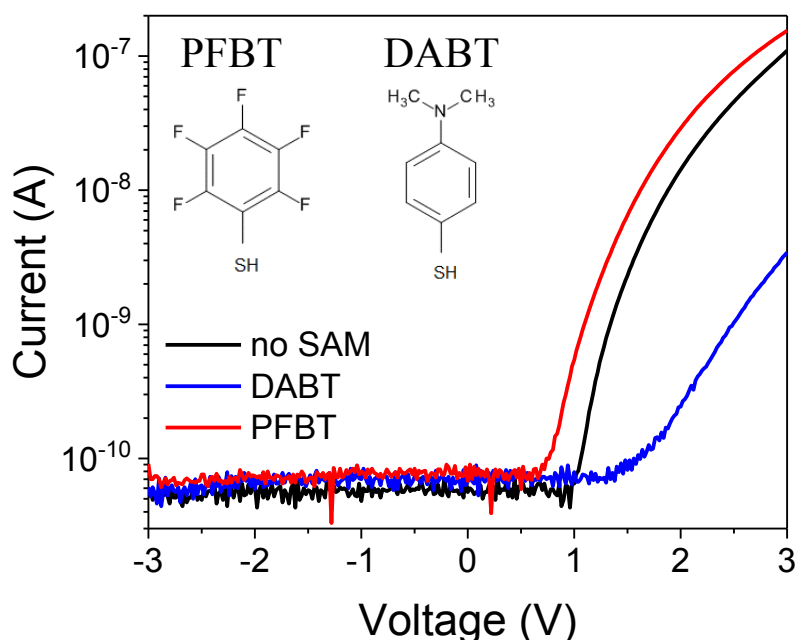


Figure 6.18: Semi-log plot of I-V characteristics without and with SAM-functionalization of Au electrode.

6.11 Conclusions

In summary, a-Lith was used to create single layer nanoscale PLEDs. First polymer devices were created using coplanar asymmetric nanogap electrodes and state of the art electroluminescent polymers; F8T2, F8BT and MDMO-PPV to create green, yellow-green and red LEDs respectively showing the versatility of the a-Lith technique in creating n-PLEDs. Next varying width devices based on the green-emitting polymer F8T2, were fabricated on

glass. Despite the active area being constrained within the <15 nm nanogap channel, the large aspect ratio of the electrodes attained upon increasing the width of device from 4 mm to 20 cm allowed for greater brightness levels.

The time response of the devices was found to be 210 μ s which is fast enough to be used in display technologies. Also shown was the stability of the devices when operated using a pulsed voltage instead of a constant voltage. The pulsing allowed for higher voltages to be placed across the electrodes without device degradation.

The effect of the high fields on the electrodes was discussed indicating the damaged caused by high voltages even when the device is under light emission. No defects were seen at low voltages (<3 V) but as the devices started to emit light electrodes were shown to be damaged. At higher voltages of $\approx$ 17 V the devices where completely destroyed, with no measurable current. Another type of the devices where light emission from the empty nanogap was observed was also presented and briefly discussed.

The n-PLEDs fabricated on PET show a stability under bending with a constant light emission seen. These results pave the way to the high throughput and low cost fabrication of arrays of nanoscale light sources on flexible substrates.

Diode characteristics and modification of the F8T2 devices was also explored. The low dimensionality of the devices allow for good device performance. This performance can be improved using workfunction modifying SAMs such as PFBT, which is known to reduce the barrier to injection from the Au as well as the turn on voltage of the device.

Future work could include using the a-Lith electrodes as test beds for novel light emitting nanomaterials, such as quantum dots [140] and 2D materials [279], which usually require coplanar rather than vertical electrodes. Following the initial work on the use of SAMs to improve charge injection, study of other SAMs for HTL and ETL layers to improve injection into the devices would also be interesting, with focus on improving electron injection from Al to the LUMO energy of organic materials.

Chapter 7

Conclusions and Outlook

7.1 Summary

For next generation devices that can be fabricated on large areas it is clear that new patterning technologies are needed. Not only do the techniques need to allow for low cost manufacture but also have to create high performance devices. Nanogap electrodes have the ability to do this but as shown in chapter 2 progress is still needed, with most technologies capable of this high resolution unsuitable for up-scaling. An interesting sector of research that may allow for this is are techniques that utilises changing of adhesion forces for the addition and subtraction of material. One such technique is adhesion lithography (a-Lith) which can not only create electrodes separated by a nanogap but can generate each electrode from dissimilar metals opening up a multitude of device applications. It has been utilised in this thesis for optoelectronics.

The first experimental chapter (chapter 4) focused on the optimisation of the a-Lith technique. The technique relies on a selective self-assembled monolayer changing the adhesive properties of a patterned metal and using this to selectively remove a second metal. It begins by explaining that whilst the electrodes created via a-Lith have an incredibly high yield (shown to be 97% when 400 devices were tested), when devices are created there are inconsistencies in

device performance showing optimisation is required. One reason suggested is change in the gap size and uniformity, dictated by the fracture mechanics of the second metal and the grain sizes of both metals. Therefore efforts were undertaken to control and understand the effect of these factors. First the grain size of the first metal was controlled via variations in the deposition rate (0.01-1 nm/s). As the deposition increased the grain size of the metal decreased. This caused greater uniformity in the nanogap and reduced variation between devices. The workfunction of the metal was also effected with decreasing values as the deposition increased with grain and roughness changes cited as the reason for this. Next the deposition rate of the second electrode was varied between 0.01- 0.1 nm/s, there was little change in the grain size and roughness of the metal but the nanogaps formed using higher deposition rates were more uniform suggesting that the increased rate allowed for the second metal to adhere more strongly to the surface, increasing the adhesion force and so reducing the impact of the cohesion of the metal to itself. Again the higher deposition rates caused the workfunction of the metal to decrease and there was a reduced variation in devices.

The effect of the change of thickness of the electrodes was also investigated. First both metals were varied at the same time from 40 nm-120nm. Here, as the thickness of the devices was increased the gap between the electrodes increased with a gap size of ~90 nm for the 120 nm thickness electrodes. This is due to a number of factors, including increased cohesion in the second metal making it more difficult to fracture. Then only the thickness of the first metal was increased which further widened the nanogap due to increased stress across the second metal due to the increase in height difference between the two metals. Last the second metal thickness was varied whilst the first metal was kept at 40 nm. Here the first metal did not allow for successful fracturing of the second metal, causing the second metal to partially remain on top of it and led to shorts across the nanogap.

Next improving the reproducibility of a-Lith on PET was investigated. It was shown that annealing the substrate before the peeling step allowed for a greater success rate in the creation of the nanogap electrodes. This was due to the intermixing of the metals with the PET as it was taken past its glass transition temperature.

This chapter was able to show that although the a-Lith technique can have a high yield, optimisation of the metal deposition is the key to repeatedly controlling the nanogap and to reduce variation in devices. It also showed that the control of adhesion forces is key to the success of the technique on any substrate.

Chapter 5 demonstrated the application of a-Lith in the creation of high performance photodiodes, with the devices created expected to have a high sensitivity and fast response times due to the small separation between the electrodes. First CuSCN was used to create solution processed deep ultraviolet photodiodes. CuSCN devices measured in the dark had a turn-on voltage of ~ 0.6 V and a rectification ratio (RR) of 10^3 at ± 2 V. This is ascribed to the ultra-low dimensionality and the co-planar architecture of the nanogap electrodes, which help minimise the series resistance. These were shown to have a photosensitivity (PS) of 7 when illuminated with a 280 nm light at low optical power ($0.2 \mu\text{W cm}^{-2}$). This value increase to 719 at an optical power density of $220 \mu\text{W cm}^{-2}$. The responsivity (R) at this power was 79 which far outperforms any other solution processed devices and is only surpassed by a couple of reported devices created using complicated fabrication techniques. Increasing the width of the devices from 1 to 10 μm increased the on-current but still allowed for reduced dark currents amplifying the PS to 4434 but decreasing R to 49 due to its dependence on device area. The response times of this device was however, not as fast as expected (on the order of seconds) attributed to defects within the material and possibly due to the semi ionic nature of CuSCN.

Ultraviolet photodiodes were created using ZnO. These devices showed a good rectification ratio (10^4 at ± 2 V) with an increase in reverse current of over 2 orders of magnitude when the device is illuminated at 390 nm light at 7 mW cm^{-2} . The mechanism for this is photochemical, with the increase of current caused by the desorption of oxygen. This however, greatly increases device response times with fall times on the order of hours showing that this device is not suitable for rapid photodetection though may be useful for continual monitoring.

PTB7-Th was utilised for visible light detection in Schottky and heterojunction (with PCBM) configurations. The heterojunction devices had an R of 33 A/W , a detectivity (D) of 6×10^{13} Jones and response times of 1.3ms. The Schottky diode had a low dark current as compared to the heterojunction device but due to reduced charge separation the responsivity was low. The response times of the device were expected to be higher but low signal to noise ratio made it impossible to accurately determine.

The last experimental chapter (chapter 6) saw a-Lith be utilised in nanoscale PLEDs. State of the art electroluminescent polymers; F8T2, F8BT and MDMO-PPV were deposited on a-Lith electrodes to create green, yellow-green and red LEDs respectively. Devices based on the green-emitting polymer F8T2 were studied more in-depth. The PL and EL from the nanogap showed a slight red shift in the emitted light with confinement the most likely cause of this.

The width of the devices were then scaled up from 4 mm to 20 cm allowing for greater brightness. The time response of the devices was found to be 210 μ s. Pulsing the diodes with a high voltage (10 V) also showed an increased device stability as compared to a constant applied voltage where devices degraded rapidly. The effect of the high fields on the a-Lith electrodes was also investigated. This showed that no damage was seen in the devices at voltages <3 V but as the devices started to emit light, electrodes had been affected by the high field with sections of the electrodes appearing melted. At $\approx$ 17 V the devices were completely destroyed with the electrodes separated by microns. Light emission from the empty nanogap can be seen at voltages between that of complete electrode failure and light emission most likely due to thermionic emission or a plasma-like discharge. F8T2 was also used to create n-PLEDs fabricated on PET. These devices demonstrated stability under bending with constant light emission observed.

7.2 Future Work

The work in this thesis shows the capabilities a-Lith in different applications. The simplicity of the technique allows for high quality nanogaps to be created from dissimilar metals which in itself is an immense feat. This thesis has shown that improvement in adhesion and metal structure can help create more uniform nanogaps. To further improve the technique to allow for less variation in the nanogap and for the technique to be more suited to industrial applications other metal deposition techniques need to be explored. One favoured by industry is sputtering, this technique would allow for reduced grain sizes and improved adhesion of the metal to the substrate due to increase in collision force between the metal and the substrate. It would however, have to be adapted for the second metal to mitigate any damage it could cause to the SAM due to this increased collision force. Modelling of the metal fracture mechanics and adhesion forces that act on the a-Lith electrodes during their fabrication could help with this. Changing the patterning technique for the first metal such as nanoimprint lithography would help in up-scaling a-Lith. Replacing the second metal with a cheaper alternative to gold would also help with this and reduce manufacturing costs. Finally development of the technique on plastic substrates to increase yield and allow for repeatable device fabrication would open up a vast number of device applications and allows for the possibility of roll to roll manufacture.

For the photodiode devices, using surface modification layers such as SAMs will allow for improved charge separation and better device performance. Using more uniform materials that are not solution processed may help enhance device response times due to the reduction of defects, the use of an encapsulate may also help with this and have the added benefit of increasing the air stability of the devices. Also for many device applications, testing devices in harsh environments is important. Further to this, materials that are sensitive to other areas of the electromagnetic spectrum (e.g. IR) using other state of the art materials would be interesting to investigate.

Following the initial work on the use of SAMs to improve charge injection, study of other SAMs for HTL and ETL layers to improve injection into the devices would also be interesting, with focus on improving electron injection from Al to the LUMO energy of organic materials. This could also be improved by using electroluminescent materials and metals that have energy levels and work functions that better match. The n-PLEDS have also shown that the a-Lith electrodes are a novel test bed for new light emitting nanomaterials and could be used to help characterise them.

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Appendix A: List of Publications

G. Wyatt-Moon, D. G. Georgiadou, J. Semple, T. D. Anthopoulos, “Deep-ultraviolet copper (I) thiocyanate (CuSCN) photodetectors based on co-planar nanogap asymmetric electrodes fabricated via adhesion lithography” ACS Applied Materials and Interfaces, vol. 9, no 48, pp 41965-41972, 2017

J. Semple, D. G. Georgiadou, **G. Wyatt-Moon**, G. H. Gelinck, and T. D. Anthopoulos, “Flexible Diodes for Radio Frequency (RF) Electronics: A Materials Perspective” Semiconductor Science and Technology, vol. 32, no. 123002, 2017.

J. Semple, **G. Wyatt-Moon**, D. G. Georgiadou, M. A. McLachlan, and T. D. Anthopoulos, “Semiconductor-Free Nonvolatile Resistive Switching Memory Devices Based on Metal Nanogaps Fabricated on Flexible Substrates via Adhesion Lithography,” IEEE Trans. Electron Devices, vol. 64, no. 5, p. 1973, 2017.

I. Isakov, H. Faber, M. Grell, **G. Wyatt-Moon**, N. Pliatsikas, T. Kehagias, G. P. Dimitrakopoulos, P. P. Patsalas, R. Li, and T. D. Anthopoulos, “Exploring the Leidenfrost Effect for the Deposition of High-Quality In₂O₃ Layers via Spray Pyrolysis at Low Temperatures and Their Application in High Electron Mobility Transistors” Advanced. Functional Materials, vol. 27, no. 22, p. 1606407, 2017.

A. F. Paterson, N. D. Treat, W. Zhang, Z. Fei, **G. Wyatt-Moon**, H. Faber, G. Vourlias, P. A. Patsalas, O. Solomeshch, N. Tessler, M. Heeney, and T. D. Anthopoulos, “Small Molecule/Polymer Blend Organic Transistors with Hole Mobility Exceeding 13 cm² V⁻¹ s⁻¹” Advanced Materials, vol. 28, no. 35, pp. 7791–7798, 2016.

J. Semple, D. G. Georgiadou, **G. Wyatt-Moon**, M. Yoon, A. Seitkhan, E. Yengel, S. Rossbauer, F. Bottacchi, M. A. McLachlan, D. C. C. Bradley, T. D. Anthopoulos, “Large-area plastic nanogap electronics enabled by adhesion lithography” npj Flexible Electronics vol. 18, no 2, 2018

G. Wyatt-Moon, D. G. Georgiadou, A. Zoladek-Lemanczyk, F. A. Castro, T. D. Anthopoulos, “Single-layer co-planar nanoscale polymer light emitting diodes fabricated via adhesion lithography on flexible substrates” Journal of Physics: Materials, Accepted 2018

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