Materials and processes to enable polymeric waveguide integration on flexible substrates

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MATERIALS AND PROCESSES
TO ENABLE POLYMERIC WAVEGUIDE INTEGRATION
ON FLEXIBLE SUBSTRATES

by

Tze Yang Hin

Ph.D. Thesis
Submitted in partial fulfilment of the requirements for the award of
Doctoral of Philosophy of Loughborough University

November 2009

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### Glossary

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<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
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<tr>
<td>CTE</td>
<td>Coefficient of Thermal Expansion</td>
</tr>
<tr>
<td>DCB</td>
<td>Double Cantilever Beam</td>
</tr>
<tr>
<td>EOCB</td>
<td>Electrical-optical Circuit Board</td>
</tr>
<tr>
<td>ESA</td>
<td>Electrostatic-induced Self Assembly</td>
</tr>
<tr>
<td>FEGSEM</td>
<td>Field Emission Gun Scanning Electron Microscope</td>
</tr>
<tr>
<td>Gbps</td>
<td>Giga bits per second</td>
</tr>
<tr>
<td>LCP</td>
<td>Liquid Crystal Polymer</td>
</tr>
<tr>
<td>MCM</td>
<td>Multi-Chip-Module</td>
</tr>
<tr>
<td>NA</td>
<td>Numerical Aperture</td>
</tr>
<tr>
<td>NIR</td>
<td>Near Infrared Region</td>
</tr>
<tr>
<td>NOA</td>
<td>Norland Optical Adhesive</td>
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<tr>
<td>PCB</td>
<td>Printed Circuit Board</td>
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<tr>
<td>PD</td>
<td>Photodetector</td>
</tr>
<tr>
<td>PGMEA</td>
<td>Propylene glycol monomethyl ether acetate</td>
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<tr>
<td>RI</td>
<td>Refractive Index</td>
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<tr>
<td>RIE</td>
<td>Reactive Ion Etching</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<tr>
<td>SIMS</td>
<td>Secondary Ions Mass Spectrometry</td>
</tr>
<tr>
<td>SWLI</td>
<td>Scanning White Light Interferometer</td>
</tr>
<tr>
<td>ToF-SIMS</td>
<td>Time-of-Flight Secondary Ions Mass Spectrometry</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra violet</td>
</tr>
<tr>
<td>VCSEL</td>
<td>Vertical Cavity Surface Emitting Laser</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectrometry</td>
</tr>
<tr>
<td>PCB</td>
<td>Printed Circuit Board</td>
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Abstract

Polymeric waveguide-on-flex has the potential to replace complex and costly light-turning devices in optoelectronic applications. As light signals are propagated and confined through the definition of core-cladding interface, the light guiding structure is required to adhere well and ensure long term interfacial stability. This thesis addresses the gap that has emerged in the fundamental material issues such as the polymeric optical waveguide materials deposited on the flexible substrates. In addition, this thesis investigates the feasibility of a new approach using electrostatic-induced lithography in micro-patterning of polymer, in optical waveguide fabrication.

Plasma treatment is applied to enhance interfacial adhesion between flex substrates and optical cladding layers. The modified flex surfaces of polyimide KaptonHN™ and liquid crystal polymer Vecstar™ materials are characterised. In addition, sonochemical surface treatment is evaluated on these flexible substrates.

ToF-SIMS depth profiling has confirmed the interface reaction mechanisms where it has shown that plasma treatment increases the interfacial interpenetration. The larger interfacial width increases the possible entanglement mechanism between the polymer chains. These results, together with the double cantilever beam testing, indicate the strengthening of the polymeric interface upon plasma treatment, which is essential for long term optical and mechanical stability of waveguide-on-flex applications.

A new method of micro-patterning of polymer material has been adopted for fabricating multimode waveguide-on-flex. The method, using an electrostatic-induced lithography, is developed to produce 50 µm x 50 µm arrays of polysiloxane Lightlink™ waveguide on flex. This thesis looks at various process recipes of the technique and reports the pattern formation of polymeric optical core. By adjusting the spin-coated liquid core thickness, pre-bake condition, UV exposure and applied voltage, the aspect ratio and profile of the optical core microstructure can be varied. As the electrostatic pressure overcoming the surface tension of spin-coated waveguide material induces the optical core formation, the core’s structure is smooth, making it ideal for low scattering loss waveguide. The propagation loss of fabricated waveguide is measured at 1.97 dB/cm at 850 nm wavelength. The result
shows that the use of electrostatic-induced lithography in optical polymer is a promising approach for low cost and low temperature (<150 °C) processing at back end optical-electrical integrated circuitry assembly.

**Keywords:** Polymer waveguide, flexible substrate, surface properties, plasma treatment, depth profiling, electrostatic-induced lithography.
Chapter 1
INTRODUCTION

1.1 The development of polymeric optical waveguide

With the introduction of multi-core processors, computing performance based on transistors and logic gates continues to grow according to Moore’s law or “More-than-Moore’s” law. As the number of components per chip, the number of chips per board and the degree of functional integration continue to increase, electrical interconnects based on copper traces are already facing fundamental bottlenecks such as speed, bandwidth, packaging, fan-out and power dissipation [1]. The expectation of replacing electrical signal lines in the body of computing devices by optical interconnection that can transfer data at very high rate is growing [2]. This expectation grows together with the recent increase of communication density, for instance the handling of graphical and video data with high quality and resolution. It is expected that the “cost per Gbps” of optical packaging will be drastically below the costs for electrical printed circuit board (PCB) at higher data rates due to the cost for layered materials and protective measures against electromagnetic interference that may result in signal distortion [3]. Recently, the development of optical waveguide-on-flex to replace fiber flexes offers an attractive alternative to optical interconnection [4]. Waveguide-on-flex allows the folding and bending of light channels without the need for a complex, costly and inefficient light turning device. Such optical flexible circuit has the advantage of being assembled in the final assembly process and is replaceable in case of failure. Along with the surge in demand of smaller, lighter yet smarter mobile devices such as smart phones and netbooks, the waveguide-on-flex realizes fast data transfer and fits in the narrow space of small mobile devices.

The first part of this chapter reviews the fundamental reasons for the demand for optical interconnection, establishes the optical interconnection hierarchy and provides an overview of a low cost polymer solution in optical waveguide
technology. This is followed by setting out the scope of this research and identifying the area of contribution to the body of knowledge.

1.1.1 Limitation of electrical interconnection

Problems with scaling electrical interconnections have been known for some time. In telecommunication applications, long distance traffic has moved away from electrical lines because the loss at high frequencies in electrical wires is too high. Inside a computer system, the electrical buses that carry information within the system run at rates much slower than the clock rate of the chips due to the physical limitation of electrical interconnection. The fundamental physical differences in optical signal compared to electrical signal as listed in Table 1.1 are higher frequency, shorter wavelength and larger photon energy [1]. These fundamental differences are translated into the high performance of optical interconnection in terms of high speed, high density and low loss signals.

Table 1.1 Physical difference between electrical and optical signal [1].

<table>
<thead>
<tr>
<th>Physical difference</th>
<th>Electronics</th>
<th>Optics</th>
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<tr>
<td>Wavelength</td>
<td>3 cm – 30 m</td>
<td>500 nm</td>
</tr>
<tr>
<td>Frequency</td>
<td>10 MHz – 10 GHz</td>
<td>500 THz</td>
</tr>
<tr>
<td>Photon energy</td>
<td>40 neV – 40 µeV</td>
<td>2 eV</td>
</tr>
</tbody>
</table>

Electrical interconnections have very substantial problems of signal distortion at high modulation frequencies. The distortion is a consequence of the signal loss at higher frequencies. In order to maintain signal integrity, the signal speed is limited by both circuit board material losses and skin effect losses [5]. On the other hand, the carrier frequency of light is very high compared to any frequency we can modulate and without frequency dependent losses. The loss in optical materials can be extremely low, e.g., 0.02 dB/cm in optical polymer. This leads to negligible distance dependent loss over the scale of interconnect distances. In addition, because of the much higher carrier frequency, optics is not vulnerable to frequency-dependent cross-talk which is a critical factor for high speed and high density interconnections. Recent development in wavelength-division multiplexing and
VCSEL arrays has amplified the application of high carrier frequency in the optical signal. As the wavelength of light is short, in the visible and infrared length scale, it is possible to image multiple sources to multiple receivers. Hence, an optical system would not have the wiring congestion problem that occurs in electrical systems.

The most important consequence of the large photon energy of light is that signals are transmitted through photon detection without any direct electrical connection with the light source. The photons carry no information about the current and voltage in the light source circuit, a phenomenon known as voltage-isolation. This provides perfect electrical isolation between the two circuits and solves an important problem in electrical systems where an impedance transformer is required for communication between two high impedance electrical logic devices via a low impedance interconnection medium.

It is clear from the physical differences that optics becomes increasingly attractive at high bit rates and higher interconnect densities at both chip and board levels. However, the realisation of optical interconnection goes well beyond the physics and lies at the material and process challenges.

1.1.2 The optical system hierarchy

The fundamental reasons and arguments for introducing optical interconnects have been reviewed in the last section. Whilst optical communication with fiber-optic has been the interconnect medium of choice for long distance links, recent research and development efforts have been focusing in intra-system optical interconnects. This section establishes the optical interconnection hierarchy, to lay out the practical problem statement for the subsequent work. Researchers in IBM Zurich have shown the application roadmap of optical interconnect technology, indicating the trend towards ever shorter optical links and a higher degree of integration in electro-optical packaging [6]. The realisation of optical links and its typical length are expected to occur in (a) rack-to-rack at 30 m; (b) board-to-board at 1m; (c) on-board at 0.1 to 0.3 m and (d) on multi-chip-module (MCM) at 5-100 mm. This research
focuses in the board-level application, which is the missing link between optical components and fibre optics technologies.

1.1.3 Polymer waveguide technology

IBM researchers have identified internet switches and large computer servers to be early adopters of optical interconnection technology [7]. The trend toward miniaturized optical components and increasing “Gbps” being squeezed into an interconnection between PCBs is a driving requirement for flexibility in packaging technology that house uncooled, high density optoelectronic devices. Optical polymer is known for its flexibility and toughness makes it suitable for an integrated electrical-optical system [8]. The challenge for the researchers in polymeric waveguide technology is to develop a low cost waveguide manufacturing technique that is compatible with PCB manufacturing and reduces the cost in alignment and connectorization with optical devices. As listed in Table 1.2, many hybrid electrical-optical board designs have been demonstrated to integrate polymer waveguides into PCB and flexible circuit [9-19].

The proposed designs can be categorised based on the different waveguide integration approaches as illustrated in Figure 1.1. Most of the proposed integrated electrical-optical board designs carry technical challenges such as integration of optoelectronic devices, connectorization, out-of-plane light turning operation, constraint of keep-out-zone and area real estate for surface mount active/passive components, thermal management, compatibility within the complex material structure and packaging reliability. While material issues such as dewetting, optical layer thickness homogeneities, material shrinkage, etc. are resolved through process optimization, the reliability issue is tackled at the product development stage. The mechanical and material failures due to thermo-mechanical stresses of the complex material structures require substantial development and accelerated aging tests.
Table 1.2 Proposed polymeric waveguide integration technologies.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer waveguide integrated on board</td>
<td>High density optical backplane; VCSEL array packaging.</td>
<td>[9-11]</td>
</tr>
<tr>
<td>Board-level fully embedded waveguide with VCSEL and PD</td>
<td>Chip-to-chip, optical bus structure; retain 100% board surface area for electronics.</td>
<td>[12,13]</td>
</tr>
<tr>
<td>Optical foil lamination with FR4 board</td>
<td>Short distance solution in backplanes, boards and modules, EOCB approach.</td>
<td>[14,15]</td>
</tr>
<tr>
<td>Waveguide with glass interlayer lamination with FR4 board</td>
<td>EOCB approach; improved thermal-mechanical stability.</td>
<td>[16]</td>
</tr>
<tr>
<td>Waveguide coupling with edge emitting laser and edge viewing photo detector</td>
<td>Light turning device eliminated; waveguide fabricated on FR4 and flex.</td>
<td>[17]</td>
</tr>
<tr>
<td>Flexible optical waveguide sheets</td>
<td>Entry level optical interconnect; optical backplane; final assembly step, replaceable.</td>
<td>[18,19]</td>
</tr>
</tbody>
</table>

As the industry is reluctant to adopt drastic change in the PCB design with the aforementioned challenges yet to be fully investigated and answered, the polymer waveguide-on-flex concept has appeared to be the entry point solution with the flexibility in assembly process and is replaceable [4]. As shown in Figure 1.1 (d), waveguide-on-flex can be surface mounted onto PCB at the final assembly step using conventional wire-bonding, ball grid array or a connector approach. Furthermore, the add-on of low cost optical flex onto an existing PCB retains all the PCB surface area for the electronics real estate. The literature survey of optical measurement on bending loss is encouraging with reports on low losses due to bend radius as summarised in Table 1.3.
Figure 1.1 Schematic view of integrated polymer waveguide technology with PCB (a) integrated waveguide on board; (b) embedded waveguide in board; (c) optical backplane between boards and (d) flexible waveguide on board.

Table 1.3 Bending losses reported in the literatures.

<table>
<thead>
<tr>
<th>Bend radius (mm)</th>
<th>Optical loss (dB) at 850 nm</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20</td>
<td>[18]</td>
</tr>
<tr>
<td>12</td>
<td>0.16</td>
<td>[17]</td>
</tr>
<tr>
<td>15</td>
<td>0.15</td>
<td>[19]</td>
</tr>
</tbody>
</table>
1.2 Details of research

1.2.1 3D-Mintegration

3D-Mintegration was a winner of EPSRC’s UK Grand Challenge competition in 2006. The team formed by 7 research institutes and 23 companies aimed to develop new ways of thinking for the design, processing, assembly, packaging, integration and testing of complete 3D miniaturised and integrated products. The “Packaging and Integration” challenge was to identify a new multi-functional integrated packaging approach and to examine the technology challenges and ultimately substantiate the research with a demonstrator.

1.2.2 Problem statement

Optical interconnect is an attractive option to replace electrical connect to relieve the bottleneck of bandwidth growth in internet servers and high end computing systems. However, the manufacturability of optical interconnects provides enormous technical challenges to enable low cost integration in electro-optical systems. Material structures, performance and reliability are the key questions to be addressed in any new technology introduction. An entry level optical interconnects that is low cost, flexible in integration and reworkable is desired. Figure 1.2 depicts the conceptual sketch developed in the early stage of research that meets such requirements. A low cost polymeric waveguide fabricated on a flexible circuitry material meets these criteria. Nonetheless, such material structures provide poor adhesion and reliability issue. Conventional approaches in polymeric optical core fabrication such as photo-etching and laser ablation result in substantial scattering losses due to surface roughness. While these approaches have been developed for electrical circuitry application, a new low cost micro-fabrication technique is required to process the optical materials.
1.2.3 Research objectives

In order to develop a low cost, flexible and 3D integrated approach in realising optical interconnects in an electro-optical system, the objectives of the research in this thesis are:

(i) To investigate a low cost entry level approach for 3D integration of optical waveguide into electro-optical systems.
(ii) To ascertain which areas of research require further development in order to manufacture and assemble the optical interconnection.
(iii) To develop a new approach in optical core patterning that yields low loss performance.
(iv) To investigate the effects of the main manufacturing process and to characterise the optical performance of the formed structures.
1.2.4 Contribution to the body of knowledge

- This thesis looks into the surface properties of both KaptonHN\textsuperscript{TM} and Vectar\textsuperscript{TM}, two candidates for flexible circuitry material in industry, and investigates the effect of plasma and sonochemical surface modification. The combined surface characterisation analysis of surface morphology, surface energy and surface chemistry has provided useful information on these materials.

- A new approach of interfacial depth profiling is demonstrated in investigating the practical adhesion of two polymeric layers. The approach uses time-of-flight secondary ions mass spectrometry (ToF-SIMS) depth profiling technique to characterise the interfacial width of two entangled polymers.

- In the waveguide fabrication front, electrostatic-induced lithography and micro-patterning of optical core is adopted to form smooth, low sidewall roughness waveguides. The relationship between process parameters and material properties are reported. Critical process properties are defined to aid future work with electrostatic-induced lithography. At the present stage of development, the process is manually operated and the fabricated waveguide is not optimised.

1.3 Structure of thesis

The research scopes are structured as illustrated in Figure 1.3. Chapter 2 reviews the optical polymer materials and summarises the development of commercial optical polymers in the industry. Specific material properties and processability of Lightlink\textsuperscript{TM} optical polymer supplied by the Dow Chemical Company (formerly known as Rohm and Haas Electronics Materials) are reported. Chapter 3 introduces flexible circuit materials, specifically on KaptonHN\textsuperscript{TM} and Vectar\textsuperscript{TM} supplied by
Dupont and Kuraray Corporation respectively. The pristine surface properties of these substrates are analysed.

**Figure 1.3 Overview of the research scopes of integrated polymeric waveguide on flexible circuit.**

In order to resolve the adhesion issue of optical polymer deposited on flexible substrates, plasma surface treatment is adopted and presented in Chapter 4. This chapter details the results of the effect of plasma recipes on surface properties. In addition, the effect of sonochemical surface treatment on these substrates is also investigated. With the surface treated substrate materials, Chapter 5 introduces a ToF-SIMS depth profiling approach to quantify the practical adhesion of two polymeric layers. The depth profiling analysis is subsequently compared with peel test results.

Chapter 6 reviews the demonstrated approaches in waveguide fabrication. Initial trials are conducted with screen printing before the adoption of the electrostatic-induced lithography. This new approach is found to produce smooth sidewalls and eliminates the development step of photo-definable material. In order to characterise the self construction of optical core due to electrostatic field, Chapter 7 identifies the process parameters and a sensitivity study is presented. As a result of the study, a process recipe for Lightlink™ waveguide material is established and defined.
Chapter 8 details the set up of an optical measurement platform. The propagation loss of the fabricated waveguide is measured using a cutback approach. The effect of electrostatic field on optical properties are discussed and assessed. The thesis ends with conclusions and further works presented in Chapter 9 and Chapter 10.

1.4 Summary

Due to the growth of bandwidth capacity, copper interconnect is expected to be rapidly replaced by optical interconnect. The industry is looking at low cost approach for electro-optical integration. Waveguide-on-flex can be the entry level technology for optical interconnect introduction. The technical challenges are materials structure design, polymeric interfacial integrity and low loss optical core fabrications. The work was funded by 3D-Mintegration which is a research consortium formed to investigate 3D multifunctional integrated issues. The research objectives are outlined in order to develop the body of research. Finally an overview and structure of the thesis are given.
Chapter 2
POLYMER WAVEGUIDE MATERIALS

Polymeric optical waveguides will play a key role in several rapidly developing optical networking and optical backplane applications due to their low cost processability and flexible integration approach into optoelectronic devices. While no specific optical material has been developed for the electrostatic-induced lithography process, there are existing materials designed for photo-definition, moulding, laser ablation and inkjetting applications. This chapter reviews the classes of polymeric optical waveguide materials and their distinctive properties; followed by a presentation of a list of commercially available waveguide materials and reported fabrication techniques and optical performance. Subsequent sections look into the material structure and processing details of both Lightlink™ and Norland Optical Adhesive (NOA) which are two optical materials selected for this research.

2.1 Classes of optical polymers

Conventional optical polymers used in waveguide fabrication include acrylates, polyimides, polystyrenes (PS), polycarbonates (PC), and epoxy resin. Commercial polymers used in waveguide fabrication include deuterated and halogenated polyacrylates, fluorinated polyimides, polyether, polysiloxanes, inorganic-organic sol-gels and various formulations of cyclic olefins.

Acrylate is a type of vinyl polymer made from acrylate monomers (\(CH_2=CHCOO\)). Acrylate monomers are esters (inorganic or organic acid with an alkyl (\(C_nH_{2n+1}\) group) which contain vinyl groups (-CH=CH\(_2\)). Some acrylates have an extra methyl (-CH\(_3\)) group attached to the carbon, and these are called polymethyl methacrylates (PMMA). The highly transparent PMMA is widely used as the material for optical waveguide [20]. As the C-H bonds in acrylates are highly absorbing in the near infrared (NIR) region, hydrogen is usually substituted with
deuterium or fluorine. The use of deuterated and fluorinated/ halogenated materials adds cost to the optical polymer. Deuterium and chemical synthesis involving fluorine are expensive while also raising questions on environmental impact when synthesized with organic material. In addition, the adhesion of fluorinated polymers to many substrates is often an issue, due to their inert nature and low surface energy. Beside acrylate, a specially formulated polyether (an organic compound with two alkyl or aryl (aromatic ring functional groups) groups) used as waveguide material is perfluorocyclobutyl aryl ether polymer (PFCB) [21]. This thermosetting PFCB polymer does not consist of bonds with high absorption losses e.g. hydroxyl O-H, amine N-H or aliphatic C-H. Cyclic olefin copolymers (COC) is a new class of optical thermoplastics that has low moisture uptake, high water barrier, low birefringence and high optical transmission [22]. COC is based on co-polymers of ethylene \( \text{(C}_2\text{H}_4) \) and a cyclic olefin such as norbornene (bridged-cyclic hydrocarbon \( \text{C}_7\text{H}_{10} \)) or cyclopentene \( \text{(CH=C}_4\text{H}_7) \). The presence of norbornene increases the glass transition temperature and reduces crystallinity for high transparency. Silicone or siloxane is another popular candidate for optical polymer. The silicon-backbone structure of siloxane \( \text{(Si-O with hydrocarbon)} \) has the unique ability to be polymeric or glass-like depending on how many oxygen (glassy) and carbon (polymeric) atoms are attached to the silicon [23]. The design of the molecular architecture and side-chains results in changes of modulus, glass transition temperature, coefficient of thermal expansion, and refractive index. With this flexibility, a variety of refractive indices against temperature, \( dn/dT \) can be obtained through controlled synthesis.

Another technique used to synthesize different organic-inorganic hybrid systems for waveguide application is the sol-gel method [24]. The sol-gel process is carried out by poly-condensation, followed by organic cross-linking reactions. The chemical solution (salkoxysilanes) reacts (undergoes hydrolysis and polycondensation) to produce colloidal particles \( \text{(Si-O-Si backbone oligomers)} \) known as sols. The materials do not gel and stay as resin which can be patterned by UV exposure. Photosensitivity and the ability to undergo a photobleaching process [25] is a characteristic of polymers. For optical waveguide fabrication, this unique characteristic is broadly employed in the crosslinking process under photo-exposure. For polysiloxanes materials, the \( \text{Si-OH} \) main chain will undergo photodecomposition
upon exposure to UV light in air and form Si-O-Si crosslinks. The organic group contains photosensitive structures such as C=C double bonds. The photo-polymerization property becomes photo-patternable upon ultraviolet (UV) light irradiation. Table 2.1 provides the summary of polymer classes used as waveguide material and their unique properties.

Table 2.1 List of different classes of optical polymers and their unique properties.

<table>
<thead>
<tr>
<th>Polymeric materials</th>
<th>Distinctive properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarbonates</td>
<td>Optical clarity, high toughness, low melt viscosity at high processing temperature (moulding), high birefringence.</td>
</tr>
<tr>
<td>Polyimides</td>
<td>Thermal stability (&gt;300 °C), high loss in NIR, high birefringence n_{TE}-n_{TM} &gt; 0.008 due to aromatic, rigid structure.</td>
</tr>
<tr>
<td>Polystyrene [26]</td>
<td>Aromatic, long-chain hydrocarbon solution; high refractive index of 1.59.</td>
</tr>
<tr>
<td>Acrylates and polymethyl methacrylates (PMMA)</td>
<td>Flexibility/ adjustability in properties, usually low temperature stability, low T_g, low birefringence, high photosensitivity.</td>
</tr>
<tr>
<td>Deuterated and halogenated polyacrylates</td>
<td>Outstanding in light transmission in NIR, low T_g at 100 °C, photo-curable,</td>
</tr>
<tr>
<td>Perfluorocyclobutyl (PFCB) aryl ether polymers</td>
<td>High temperature stability (T_g = 120 – 350 °C), low optical loss (&lt;0.25 dB/cm) at 1310 and 1550 nm, low birefringence.</td>
</tr>
<tr>
<td>Cyclic olefins copolymers (COC)</td>
<td>Polymeric isotropic, low birefringence under stress, low moisture uptake,</td>
</tr>
<tr>
<td>Siloxanes or silicone</td>
<td>Resistance to high and low temperatures, water, oxidation and inertness, low shrinkage &lt;0.1%, solvent free.</td>
</tr>
<tr>
<td>Polydimethylsiloxane (PDMS) [27]</td>
<td>High temperature stability &gt;290 °C, thermal crosslinking</td>
</tr>
</tbody>
</table>
2.2 Requirement of optical polymers

Polymers are the industry’s material of choice for low cost integrated optical system compared to the conventional optical materials [29]. When synthesized and processed properly, they offer high performance, tunability, environmental stability, high yields and low cost. An optical polymer is highly transparent, with absorption loss of 0.1 dB/cm or lower at datacom and telecommunication operating wavelengths. The scattering loss can be minimized in polymer waveguides by improving the surface roughness between core and cladding layers. The scattering loss can also be improved by ensuring homogeneity in optical core processing, with minimum phase separation, voids and particles. Optical polymer layers are designed to be stress-free, thus eliminating stress-induced scattering loss and polarization effects. Another source of polarization-dependent loss is the unequal degree of roughness of the vertical and horizontal sidewall inherited from processing conditions. The birefringence (\(n_{\text{TE}} - n_{\text{TM}}\)) can be extremely low in the polymeric waveguide fabrication process that undergoes little molecular orientation during processing. These are important factors to consider in the development of a new waveguide fabrication approach [29].

There are limited investigations published in the literature regarding the reliability testing of polymeric optical waveguides [23, 30-32]. Environmental stability of optical polymers is critical as most polymers are vulnerable to thermal and humidity attack. Mechanical and thermal stresses during fabrication or operation can affect the functional optical properties such as refractive index or transparency. Furthermore, they can cause birefringence and increase polarization dependent losses. Organic materials are exposed to oxidation due to reactive double bond species and maybe subjected to yellowing upon thermal aging [31]; while moisture absorption may result in optical absorption due to \(OH\)-stretch of water. The typical material requirements for polymeric waveguide application are summarized and listed in Table 2.2.
**Table 2.2 Summary of waveguide material requirements for datacom and telecom operation wavelengths at 850, 1310 and 1550 nm.**

<table>
<thead>
<tr>
<th>Responses</th>
<th>Market Requirements</th>
<th>Material Designs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive index controllability</td>
<td>1.45 – 1.55</td>
<td>High RI from dense crystal structure, aromatic, phenyl groups and less free volume.</td>
</tr>
<tr>
<td>Low birefringence</td>
<td>&lt; 0.0001</td>
<td>Homogenous, isotropic, amorphous polymer with aliphatic groups; stress-free optical layers.</td>
</tr>
<tr>
<td>Low absorption loss</td>
<td>≤0.1 dB/cm</td>
<td>Break C=C bond by crosslinking, reduce C-H, O-H and N-H bonds and introduce deuterated or halogenated polymer.</td>
</tr>
<tr>
<td>Low polarization dependent loss (PDL)</td>
<td>Minimum</td>
<td>Low birefringence, symmetric waveguide design and equal degree of roughness at sidewalls vertically and horizontally.</td>
</tr>
<tr>
<td>Low scattering loss</td>
<td>Cutback losses ≤ 0.1 dB/cm</td>
<td>Low core-clad interface roughness &lt;40 nm; remove particles, voids during fabrication.</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>no “yellowing” effect; ideally stable &gt;200 °C</td>
<td>Avoid oxidation due to C=C bonds; process in inert gas or nitrogen atmosphere to reduce decomposition; highly crosslinked material to avoid oxidation at high temperature.</td>
</tr>
<tr>
<td>Humidity stability</td>
<td>Stable at 85 °C/ 85%</td>
<td>Highly crosslinked material to achieve low level of voids.</td>
</tr>
</tbody>
</table>
2.3 Development of commercial optical polymers

There is a wide range of commercialized optical polymers developed by polymer scientists for optical waveguide applications. Unfortunately, few materials from the commercially available optical polymers exhibit all of the required characteristics. Depending on the specific applications, some trade-offs among material characteristics are required. Waveguide designers have to interact closely with polymer scientists in order to optimize and tailor the desired optical polymers. Prior reviews have been conducted to provide a comprehensive list of optical polymers developed globally [8, 29]. The list is compiled and presented as Table 2.3. All propagation loss values are measured from fabricated waveguide values unless otherwise specified.

Table 2.3 Commercially available optical polymers.

<table>
<thead>
<tr>
<th>Manufacturer/commercial name</th>
<th>Polymer class</th>
<th>Reported loss* (dB/cm), wavelength (nm)</th>
<th>Fabrication Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exxelis/Truemode [19, 33, 34]</td>
<td>Acrylate</td>
<td>0.04 (850-slab) 0.15 (850)</td>
<td>Spin-coating, UV-patternning, wet-etching, laser ablation, doctor blading, inkjet printing</td>
</tr>
<tr>
<td>Dupont/Polyguide [35]</td>
<td>Acrylate</td>
<td>0.18 (800) 0.2 (1300) 0.6 (1550)</td>
<td>Monomer diffusion, UV-polymerization</td>
</tr>
<tr>
<td>Corning (formerly Allied Signal) [31]</td>
<td>Acrylate and fluorinated acrylate</td>
<td>0.02; 0.001 (840) 0.15; 0.03 (1300) 0.45; 0.05 (1550)</td>
<td>UV-lithography, laser direct write;</td>
</tr>
<tr>
<td>Zen Photonics/OMR20, WIR30-RI [15]</td>
<td>Fluorinated acrylate</td>
<td>0.05 (850) 0.45 (1550)</td>
<td>Dry etching, UV wet etching, hot embossing</td>
</tr>
<tr>
<td>ORMOCER* [19, 24, 28, 36]</td>
<td>Silicate-based sol-gel hybrid</td>
<td>0.5 (850) 0.7 (1320)</td>
<td>Spin-coat, UV lithography, PDMS-</td>
</tr>
<tr>
<td>Company/ Material</td>
<td>Polymer Type</td>
<td>Refractive Index Range</td>
<td>Surface Process</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-------------------</td>
<td>------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Dow Chemical/ Lightlink</td>
<td>Polysiloxane</td>
<td>0.08 (850) 0.24 (1320)</td>
<td>Based moulding, laser-ablation</td>
</tr>
<tr>
<td>Dow Corning/Silicones</td>
<td>Polysiloxane</td>
<td>0.06 (850-slab) 0.35 (1550-slab)</td>
<td>UV-cure, wet developing, RIE, inkjet printing</td>
</tr>
<tr>
<td>Nippon Paint/GlassiaWG</td>
<td>Polysilane</td>
<td>0.1 (850)</td>
<td>UV irradiation, bond with glass</td>
</tr>
<tr>
<td>Wacker Chemie/SLM7</td>
<td>Polydimethylsiloxane (PDMS)</td>
<td>0.06 (850)</td>
<td>Moulding, doctor blading, heat cure</td>
</tr>
<tr>
<td>Ticona/ TOPAS*</td>
<td>Cycloolefin copolymer (COC)</td>
<td>0.5 (830) 0.5 (1330) 0.7 (1550)</td>
<td>Spin-coat, RIE, hot-embossing</td>
</tr>
<tr>
<td>Goodrich</td>
<td>Polynorbornene</td>
<td>0.14 (820)</td>
<td>Moulding, RIE, laser ablation</td>
</tr>
<tr>
<td>Asahi/Cytop</td>
<td>Fluorinated polyether</td>
<td></td>
<td>Spin-coat, RIE, photolithography</td>
</tr>
<tr>
<td>Dupont/Teflon</td>
<td>Fluorinated polyether</td>
<td>0.06 (800) 0.35 (1550)</td>
<td>RIE, photo-patterning, nanoimprint</td>
</tr>
<tr>
<td>Dow Chemical/Cyclotene</td>
<td>Benzocyclobutene</td>
<td>0.51 (633) 0.8 (1300) 1.5 (1550)</td>
<td>RIE, photolithography</td>
</tr>
<tr>
<td>Zenphonotics/ZP2145M</td>
<td>Fluorinated polyether</td>
<td>0.3 (1550 – slab) 0.67 (1550)</td>
<td>Hot-embossing, thermal cure</td>
</tr>
<tr>
<td>Amoco/ Ultradel</td>
<td>Fluorinated polyimide</td>
<td>0.4 (1300) 1.0 (1550)</td>
<td>Photo-exposure, wet etch</td>
</tr>
<tr>
<td>Luvantix</td>
<td>Fluorinated</td>
<td>0.2 (850)</td>
<td>UV embossing, soft</td>
</tr>
<tr>
<td>Efiron [43]</td>
<td>urethane oligomer epoxy resin</td>
<td>litho, moulding</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>------------------------------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td>Norland/NOA* series [44]</td>
<td>Mercapto-ester with acrylates</td>
<td>0.4 (633)</td>
<td>Dispense, UV light cure</td>
</tr>
<tr>
<td>MicroChem/SU-8 [13, 33]</td>
<td>Epoxy</td>
<td>0.55 (850)</td>
<td>Doctor-blading, UV cure</td>
</tr>
<tr>
<td>Epoxy Tech/OG169, 146 [45, 46]</td>
<td>Epoxy</td>
<td>0.28 (1300) 0.26 (1550)</td>
<td>UV light cured, moulding</td>
</tr>
</tbody>
</table>

*TOPAS (Thermoplastic Olefin-Polymer of Amorphous Structure)
*ORMOCER (ORganically Modified CERamics)
*IPG (Inorganic Polymer Glass)
*NOA (Norland Optical Adhesive)

### 2.4 Optical polymers of choice

We chose two photo definable polymer materials – epoxy based **Norland Optical Adhesive (NOA)** from Norland Corporation and liquid polysiloxanes based **Lightlink™** polymer from Dow Chemical. Lightlink™ is selected as the high performance waveguide polymer while NOA is studied as the low-cost option useful for rapid prototyping.

#### 2.4.1 Polysiloxane - Lightlink™

Polysiloxane also known as silicone, is a photo definable system based upon an organo-silsesquioxane photo-curing material platform [37, 38]. Silsesquioxane structure as shown in *Figure 2.1* is known for its low moisture absorption and good thermal stability. The structure can be configured with various combinations of aliphatic or aromatic groups attached to the main chain as $R_1, R_2, R_3$ and $R_4$. As a result, various material performances can be designed into the structure including
dissolution rate, refractive index, birefringence, lithographic response and optical loss.

Figure 2.1 Polymer structure of Lightlink™ material.

These polymers are made via a silanol (Si-OH) condensation reaction in solvent (65% solids). In this condition, the as-supplied liquid optical core product is at low viscosity approximately 130 cP at 25 °C. Such a diluted solution with propylene glycol monomethyl ether acetate (PGMEA) solvent allows low temperature deposition at 30 – 35 °C. Curing is accomplished by photo-generating a strong acid followed by thermal curing. The photoacid generators break down to the corresponding strong acids under the influence of light. The acid then catalyzes a curing process wherein two -OH groups are condensed to crosslink two silicone polymer moieties with the by product of a water molecule (Figure 2.2) [37]. As a result, a highly stable Si-O-Si bonding is formed upon the crosslinking process. An intrinsic loss from the optical polymer is induced from the presence of aliphatic and hydroxyl groups usually at 1550 nm, while the fabrication of the waveguide core contributes to the extrinsic loss due to the light scattering off roughness of the wall.

Figure 2.2 Silanol condensation (crosslinking) reaction described in [37]
The Lightlink™ material has been used in spin coating and photo-patterning processes. Other processing approaches and development demonstrated with this material reported are excimer laser ablation, electroless copper plating process and through holes or vias formed into PCB with embedded optical layer, a Z-turning approach with angled face milled by an aligned ion beam and off-board connectors [38]. For the purpose of this study, Lightlink™ XP-6701A and XP5202A are used as core and cladding materials respectively. It is also worth noting that a new development of Lightlink™ cladding material is introduced into this research, namely Lightlink™ XP-07423A, for the formation of planar waveguides on flexible substrates [39]. A proprietary solvent formulation is added to this material to promote swelling on the substrate’s surface, thus improving the adhesion between cladding and substrate. The composition of the Lightlink™ material is listed in Table 2.4.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic grade propylene glycol monomethyl ether acetate (PGMEA)</td>
<td>20 – 40%</td>
</tr>
<tr>
<td>Organosiloxane polymer</td>
<td>50 – 70%</td>
</tr>
<tr>
<td>Amido ether</td>
<td>&lt; 5.0%</td>
</tr>
<tr>
<td>Aromatic photoinitiator</td>
<td>&lt; 1.0%</td>
</tr>
</tbody>
</table>

2.4.2 Norland Optical Adhesive (NOA)

NOA is a composite mix of mercapto-ester with acrylate monomer [47]. Mercaptans (also known as thiol), is a compound that contains the functional group composed of a sulphur atom and a hydrogen atom (–SH). Common photoinitiators include benzophenone ((C₆H₅)₂CO). Upon UV exposure, photoinitiators undergo a change and create free radicals, which then react with monomers to create monomer chains. In the cured state, the monomer chains convert to cross-linked chains. For NOA, their absorption spectra are localized at UV region λ = 300nm. The recommended
energy required for cure is 4.5 J/cm². Blanketing with nitrogen is necessary to avoid the presence of oxygen during acrylate cross-linking.

2.4 Summary

A literature review of optical polymer is given. Various classes of optical polymer and their distinctive properties are discussed. The specific requirements for multimode waveguide fabrication have been identified. While there is a large range of commercial optical polymers available in the market, depending on application, specific trade-offs of material characteristics are required. To aid the subsequent analysis work, this chapter discusses the detailed polymer structures and material characteristics of both optical polymers used in this research.
Chapter 3

FLEXIBLE CIRCUIT MATERIALS AND SURFACE CHARACTERISATION

In depositing waveguide polymers onto flexible substrates, the critical issue lies in the polymeric layers formation that will determine adhesion strength and long term structural integrity. The strength of adhesive joints mainly depends on the surface structure and property that controls the state of adhesion. Several key factors are to be considered in material selection and surface preparation in order to achieve mechanically reliable waveguide-on-flex:

1. Minimum coefficient of thermal expansion (CTE) mismatch to avoid build-in residual stress during processing as well as thermal life cycles.
2. Good wettability by reducing interfacial tension to allow maximum contact for interface formation.
3. Ease of surface preparation and modification to promote adhesion and interfacial formation.

The aim of this chapter is to study the candidate flexible substrates and analyse their surface properties.

3.1 Flexible substrate candidates

Over the last decade the demand for flexible substrates has been constantly growing due to the surge in flexible electronics applications. The use of flexible substrate can lower the overall product thickness, ease the product assembly, fit into compact product design and enable low cost assembly such as roll-to-roll fabrication. Inevitably, the growth of flexible substrate application is parallel with the growth of portable electronics. The most widely used material as flexible substrate in the industry is polyimide film.
Polyimide is a dielectric material with many applications in microelectronics. It is also widely used as flexible circuit in electronic applications. As the form factor requirements for portable electronics demand lighter, thinner, and more flexible packages and interconnection, polyimide films offer unique advantages when compared to rigid substrates. Its useful material properties include low dielectric constant, high thermal stability, good reliability and ability to absorb bending stresses. The thermal transfer through a thinner substrate is also better while multilayer flex for high density electrical interconnection has been demonstrated in real product. There are a number of commercial polyimide films, namely Kapton, Upilex, VTEC, Apical, Espanex, etc.

KaptonHN™ used in this study was introduced by DuPont in 1980s, who first commercialized the Kapton® material in 1960. It has two thicknesses, 50 µm and 127 µm. Kapton® is made of poly(pyromellitic dianhydride) (PMDA) linked with oxydianiline (ODA). PMDA and ODA react to form the intermediate polyamic acid (PAA). Heating to temperature >200 °C causes imidization to occur, resulting in the release of water and the formation of polyimide chains [48]. The polymer structure for polyimide is depicted in Figure 3.1.

_Figure 3.1 KaptonHN™ – a flexible substrate and its polymer structure as supplied by DuPont Corporation._

Besides polyimide film, liquid crystal polymer (LCP) film is evaluated in this research as the alternative material in the development of waveguide-on-flex. LCP, a polymer class made of aromatic polyester, is a thermoplastic polymer with unique
structural and physical properties. It is highly crystalline with aromatic ring-structured compounds after polymerizing. It contains rigid and flexible monomers that link to each other. When flowing in the liquid crystal state, rigid segments of the molecules align next to one another in the direction of shear flow. Once this orientation is formed, their direction and structure persist when cooled below the melting temperature [49]. As a result, the mechanical and chemical properties of LCP are strongly dependent on the molecular orientation, order and density. To overcome the anisotropic behaviour of LCP, biaxially oriented film with equal transverse and longitudinal direction properties can be made.

The LCP film, Vecstar™ used in this study is supplied by Kuraray Corporation, with a thickness of 100 µm and consists of thermotropic aromatic copolyester made of hydroxybenzoic acid (HBA) linked with hydroxy-naptholic acid (HNA). The polymer structure of Vectra is illustrated in Figure 3.2.

*Figure 3.2 Polymer structure of LCP Vecstar™ as provided by Kuraray Corporation.*

Table 3.1 compares the material properties of base materials used in electronic circuit manufacturing, e.g. rigid substrate flame retardant 4 (FR4), polyimide KaptonHN™ and LCP Vecstar™. These materials are widely used in the fabrication of printed circuits. Compared to FR4 and polyimide, LCP gives lower dielectric constant, which allows faster electric signal transfer and lower moisture absorption leads to significant lower loss in high frequency interconnect application [50].
Table 3.1 Comparison of material property for base material candidates.

<table>
<thead>
<tr>
<th>Material Property</th>
<th>FR4</th>
<th>KaptonHN™</th>
<th>Vecstar™</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg.m$^{-3}$)</td>
<td>1200</td>
<td>1420</td>
<td>1400</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>63 - 276</td>
<td>231</td>
<td>294</td>
</tr>
<tr>
<td>Young modulus (GPa)</td>
<td>17</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Coefficient of thermal expansion, CTE (ppm/°C)</td>
<td>11 - 20</td>
<td>20</td>
<td>17</td>
</tr>
<tr>
<td>Glass transition temperature, $T_g$ (°C)</td>
<td>130 - 200</td>
<td>250</td>
<td>220</td>
</tr>
<tr>
<td>Thermal conductivity (W/m.K)</td>
<td>0.27</td>
<td>0.12</td>
<td>0.3</td>
</tr>
<tr>
<td>Moisture absorption (%)</td>
<td>0.1 – 1.5</td>
<td>2.8</td>
<td>0.04</td>
</tr>
<tr>
<td>Dielectric constant (1 GHz)</td>
<td>4.40</td>
<td>4.06</td>
<td>2.85</td>
</tr>
<tr>
<td>Relative cost</td>
<td>1</td>
<td>2 – 4</td>
<td>2 - 4</td>
</tr>
</tbody>
</table>

### 3.2 Surface characterisation techniques

Surface analysis plays an important role in the study of adhesion and interfacial formation. There are differences between the properties of materials in bulk and those close to surfaces. In many cases, the definition of surface is set by atomic or molecular length scales (0 – 10 nm). In this work, the investigation is focusing on the analysis of surface morphology, surface energy and surface chemistry. Surface morphology looks at physical structure, shape and surface roughness of the polymer. SEM and AFM are used to investigate the surface morphology of the polymer substrates. In contrast to the surface physical structure, the unique characteristic of the end-of-chain of a polymer structure gives surface tension that is a result of intermolecular cohesive forces. Surface chemistry investigation provides the chemical composition on the polymer surface, which aids in identifying the presence of appropriate functional groups for interfacial formation. In this study, both XPS and ToF-SIMS are used to analyze the surface chemistry of the flexible substrates.
3.3 Surface morphology of flexible substrates

The surface morphology of the flexible substrates was initially assessed using an optical microscope, Zygo NewView scanning white light interferometer (SWLI), scanning electron microscope (SEM) and atomic force microscope (AFM). While the images taken with optical microscope and Zygo are simple and non-destructive, there are limited details of surface morphology that can be extracted from the images. Knowing that the organic sample is not conductive and vulnerable to electron beam damage, imaging with an SEM requires the polymeric surface to be coated with conductive material. In this case, SWLI and SEM are ideal for surface profile scanning in micro-scale, whereas AFM is preferred to examine the surface morphology of polymeric surfaces. AFM can generate images containing surface morphology details that are beyond the resolution capability of optical microscope and SEM. Additionally, samples viewed by AFM do not require further treatments that would alter or damage the surface. AFM also work well in an ambient air environment. The polymeric surface morphology was examined with a Nanoscope tapping mode AFM, scanning an area at tip scanning rate of 1 Hz and 256 lines per image using standard silica nitride cantilever probes derived surface micrographic images. For highly reflective and soft polymeric surfaces, tapping mode is preferred over contact mode to avoid interference between the incident and reflected light from the surface that can result in image artefacts.

3.3.1 Polyimide KaptonHN™

It was reported that KaptonHN™ contains calcium hydrogen phosphate (CaHPO₄) as a slip additive [51]. It is believed that the addition of the slip additive into the material is designed to reduce the coefficient of friction, hence lowering the friction between film layers and other surfaces. Due to the incompatibility with the polymer matrix, the majority of the slip additives will exude to the film’s surface. Therefore this prevents direct film-to-film contact. The addition of a slip additive can prevent film sticking and pulling, helping to increase throughput of film productivity. A similar observation has been seen with the KaptonHN™ sample received for this work as shown by the optical image in Figure 3.3. The slip additives observed are
large, some are in microns. The presence of such micro-features on the substrate surface is unwanted for coating application. This can result in poor adhesion and weak interface formation due to the void formation and wettability issue during the coating process. As a result, surface modification is required to improve the surface homogeneity prior to material deposition.

*Figure 3.3 Large particles observed on the optical image of KaptonHN™ surface.*

Similar observation is obtained using the AFM analysis. *Figure 3.4* shows the AFM image of a KaptonHN™ sample. Although the surface roughness measurement indicated smooth substrate surface, particles several microns in size can be detected on the surface. The arithmetic mean surface roughness, $R_a$ of three KaptonHN™ samples, measured at 10 x 10 μm area are 3.764, 6.586 and 7.841 nm respectively.

Generally, the cleaned surface of the polyimide film is smooth except for the presence of additives that can induce adhesion problems such as the crack initiation of an interface during processing or operational stage. Poor wetting can result in poor adhesion and interface formation. Voids at the interface due to processing can lead to stress concentration in the operational stage.
Figure 3.4 Large scale tapping mode AFM image of 10 µm x 10 µm area of KaptonHN\textsuperscript{TM} with $R_a$ of 7.841 nm.

3.3.2 \textit{LCP Vecstar}\textsuperscript{TM}

The surface morphology of Vecstar\textsuperscript{TM} film was studied under AFM. As shown in Figure 3.5, the images obtained reveal that ribbon like fibrils are the dominant surface features of these LCPs. Large fibrils, in 1-2 µm width and 5-6 µm in length are contributing to local non-homogeneity, disorder structures, surface debris and localized amorphous regions. This phenomenon has been reported elsewhere [52, 53]. The existence of fibrils is believed to be induced from the polymer extrusion process during liquid crystallization. As shown in Figure 3.5, the arithmetic mean surface roughness, $R_a$ of the Vecstar\textsuperscript{TM} surface can be very high due to the localized fibril-like structure. Further $R_a$ measurements were taken on the sample in the highly amorphous regions excluding the fibrils, and the $R_a$ readings are 7.304, 8.016, 13.933 nm. The existence of localized microfibrils provides the onset for crack initiation when the surface is deposited with coating materials. Therefore, surface treatment is necessary to improve the surface homogeneity on the Vecstar\textsuperscript{TM} surface.
3.4 Surface energy of flexible substrates

3.4.1 Advancing contact angles

The liquid optical polymer is deposited by spin coating on the substrate surface. Here, it is important that good wetting behaviour occurs between the liquid deposited and the underlying surface. One method to test the wetting behaviour is to look at contact angle measurement. The calculation of the solid’s surface tension is then possible from contact angles formed on its surface by several different test liquids.

In this study, dynamic advancing contact angle was measured with a Dataphysics OCA20 apparatus, using the test liquids of deionised water and diiodomethane. As shown in Figure 3.6, the contact angle, \( \theta \) is obtained by drawing a tangent to the profile at the point of three phase (vapour, liquid and solid) contact where the drop profile has been enlarged by the image projection. Measurements are made
immediately after the three phase line has come to rest. The test liquid is advanced over the surface by increasing the volume which is dispensed by a needle from a syringe. The needle remains in the droplet during measurements to avoid unnecessary vibration or distortion of the droplet, and has no effect on the contact angle. In this case, the measurement was taken from the second dispense onwards, and three advances were dispensed on a sample.

Figure 3.6 Screen shots from an advancing contact angle measurement

The result in Figure 3.7 is the advancing contact angle measurement of three samples each for both types of substrates. Three locations of each sample were measured and three contact angle readings were taken each. The average contact angle, \( \theta_{\text{mean}} \) of both \( \theta_{\text{right}} \) and \( \theta_{\text{left}} \) was plotted in the result. The mean of the contact angles for KaptonHN\textsuperscript{TM} as shown in the figure are 71\(^\circ\) (water) and 28\(^\circ\) (diiodomethane); and for Vecstar\textsuperscript{TM} are 80\(^\circ\) (water) and 35\(^\circ\) (diiodomethane) respectively. The LCP surface has higher water contact angle than the polyimide surface. The measured advancing contact angle data of KaptonHN\textsuperscript{TM} is comparable to the literature [48].
3.4.2 Surface energy estimation

Young first established the relationship between surface tension and the angle of a droplet on a solid surface. Fowkes then proposed the concept of surface free energy components, \( \gamma \) of the films can be resolved into a London dispersive component, \( d \) and polar component, \( p \). Owens and Wendt extended the work of Young and Fowkes by stating the interfacial tension between a liquid and a solid surface can be expressed as [54]:

\[ \gamma = d + p \]
The Owens-Wendt approach is adopted for solid surface free energy estimation by using two known test liquids from literature while $\theta$ can be measured. Based on Strom et al., measurement of distilled water ($\gamma_L = 72.80$ mN/m; $\gamma_L^d = 21.80$ mN/m and $\gamma_L^p = 51.00$ mN/m) and diiodomethane ($\gamma_L = 50.80$ mN/m; $\gamma_L^d = 50.80$ mN/m and $\gamma_L^p = 0.00$ mN/m), a straight line can be drawn using a series of liquids to calculate $\gamma_S^d$ and $\gamma_S^p$.

A summary of the calculated solid surface free energy values is shown in Table 3.2. For both substrates, the pristine surfaces contain low contribution from the polar component. The polar components are 2.50 mN/m and 4.93 mN/m respectively for both KaptonHN$^\text{TM}$ and Vecstar$^\text{TM}$. The overall surface energies calculated are 49.76 mN/m and 38.81 mN/m respectively for both KaptonHN$^\text{TM}$ and Vecstar$^\text{TM}$. The result obtained from the experiment is comparable to the values reported in literature ranges between 43.2 – 46.0 mN/m (Kapton) and 35.7 – 37.1 mN/m (Vectra). These values can be used for comparison when surface treatment is applied to the substrates. Surface treatment is required to improve the wettability of the surface by increasing the polar component.
Table 3.2 Comparison of surface energy estimation using Owens-Wendt method on both measured pristine KaptonHN\textsuperscript{TM} and Vecstar\textsuperscript{TM}; and additional data from the literature.

<table>
<thead>
<tr>
<th>Material</th>
<th>Total Surface Energy (mN/m)</th>
<th>Dispersive component (mN/m)</th>
<th>Polar component (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KaptonHN\textsuperscript{TM}</td>
<td>49.8</td>
<td>47.3</td>
<td>2.5</td>
</tr>
<tr>
<td>KaptonHN\textsuperscript{TM}[54]</td>
<td>46.0</td>
<td>44.0</td>
<td>2.0</td>
</tr>
<tr>
<td>KaptonH\textsuperscript{TM}[54]</td>
<td>43.2</td>
<td>41.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Vecstar\textsuperscript{TM}</td>
<td>35.8</td>
<td>30.9</td>
<td>4.9</td>
</tr>
<tr>
<td>Vectra\textsuperscript{TM} A [55]</td>
<td>35.7</td>
<td>31.1</td>
<td>4.6</td>
</tr>
<tr>
<td>Vectra\textsuperscript{TM} B [55]</td>
<td>37.1</td>
<td>32.7</td>
<td>4.4</td>
</tr>
<tr>
<td>Xydar\textsuperscript{TM} [55]</td>
<td>37.21</td>
<td>31.95</td>
<td>5.26</td>
</tr>
</tbody>
</table>

3.5 Surface chemistry of flexible substrates

3.5.1 Combined XPS and SIMS analysis

A variety of mechanisms can be responsible for the adhesion between two materials. These range from covalent bonding, van der Waals attraction, mechanical interlocking, electrostatic attraction, etc. With the possible exception of mechanical locking, these mechanism are each dependent upon the chemistry and composition at the interface. The study of interface formation and adhesion require surface analytical techniques for the characterisation of pre-bonded surfaces. In this section, surface spectroscopy techniques are used to analyse the surface chemical species on the polymer samples.

Surface chemical composition of approximately 5 - 10 nm in depth was analyzed using a VG Escalab X-ray photoelectron spectroscopy (XPS) with an Al K\textalpha{} X-ray source (1486.6 eV). The vacuum in the analysis chamber was maintained between 10\textsuperscript{-7} and 10\textsuperscript{-8} Torr. The X-ray source was run at a power of 160 W (anode voltage of 8 kV with current level at 20 mA). The broad scan started at 0 - 600 eV and followed by a 40 eV width narrow scan. All spectra were obtained at a take-off
angle of 90° relative to the surface. An electron kinetic energy analyzer plotted the intensity of the emitted photoelectron according to their binding energies. The analyzer was operated at pass energy of 20 eV with step energies of 0.4 eV (broad scan) and 0.05 eV (narrow scan). The XPS data was analyzed with the XPSPEAK software version 4.1 (developed by R.W.M. Kwok, Chinese University of Hong Kong). The surface chemical composition was calculated from the areas of relevant spectra peaks.

Further molecular and structural information of the polymer surfaces were obtained using a time-of-flight secondary ions mass spectroscopy (ToF-SIMS) IV instrument (ION-TOF GmbH, Münster, Germany) fitted with a Bi⁺ liquid metal ion source. SIMS measurements have been used to explore the nature of surfaces prepared for bonding [56]. Using a static SIMS approach, a spectral analysis and ion fragmentation identification can be performed on the polymeric surface. The relative ratios of the sputtered ions provided a direct measure of the composition of the layer that had been removed. All data analysis was carried out using IonSpec and IonImage (version 4.0) software which were specifically attached with ToF-SIMS IV instrument.

3.5.2 Polyimide KaptonHN\textsuperscript{TM}

The XPS broad scan spectrum of KaptonHN\textsuperscript{TM} surface in Figure 3.8 is not unexpected and indicates the primary C, N and O peaks with binding energies of 285, 400 and 532 eV respectively. Based on the areas of each peak in the spectrum, the C, N and O atomic concentrations were calculated with C 1s at 79.7%; O 1s at 12.8% and N 1s at 5.7%. The slightly higher carbon concentration when compared to the nominal stoichiometry of the repeating unit of polyimide at 75.9% is probably due to surface contamination when exposed to the ambience.
In order to understand the chemical binding states in detail, the narrow scan XPS spectrum of \( C\,1s \) was analysed. Characteristic peaks of polyimide pristine surface are assigned as recommended in the work by Briggs et al. [57] and shown in Figure 3.9. The main problem for narrow scan analysis is the exact calibration of the binding energy scale in the absence of a well defined aliphatic \( C\,1s \) line and the number of peaks to be included into the fit of the \( C\,1s \) line. Nevertheless, in this case the \( N\,1s \) signal with single \( N-C \) binding state is chosen as the reference energy at 400.6 eV. The peaks-fitting of \( C\,1s \) line of KaptonHN\textsuperscript{TM} sample is limited to 4 peaks. The binding energy for aromatic \( C-C \) in the ODA benzene rings is assigned at 284.7 eV. The peak assigned at 285.6 eV contains two non-separable peaks i.e. \( C-C \) and \( C-N \) bonds in the PMDA imide-groups. The subsequent two peaks are assigned as \( C-O-C \) in the ODA unit (286.3 eV) and \( C=O \) in the imide group (288.6 eV) respectively.
Despite the above efforts, a surface scan using ToF-SIMS was conducted to provide further evidence of specific chemical species. The molecular ion species identified by ToF-SIMS allow the identification of specific molecular fragmentation. The ToF-SIMS data obtained for the pristine KaptonHN™ surface, as shown in Figure 3.10, is compared with the findings from literature [58]. As expected, a positive spectrum indicates the organic skin of hydrocarbon clusters (\(C_6H_n\)) from the sample’s surface with fragments induced from the aromatic benzene rings; whereas the acidic-ion with additional hydrogen fragmentations were shown in a negative spectrum. The identified hydrocarbon clusters in the positive spectrum are \(C_3H_3 = 27\) amu, \(C_4H_3 = 39\) amu, \(C_4H_5 = 51\) amu, \(C_5H_3 = 63\) amu, \(C_6H_3 = 75\) amu and \(C_8H_7 = 115\) amu. The identified negative ions are \(O = 16\) amu, \(CN = 26\) amu and \(CNO = 42\) amu. The strong peaks of \(CN\) and \(CNO\) are the characteristic marker of KaptonHN™. From the combined XPS and ToF-SIMS analysis, there is limited evidence of the functional groups presence e.g. hydroxyl, carboxylic acid, that will provide active surfaces for bonding with the deposited coating material.
3.5.3 LCP Vecstar™

While there have been plenty of researchers’ data on KaptonHN™ material, it is worth noting here that there is limited data available in the literature for references on Vecstar™ or Vectra™ related materials. Howlader et al. reported a brief XPS analysis of LCP surface before and after the argon plasma and copper deposition [65]. This work provides both the broad scan and narrow scan of XPS analysis with further ToF-SIMS spectra analysis on the LCP sample. The XPS broad scan spectrum on pristine Vecstar™ surface, as shown in Figure 3.11, indicates the primary C and O peaks with the atomic ratio of C 1s at 81.9% and O 1s at 18.1% respectively.
As there is no third element present in the Vecstar™ polymer structure, the $O\,1s$ narrow scan spectrum is analysed and depicted in *Figure 3.12* highlighting the two peaks of single bond $C-O$ at 532.0 eV and double bond $C=O$ at 533.7 eV respectively.
Similarly to the ToF-SIMS spectra of KaptonHN\textsuperscript{TM}, the positive spectrum - Figure 3.13a of the Vecstar\textsuperscript{TM} surface, indicates the ion fragments of organics species from the benzene rings ($C_nH_n$). The identified hydrocarbon clusters are $C_2H_3 = 27$ amu, $C_3H_3 = 39$ amu, $C_4H_3 = 51$ amu, $C_5H_3 = 63$ amu, $C_6H_4 = 76$ amu and $C_7H_3 = 87$ amu. Figure 3.13b highlights the negative ions which consist of mostly acidic species. The identified negative ions are $O = 16$ amu, $C_2H = 25$ amu, $C_2OH = 41$ amu and $C_4H = 49$ amu. The subsequent clusters of peaks are the fragmentation of hydrocarbon from the benzene rings. Similar to the finding for the KaptonHN\textsuperscript{TM} surface, both XPS and ToF-SIMS analysis conclude with the lack of functional groups present that provide the active species for interface bonding.

*Figure 3.13 ToF-SIMS (a) positive and (b) negative spectra of pristine Vecstar\textsuperscript{TM}.*
3.6 Summary

Two types of industrial grade polymeric substrates for flexible circuitry were identified as candidates for the waveguide-on-flex application, i.e. polyimide KaptonHN™ and LCP Vecstar™. While KaptonHN™ has been widely used in various applications, LCP films are recently introduced with the advantage of lower dielectric constant and better resistance to moisture absorption. The LCP film obtained from Kuraray Corporation is made of Vectra resin supplied by Ticona, and several surface analysis results were conducted and compared with KaptonHN™. The summary of the results is as following:

1. Surface treatment is required to remove localised surface inhomogeneity found on the samples i.e. slip additives on KaptonHN™ and microfibrils on Vecstar™ surfaces.

2. Based on Owens-Wendt method of surface energy estimation, the surface energy of KaptonHN™ and Vecstar™ are 49.8 mN/m and 35.8 mN/m respectively. Surface treatment is needed to improve the polar contribution of the surface energy.

3. Surface chemistry analysis reveals that the surfaces of both substrates primarily consist of carbon-rich skins and lack functional groups for interfacial bonding. Appropriate surface treatment is required to prepare the surface with active species for improved adhesion.
Chapter 4
SURFACE MODIFICATION OF FLEXIBLE SUBSTRATES

4.1 Introduction

As concluded from the previous chapter, surface treatment is required to prepare the flexible substrates for interfacial formation and improved adhesion. As light signals are propagated and confined through the polymeric waveguide, the light guiding structure is required to adhere well and ensure long term reliability. High adhesion strength is a critical parameter of multi layer materials structures, which can be fragile to thermal-mechanical stresses encountered during fabrication, handling and product life cycle. Poor adhesion, dewetting and thermal expansion mismatch phenomena are fundamental issues that will affect the overall performance of optical waveguide-on-flex.

Choi et al. demonstrated a waveguide foil integrated onto flexible circuit without discussing the potential thermal mismatch issue [13]. Similarly, Kopetz et al. reported the use of Kapton\textsuperscript{TM} as carriers to laminate a polysiloxane waveguide foil [59]. The Kapton\textsuperscript{TM} carrier was pressed against the mould of the liquid phase optical polymer and thermally cured. A similar process was repeated for the top cladding to maintain symmetry in the material structure. To reduce the build-up of residual stress from inner layers, Bosman et al. also adopted the symmetrical approach by sandwiching the optical track between two spin-coated polyimide layers [19]. An adhesion promoter and plasma treatment were applied to the polyimide layers for optimized adhesion. The concern of a spin-coated polyimide layer is vulnerability to moisture absorption and wrinkle formation during the drying process [60]. The wrinkle formation is due to the inhomogeneous in solvent evaporation that results in skin layer at the top surface. This will result in poor wettability during the optical cladding layer deposition. Kehagias et al. reported poor adhesion between the optical core material of polystyrene and cladding layer made of Teflon [26]. In his work,
plasma treatment and silane coupling agent were attempted to enhance the adhesion of optical layers. Similar dewetting observation was reported by Uhlig et al. in processing the ORMOCER materials [61]. However, Uhlig adopted small or moderate changes in the chemical composition to avoid dewetting problems.

In this chapter, a systematic approach was adopted to investigate the plasma treatment effect on surface properties. The effect of argon, nitrogen and oxygen plasma treatments was characterized. While the plasma treatment on KaptonHN™ substrate has been widely discussed in literature, the detailed characterisation of both pristine and different plasma surface modified Vecstar™ films is reported and compared for the first time. In addition, the investigation was extended to a sonochemical surface treatment method in collaboration with the Sonochemistry Center of Coventry University.

4.2 Plasma treatment

4.2.1 Influence of plasma treatment

As discussed in Chapter 3, commercially available flexible circuit foils are usually produced with poor surface wetting characteristics for ease of fabrication. The pristine surfaces of the samples are very smooth except with contaminants and micro-fibril like structures. Surface treatment is required to improve local inhomogeneity. The presence of such micro-features on the surface during liquid polymer deposition process can lead to the introduction of voids in the interface. Such voids are the potential defects in the interface formation where stress concentration can occur, leading to crack initiation and propagation. The substrate in this investigation is usually subjected to thermo-mechanical stress during the assembly process as well as during product life cycle.

Beside the existence of contaminants and microfibrils, the substrate’s surface is chemically stable before the deposition of the cladding material. Due to the poor wetting and non-reactive characteristics, only a few or no ester linkages (−COOH)
can be formed when the optical material is spin-coated onto the substrates. As illustrated in Figure 4.1, the weak boundary layer formed with a lack of crosslinking, exhibiting poor adhesion through polymer chain entanglement and Van der Waals bonding only.

*Figure 4.1 Illustration of entanglement between two miscible polymer chains (a) weak boundary layer formation and (b) crosslinked interface.*

Many surface treatment methods have been deployed to improve the adhesion of flexible substrate with other materials. These include wet chemical treatments [54, 62], plasma treatment [63-66], ion beams [67], laser irradiation [68] and silane coupling agent [69]. This work used plasma treatment approach to modify the surface properties without altering the bulk properties. Plasma pre-treatment is commonly used in the industry for surface cleaning and preparation. This dry treatment approach avoids problems caused by wet chemical pre-treatment such as residual solvent and swelling on the surface of the substrate. The high energy state of plasma irradiation composed of a mixture of charged particles, electrons and neutral atoms, is generated mainly from the particle collision and photon energy absorption at low pressure. The plasma energy penetrates into the polymer surface surrounded by disordered chains to initiate both physical and chemical reactions [70]. In a physical sense, the plasma-polymer interaction with electrons, ions and radicals is an etching reaction. In a chemical sense, the interactions are chain-scission, surface crosslinking or introduction of functional species. Selective plasma treatment can improve surface homogeneity, wetting characteristic, increase the mechanical interlocking mechanism and introduce new functional species to
promote covalent bonding with the spin-coated material at a temperature below melting point.

### 4.2.2 Experiment

Flexible films of KaptonHN™ and Vecstar™ were cut to 5 x 5 cm sheets. The samples were subsequently cleaned with methanol in an ultrasonic bath followed by rinsing in deionised water and drying in air. The plasma treatment was carried out using a Plasmalab 80 Plus as shown in Figure 4.2. Gas plasma was introduced at the pressure level maintained at 0.05 Torr. The plasma treatment was achieved by a radio frequency (RF) power of 300 W and flow rate of 100 sccm. The minimum processing pressure, maximum RF power and flow rate of the Plasmalab 80 Plus were selected to maximize the plasma efficiency [71]. Three different gases were used in the experiment i.e. argon, nitrogen and oxygen. The surface temperature of the substrates was observed to increase after plasma treatment. However, due to the high temperature stability of both KaptonHN™ and Vecstar™ substrates, these processing temperatures are not critical for the materials. The default processing parameters used in the plasma treatment is listed in Table 4.1.

*Figure 4.2 Sample preparation (a) pre-cleaned samples and (b) Plasmalab 80 Plus.*
Table 4.1 Default parameters used in the plasma treatment.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Default parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>argon, oxygen, nitrogen</td>
</tr>
<tr>
<td>Pressure</td>
<td>0.05 Torr (1 atm = 760 Torr)</td>
</tr>
<tr>
<td>Flow rate</td>
<td>100 sccm</td>
</tr>
<tr>
<td>Time</td>
<td>0 – 10 minutes</td>
</tr>
<tr>
<td>Discharge power</td>
<td>300 Watts</td>
</tr>
</tbody>
</table>

4.2.3 Surface morphology analysis

The surface morphology is of great importance for the wettability of the polymer films. Plasma treatment is used to increase the micro roughness of the surface as well as removing the local inhomogeneity caused by the presence of slip additives and microfibrils. The high energy irradiation of plasma initiates the etching reaction of the polymer surfaces and modifies the surface morphology. The plasma treated surfaces were imaged using SEM and AFM. Figure 4.3 shows the oxygen-plasma treated KaptonHN\textsuperscript{TM} surface under 10,000X magnification.

Figure 4.3 SEM images of oxygen-plasma treated KaptonHN\textsuperscript{TM} surfaces at 0.05 Torr, 100 sccm, 300 watts with treatment time at 2, 5 and 10 minutes respectively.

Figure 4.4 shows the morphological change of the polymer surfaces as a result of intense plasma irradiation, as analyzed using AFM. Both SEM and AFM analysis indicate the conversion of the smooth surface to a uniformly roughened surface. Such conversion is expected to improve the overall wettability through the capillary
effect. The adhesion between the depositing liquid polymer and the plasma-roughened surface is enhanced with a mechanical interlocking mechanism when cured. However, different types of gas plasma produce different effects on the polymer surfaces as shown in Figure 4.4. Hence, a subsequent experiment investigated the surface morphological changes of argon, nitrogen and oxygen with respect to plasma treatment time.

Figure 4.4 Plasma treatments convert smooth surface to a uniformly roughened surface.

(a) Pristine KaptonHN™ surface

(b) Argon-plasma treated KaptonHN™ surface
100 sccm, 0.05 Torr, 300 W, 10 mins

10 x 10 µm, $R_a$ of 7.841 nm

10 x 10 µm, $R_a$ of 34.865 nm

(c) Pristine Vecstar™ surface

(d) Oxygen-plasma treated Vecstar™ surface
100 sccm, 0.05 Torr, 300 W, 5 mins

10 x 10 µm, $R_a$ of 13.933 nm

10 x 10 µm, $R_a$ of 62.785 nm
The effect of various plasma treatment times was further studied at 2, 5 and 10 minutes treatment time. *Figure 4.5* depicts the transition of the morphological changes of KaptonHN™ surface under intense plasma irradiation. At the initial stage of plasma treatment, etch pits are observed on the polyimide samples. These etch pits are formed and evolved into surface cracks during further plasma irradiation and propagated, leading to the formation of micro-roughness on the top surface. Surface contaminants are removed. Both argon and nitrogen plasma treated surfaces observe similar morphological changes with improved uniformity in surface roughness.

*Figure 4.5 Atomic force micrographs (5 x 5 µm) of various gases plasma treatment on KaptonHN™ at 0.05 Torr, 100 sccm and 300 watts.*

Similar observation was made on the LCP Vecstar™ surface and shown in *Figure 4.6*. Micro-fibril and subdivided fibril structures are revealed on the Vecstar™ surface at the early stage of plasma treatment before prolonged plasma treatment.
leads to the similar development of micro-roughness surface as seen in KaptonHN\textsuperscript{TM}. It is believed that prolonged treatment time of intense plasma irradiation etches the fibrils and deforms the skin layers before the formation of micro roughness. Similar to the observation in the case of KaptonHN\textsuperscript{TM}, the effect of oxygen plasma treatment on LCP surface morphology indicates more volatile species generated on the samples’ surface. The structure becomes deeper and wider as a result of surface erosion by chemical and physical effects of the reactive oxygen plasma. This observation is further validated with the increase of the polar contribution to surface free energy as well as the surface chemical analysis.

*Figure 4.6 Atomic force micrographs (5 x 5 \(\mu m\)) of various gases plasma treatment on Vecstar\textsuperscript{TM} 0.05 Torr, 100 sccm and 300 watts.*

The arithmetic mean roughness \(R_a\) is used to compare the roughness of surfaces and the data is plotted in *Figure 4.7*. It is observed that longer treatment time resulted in increased of \(R_a\) values due to the etching effect on the polymer surfaces. In both
substrates, larger roughness values observed in the oxygen plasma treatment compared to the inert gases treatment. The surface morphological analysis concludes that the high energy irradiation of plasma treatment successfully initiates etch pits on both polyimide KaptonHN™ and LCP Vecstar™ films, and results in the introduction of micro roughness upon prolonged irradiation. Such a finding is essential in preparing the surface for improved adhesion with depositing material.

Figure 4.7 Arithmetic mean roughnesses, $R_a$, of flexible substrates (a) KaptonHN™ and (b) Vecstar™ before and after plasma treatment.
4.2.4 Surface free energy analysis

Higher surface energy results in greater wettability. The ability of a liquid to wet a solid surface is critical in order to optimize the interfacial adhesion. Therefore, the surface free energy of a plasma modified surface was quantified to assess the attractive forces between two materials in intimate contact. The measured contact angles of KaptonHN™ changed significantly upon plasma treatment as listed in Table 4.2. The surface energy estimation was calculated based on Owens-Wendt method as discussed in previous chapter. Upon exposure to 5 minutes of plasma treatment, the total surface free energy, $\gamma_s$ increases from 50 mN/m of pristine surface to 54, 57 and 65 mN/m of argon, nitrogen and oxygen plasma-modified surfaces respectively. It is observed that the polar component, $\gamma_{sp}$ of surface free energy is largely increased after plasma treatment of the polymer substrate. Similar to the observation in the AFM analysis, the oxygen plasma has the most significant repercussion than argon and nitrogen plasma in surface free energy changes. It is found that oxygen plasma is more effective in introducing polar groups onto the polymer surface. As a result, the wettability enhanced by the increase of polar components from plasma treatment, promotes spreading of liquid polymer to fill voids in the polymer surface for better bonding. Therefore, the liquid polymer can react with surface functional groups for covalent bonding upon curing process.

Table 4.2 Advancing contact angle and surface free energy of 5 minutes plasma treated KaptonHN™ substrates.

<table>
<thead>
<tr>
<th>Plasma</th>
<th>Advancing contact angle (°)</th>
<th>Surface energy (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>Di-iodomethane</td>
</tr>
<tr>
<td>Pristine</td>
<td>72</td>
<td>28</td>
</tr>
<tr>
<td>Argon</td>
<td>58</td>
<td>38</td>
</tr>
<tr>
<td>Oxygen</td>
<td>32</td>
<td>56</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>50</td>
<td>62</td>
</tr>
</tbody>
</table>
Figure 4.8 shows the results of surface free energy of the oxygen plasma treated Vecstar\textsuperscript{TM} as a function of plasma treatment time. As the contact angle measurement is insensitive to the depth of surface modification, the polar groups on the polymer surface has largely increased with increasing treatment time. The decrease of the dispersive component of surface free energy upon extended plasma treatment indicates a chain scission phenomenon on the polymer surface structure as well as the etching effect of the roughened surface [72]. However, practical adhesion between polymer surfaces and other depositing materials cannot always be correlated with wettability. The presence of highly wettable, but possibly weak boundary layers due to an excessive chain scission process may leads to low practical adhesion. Further characterization of the surface chemistry is required to understand the overall package of surface modification by plasma treatment.

Figure 4.8 Surface free energy of oxygen plasma treated Vecstar\textsuperscript{TM}.

4.2.5 Surface chemistry analysis

Plasma treatment induces mechanical interlocking by producing a micro-roughness surface and promotes wettability by increasing surface polar groups. Yet the
interfacial characteristic is determined primarily by the strength of chemical bonding between the two joining surfaces. It was suggested that the plasma treatment resulted in relatively more interfacial crosslinking [66]. Selective gases plasma treatment can introduce the appropriate functional species to promote interfacial covalent bonding with increased molecular mobility. Therefore, surface chemical changes of both KaptonHN™ and Vecstar™ upon various plasma treatments were analyzed using combined XPS and ToF-SIMS techniques.

4.2.5.1 Surface chemistry analysis on plasma-treated KaptonHN™

Both the XPS broad and narrow scan spectra of the pristine KaptonHN™ were discussed in the previous chapter. Figure 4.9 shows the relative intensity of C, N and O peaks with different gas plasma-treated KaptonHN™ samples. The samples were plasma-treated for 2 minutes for analysis. Upon plasma irradiation, there are sharp rises observed in oxygen and nitrogen peaks based on the intensity plot.

*Figure 4.9 XPS broad scan spectra of pristine, argon, nitrogen and oxygen plasma-treated KaptonHN™ samples.*
Calculating the areas of each peak in the spectra, the C, N and O atomic concentrations were calculated and summarized in Table 4.3. All gas plasma treatments reported in this work observe the increase of oxygen concentration. The increase of O/C in all gas plasma treatments is probably explained by the water vapour trapped in the chamber during plasma treatment and the recombination phenomenon of oxygen radicals in the atmosphere. Nitrogen concentration is unaltered for both argon and oxygen plasma treatments. However, N/C ratio increases significantly from 0.07 to 0.16 after nitrogen plasma treatment for 2 minutes.

Table 4.3 Atomic composition of plasma treated KaptonHN™ surface.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment Time (minutes)</th>
<th>Elemental Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>0</td>
<td>0.19</td>
</tr>
<tr>
<td>Nitrogen-plasma treated</td>
<td>2</td>
<td>0.23</td>
</tr>
<tr>
<td>Oxygen-plasma treated</td>
<td>2</td>
<td>0.30</td>
</tr>
<tr>
<td>Argon-plasma treated</td>
<td>2</td>
<td>0.27</td>
</tr>
</tbody>
</table>

As derived from Table 4.3, a significant amount of oxygen uptake is found post plasma treatment. Further XPS narrow scan analysis of C 1s line was carried out to fit the potential new chemical species introduced onto the surface. The noticeable change of the C 1s line-shapes after plasma treatment is the shoulder broadening at ~287.0 eV and a new peak is assigned accordingly for carboxylates (-COO) in Figure 4.10b, c and d. The formation of COO- complex after oxygen plasma treatment is possibly due to the chain scission of C-C, C-N (PMDA) and C-O-C (ODA) bonds. Besides the addition of the COO- functional group, there is a possibility of amine functional group (N-C=O) introduction during bond scission of the aromatic benzene rings under nitrogen plasma treatment. Table 4.4 shows the relative binding component ratio of pristine and various plasma treated samples based on the area of the component peaks of the C 1s spectra in Figure 4.10.
Figure 4.10 C 1s core level XPS spectra of 2 minutes plasma treated KaptonHN™ surface.

Table 4.4 Binding component ratios of pristine, oxygen, argon and nitrogen-plasma treated KaptonHN™.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C-C (benzene ring)</th>
<th>C-C &amp; C-N (imide group)</th>
<th>C-O-C (ODA)</th>
<th>C=O (PMDA)</th>
<th>COO-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>62.9</td>
<td>14.5</td>
<td>10.9</td>
<td>11.6</td>
<td>-</td>
</tr>
<tr>
<td>2 minutes oxygen plasma</td>
<td>63.6</td>
<td>9.8</td>
<td>7.5</td>
<td>13.5</td>
<td>5.6</td>
</tr>
<tr>
<td>2 minutes argon plasma</td>
<td>67.6</td>
<td>8.3</td>
<td>7.0</td>
<td>7.3</td>
<td>9.7</td>
</tr>
<tr>
<td>2 minutes nitrogen plasma</td>
<td>56.9</td>
<td>15.7</td>
<td>9.4</td>
<td>7.5</td>
<td>10.5</td>
</tr>
</tbody>
</table>
To further aid the identification of new chemical species introduced to the plasma-treated surfaces, ToF-SIMS analysis was performed to allow the identification of specific plasma-induced fragmentation and confirm the surface reaction mechanisms deduced from the XPS results. As expected, positive spectra are not indicating the characteristic changes of the polyimide structure. Nonetheless, there is a noticeable removal of the carbon-rich skin and benzene ring \((C_dH_n)\) bond scission effects upon plasma treatment that occurred at mass ranges of 73-78 m/z (Figure 4.11). This finding is supported by the increase of the \(O/C\) ratio as summarized in the XPS results listed in Table 4.3.

*Figure 4.11 Positive ToF-SIMS spectra of KaptonHN\textsuperscript{TM} surface, removal of C-rich skin \((C_dH_n)\) after plasma surface modification.*

In the negative spectra, the oxygen-rich functional group created by plasma modification is observed at 44.99 m/z \((-C(=O)OH\), as shown in *Figure 4.12*. The increase of carboxyl group is most significant in oxygen plasma treatment. Upon plasma irradiation, the imidized surface of KaptonHN\textsuperscript{TM} is turned into poly(amic acid) (PAA) through the bond scission of the imide ring. The surface polyamic acid serves as a useful precursor for subsequent chemical reactions.
Figure 4.12 Introduction of carboxylate (-COOH) functional group on KaptonHN™ surface after plasma treatment.

4.2.5.2 Surface chemistry analysis on plasma-treated Vecstar™

The atomic composition of various plasma treated Vecstar™ surfaces were studied with XPS broad scan as shown in Figure 4.13. The elemental composition ratio is summarized in Table 4.5. An increase of carbon concentration is observed upon argon plasma obtained from XPS broad scan analysis. This can be explained by the possibility that the C-O and C=O bonds underwent degradation by argon plasma treatment. The effect of argon plasma treatment on the liquid crystallised organic surface is possibly physical bombardment, chain scission and exposure of the active radicals. The emergence of a nitrogen peak at 400.6 eV from the surface indicates additional nitridation on the organic surface; possibly amino and amido functional groups are generated during nitrogen plasma treatment. Oxygen plasma successfully increases oxygen concentration on the Vecstar™ surface. The possibility of increase in single- and double- bonded oxygen promises more O-rich sites for improved bondability.
Figure 4.13 XPS broad scan spectra of pristine, argon, nitrogen and oxygen plasma-treated Vecstar™ samples.

Table 4.5 XPS atomic ratio of Vecstar™ surface with various plasma treatments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O/C</td>
</tr>
<tr>
<td>Pristine</td>
<td>0.22</td>
</tr>
<tr>
<td>5-minutes argon plasma treatment</td>
<td>0.18</td>
</tr>
<tr>
<td>5-minutes oxygen plasma treatment</td>
<td>0.45</td>
</tr>
<tr>
<td>5-minutes nitrogen plasma treatment</td>
<td>0.28</td>
</tr>
</tbody>
</table>

The effect of oxygen plasma treatment time on Vecstar™ surface was further investigated and the result is shown in Figure 4.14. The O/C ratio increases from 0.22 on pristine surface to 0.38, 0.45 and 0.63 following 2, 5 and 10 minutes of treatment time respectively. The prolonged oxygen plasma treatment leads to the possible introduction of carbonyl, carboxyl and hydroxyl moieties as oxygen functionalities at the surface.
The negative ToF-SIMS spectra of both nitrogen and oxygen plasma treatments indicate functional group generation on the Vecstar\textsuperscript{TM} surface. Figure 4.15 shows the introduction of $\text{COOH}$ (m/z = 45) functional group after oxygen plasma whereas functional species such as $\text{CN}$ (m/z = 26), $\text{CNO}$ (m/z = 42), $\text{CNOH}$ (m/z = 43) are introduced after nitrogen plasma. The nitrogen radicals generated in the oxygen and nitrogen plasma can react with the organic surface and form covalent nitrogen bonds at energetically favourable sites. The introduction of functional species into the Vecstar\textsuperscript{TM} surface is possibly via hydrogen abstraction from aromatic polymer chains, and then recombination with radical plasma to form functional species. It is noted that nitridation introduced after oxygen plasma treatment is captured in the ToF-SIMS spectrum. It is believed that the source of nitrogen ions is from the atmosphere/ vapor in the chamber, which recombines with the active surface to form functional species.
4.3 Sono-chemical treatment

The surface modification of polymer materials is essential in order to obtain functional polymers by controlling their surface properties. However, whatever surface modification technique is employed it must restrict the modified layer to a very shallow depth. Ideally the modified layer should be a monolayer of the polymer surface in molecular size, and the deeper layer into the bulk materials should never be modified. The conventional “wet” chemical surface treatment processes have been successful over the years but are often characterised by the use of hazardous chemistry, operated at high temperature and require copious rinsing. Therefore, increasing environmental, health and safety issues and legislation have led to the re-evaluation of alternative surface modification processes [73].

In this work, a “clean” and “green” sonochemical method was investigated to functionalize the surfaces of polyimide KaptonHN™ and LCP Vecstar™ as an alternative to plasma treatment. The sonochemical process uses deionised (DI) water as the liquid medium and combines mechanical abrasion and chemical attack of the substrate surface to enhance the adhesion of a coating to the substrate. Both effects are induced by the collapse of acoustic cavitation bubbles near the surface. It has been reported that ultrasound can surface modify materials such as ceramic, polyphenylene/ polystyrene (Noryl HM4025) and FR4 laminate Isola Duraver 104 [74], acrylonitrile-butadiene-styrene (ABS) [75], polyvinyl chloride (PVC) [76] and...
polyethylene (PE) [77]. A similar approach was adopted in this study to evaluate the efficacy of this treatment on polymeric flexible circuit materials.

4.3.1 Influence of sonochemical treatment

The sonochemical treatment on the flexible substrates is expected to change the closed-ring structure of the surface thereby to enhance the adhesion. Surface cavitation leading to microjetting during the ultrasonic process produces a number of effects that are useful for surface modification. Surface abrasion is the direct result of the impact of powerful microjets on the surface generated by cavitation bubble collapse. Chemical attack on a surface induced by cavitation is also possible since cavitation collapse is known to generate highly reactive but short-lived hydroxyl radicals that have been used to oxidise and destroy chemical pollutants in waste water [78]. When this oxidant is generated by bubble collapse close to a surface then the surface itself can be chemically modified. This work was set up to investigate the possibility of both physical and chemical effects on the candidate substrates.

4.3.2 Experiment

To enable samples of the flexible substrates to be treated using sonochemical techniques described in [74], samples were cut to 2.5 x 3 cm in size, and attached onto a rigid carrier. This set up allowed the thin foil substrates to be held securely while the ultrasonic horn was turned on. Using DI water as the liquid medium, a 20 kHz ultrasonic horn was set to an applied power of 25, 50 and 80 W, equivalent to an ultrasonic intensity of 2.9, 4.8 and 8.3 W.cm\(^2\) respectively. A water jacket was used to maintain a low temperature ranging from 0 – 12 °C and the experiment was run at 30 minutes intervals. The set up is illustrated in Figure 4.16.
4.3.3 Surface morphology analysis

Using the deionised water as the solution in this experiment, no physical effect was observed on KaptonHN™ material. It is found that the impact of the microjets generated from the bubbles collapse is not sufficient to initiate the etching of the smooth surface. However, various spots of visible physical damage were observed on LCP Vecstar™ surface, directly underneath the perimeter of the ultrasonic horn. The reason the LCP Vecstar™ surface is more susceptible than KaptonHN™ to the etching effect as shown in Figure 4.17, can be explained by the presence of the microfibril-like structure on its surface, as discussed in the last chapter. These 5 – 10 µm in size bundles and subdivided microfibrils provide etch pits which lead to physical damage and destroy the physical layers of the surface.
Figure 4.17 FEGSEM imaging on sonochemical treated flexible substrates with 20 kHz horn, 2.9 W/cm², de-ionised water and measured temperature at 0 – 12 °C.

As received          30 minutes sonication

The surface physical damage from the localized spot of the treated LCP Vecstar™ surface was examined using FEGSEM and the results are shown in Figure 4.18. It is later found that the ultrasonic horn used in this experiment produces horizontal mode of vibration. Due to the nature of the experimental set up using a cylindrical ultrasonic horn in horizontal agitation, the effect of sonochemistry on the treated surface was found to be minimal and occurred locally underneath the edge of the ultrasonic horn. Figure 4.19 illustrates the explanation to the observation obtained in this experiment. Less physical damage was observed as the images travel away from the ultrasonic horn perimeter. There is a need to improve the set up by scanning over an area or by using vertically-agitated horn if large and uniform areas of surface treatment are desired.
Figure 4.18 FEGSEM images of the gradual surface physical damage effect (away from the localised spot center) of the sonochemical treatment due to the cylindrical ultrasonic horn set up.

Figure 4.19 Schematic explanation of the localized surface effect due to the experimental set up as observed in the sonochemical surface treatment.

In this experiment, it is noted that the physical damage increased with the lowering of ultrasonic intensity. The physical erosion of a surface by the violent collapse of acoustic cavitation bubbles is affected by parameters such as the surface tension, viscosity and vapour pressure of the sonicated liquid. Performing
sonochemical surface modification in water at low temperature will reduce the vapour pressure of the liquid medium and therefore less vapour will enter the cavitation bubble. The subsequent collapse of such a bubble will therefore be more energetic as it will be less ‘cushioned’ by entrapped vapour. In this experiment a relatively small volume of water was used (200 ml) and as the ultrasonic intensity was increased the temperature of the solution increased and, even using a chiller, it was difficult to maintain a low temperature. At lower ultrasonic intensities it was easier to maintain a low temperature (and thus a low vapour pressure) and this is the probable explanation for the improved results found using low power. The experiment studying the effect of temperature on the surface damage of LCP Vecstar™ surface is summarised in Table 4.6.

*Table 4.6 LCP Vecstar™ sample configuration for the investigation of temperature effect on physical damage induced by sonochemistry method, using de-ionised water and a 20 kHz horn.*

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Applied power</th>
<th>Treatment time</th>
<th>Thermal couple reading</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>9.3 W/cm²</td>
<td>15 minutes</td>
<td>16 – 18 °C</td>
<td>No physical damage.</td>
</tr>
<tr>
<td>Test 2</td>
<td>9.3 W/cm²</td>
<td>30 minutes</td>
<td>16 – 18 °C</td>
<td>No physical damage.</td>
</tr>
<tr>
<td>Test 3</td>
<td>5.8 W/cm²</td>
<td>15 minutes</td>
<td>10 – 11 °C</td>
<td>Small spots of discoloration, physical damage.</td>
</tr>
<tr>
<td>Test 4</td>
<td>5.8 W/cm²</td>
<td>30 minutes</td>
<td>10 – 11 °C</td>
<td>Small spots of discoloration, physical damage.</td>
</tr>
<tr>
<td>Test 5</td>
<td>2.9 W/cm²</td>
<td>30 minutes</td>
<td>5 – 6 °C</td>
<td>Large area of discoloration, severe physical damage.</td>
</tr>
</tbody>
</table>

4.3.4 Surface chemistry analysis

Further molecular and structural information of the optical polymers were obtained using time-of-flight secondary ion mass spectrometry (ToF-SIMS). The negative
spectrum of the treated KaptonHN™ surface observed a slight increase of oxidised surface with the functional species of $CNOH$ and $COOH$ as shown in Figure 4.20. The sonochemical effect on KaptonHN™ surface was less effective compared to the result of plasma treatment as discussed earlier. However, the negative spectra of treated LCP Vecstar™ surface clearly indicated the introduction of functional species such as $CNO$, $CNOH$ and $COOH$ as depicted in Figure 4.20b. The presence of amino in the nitrogen-free polymer structure of LCP Vecstar™ can be explained with contamination from the atmosphere/ water during the sonochemical process. While the sonochemical treatment has not produced significant surface modification to KaptonHN™ substrate, the liquid crystallised surface of the Vecstar™ surface is observed to undergo significant physical surface damage. In a physical sense, the microjetting localised high temperature and pressures initiate an etching reaction on the polymer surface. In a chemical sense, the interaction of radicals and oxidizing species as a result of the etching reaction, introduces functional species to the polymeric chains. However, the degree of contribution to the practical adhesion from these observed surface modifications is still to be determined.
Figure 4.20 Negative ToF-SIMS spectra of pristine and sonochemical treated (a) KaptonHN<sup>TM</sup> surface and (b) LCP Vecstar<sup>TM</sup> surface.

(a) Pristine KaptonHN<sup>TM</sup>

(b) Pristine Vecstar<sup>TM</sup>
4.4 Summary

In order to realize optical waveguide-on-flex, surface treatment is required to modify and prepare the surface properties of the flexible substrates for the deposition of liquid optical polymer. This chapter performs a systematic investigation into the surface properties of the flexible substrate candidates upon plasma and sonochemical treatment. The results of the investigation can be summarized as follows:

- Plasma treatment successfully introduces etch pits onto both KaptonHN™ and Vecstar™, and prolonged plasma treatment generates uniform micro roughness for improved adhesion.
- The increase of surface energy of the substrates as a result of plasma treatment will improve the wettability of the depositing liquid optical polymer.
- Functional species such as \( COOH \) and \( CNOH \) are introduced onto the substrate surface upon plasma treatment. The chemically active surface will promote covalent bonding and crosslinking of surfaces with the depositing material.
- The microjetting bubbles due to horizontally agitated 20 kHz ultrasonic horn in de-ionised water do not generate sufficient energy for surface etching of KaptonHN™. Consequently, insignificant changes are introduced to the surface chemistry.
- The microjetting bubbles result in aggressive surface damage to the LCP Vecstar™ surface. Furthermore, significant amount of functional species i.e. \( CNOH \) and \( COOH \) are introduced to the surface chemistry. However, the practical adhesion of such aggressive surface physical damage is yet to be determined.
Chapter 5
SAMPLING DEPTH ANALYSIS OF POLYMER INTERFACE

The structural integrity of the polymeric interface is critical for a number of micro- and optoelectronic applications. Previous chapters have discussed the surface properties and reported the surface modification results. This chapter investigates the strengthening of the polymeric interface between spin-coated polysiloxane waveguide material and the plasma surface treated flexible substrates. In this study, the surfaces of both polyimide KaptonHN™ and liquid crystal polymer Vecstar™ flexible substrates were plasma treated. Polysiloxane Lightlink™ material was then spin-coated and cured on the flexible substrates. Conventional approaches in determining the adhesion strength of polymeric interface include the peel test, double beam test and indentation-induced debonding methods. These methods approach the adhesion characterization by introducing an external force to induce delamination at the interface so that the critical interfacial strength can be quantified. To further investigate the fundamental interface formation of two immiscible polymers, an interface depth profiling technique is implemented. The ToF-SIMS depth profiling approach investigates the interpenetration of polymer chains at the interface as a result of plasma surface modification. The quantitative analysis on interfacial width provides an insight into the possible entanglement between the polymer chains, which translates into adhesion characteristics. Such information is essential in the effort to overcome the adhesion failure and strengthen the polymeric interface for long term optical and mechanical stability in waveguide-on-flex applications.
5.1 Adhesion and interface of two immiscible polymers

Optical layers have been previously deposited on rigid substrates [79]. For flexible substrates, poor adhesion [26, 80] due to the difference in coefficient of thermal expansion and dewetting phenomenon [61] are two fundamental issues affecting polymer waveguide-on-flex. During material processing, the internal stresses between the optical material and the substrate become too high, causing delamination when exposed to minimal curvature. In the waveguide-on-flex and many other applications, the polymeric interface should adhere well and possess both high fracture energy and good resistance to crack growth under thermal and hydrothermal conditions. However, because of their closed ring structure, polyimide and LCP surfaces adhere poorly to the polysiloxane, leading to poor fracture energy and poor resistance to crack propagation. Hoontrakul et al. has given a set of measurements of the fracture energy of unmodified interfaces between four different polyimides and a bisphenol-F epoxy [81]. Figure 5.1 shows the poor adhesion of the optical polymer Lightlink™ deposited on polyimide KaptonHN™. The delamination of optical polymer sheet from the flexible substrate upon curing confirms the theory that interface formation between two polymers is weak due to chemically non-reactive surfaces.

*Figure 5.1 Poor adhesion of Lightlink™ spin-coated onto pristine KaptonHN™ surface.*
The purpose of this work is to study the adhesion strength and interfacial formation of the optical cladding layer as a result of oxygen plasma treatment on flexible substrates. As shown in the previous chapter, the plasma effect on flexible substrates changes the surface properties. The plasma-polymer interaction with electrons, ions and radicals generates an etching reaction. Chemically, the interactions are chain scission, surface crosslinking or introduction of functional species. In addition, oxygen plasma treatment increases the area available for chemical interactions as well as introduction of functional species such as \( COOH \) and \( CNOH \). Plasma treatment can provide a highly wettable surface, increase the mechanical interlocking mechanism and introduce new functional species to promote covalent bonding with the spin-coated material at a temperature below melting point.

According to Brown et al., the primary mechanism of adhesion in most situations is generally accepted as the diffusion across the interface, which allows chains to entangle [82, 83]. Despite the immiscibility of most polymers, an interphase region with finite thickness is always created between two polymers during solvent processing. A transition region is created in which polymer chains of one type polymer gradually decrease in density as polymer chains of a second type increase in density. Within this interfacial region, polymer chains of both polymer types become entangled. Such entanglements with sufficient chain mobility form readily during melting and/or solvent evaporating. As solvent is evaporated, the entanglements formed are frozen in place thus providing a physical link. Due to the chain-scission of plasma treatment, the treated surfaces have a smaller molecular weight, \( M_w \), which promotes mobility in molecular entanglement and interpenetration. The number of entanglements, thus the width of the interface that bonds the two materials, is directly affected by varying the bonding temperature or the chemistry of the polymeric components [84].

Verifying that such chemical bonds actually form and strengthen the interface is a difficult task. A quantitative analysis of any material transfer and interpenetration to determine the interfacial width is needed to verify the possible mechanism of enhanced entanglements or diffusion between the polymer chains in the interface, as depicted in Figure 5.2.
Figure 5.2 Possible mechanisms of interfacial formation with covalent bonds, interface interpenetration and polymer chains entanglement.

As shown in Figure 5.3, high resolution optical and electron microscope images could give a relatively coarse assessment of the interface, but could not give a quantitative value of the interface interpenetration, which is essential in determining the interfacial strength of two immiscible polymers. Hence, a depth profiling technique at the interface is proposed and chemically analyzed using the ToF-SIMS approach [85, 86]. The depth profiling technique is used to determine the composition ratio of the various chemical species as a function of depth.

Figure 5.3 Optical (a) and SEM (b) images of the cross-sectional specimen of polysiloxane Lightlink™ deposited onto KaptonHN™ substrate.
5.2 Interfacial depth profiling

5.2.1 Experiment

Polymeric waveguide material was deposited on KaptonHN™ (125 µm thick) and Vecstar™ (100 µm thick) films for comparison. Figure 5.4 shows the schematic of a waveguide-on-flex structure design. Prior to spin-coating, the substrate’s surface was pre-cleaned with methanol in an ultrasonic bath followed by rinsing in deionized water and drying in air. The flex surface was then plasma-treated using a Plasmalab 80 Plus. The plasma was excited by a top electrode driven by radio frequency generator (13.56 MHz). Oxygen was fed into the vacuum chamber at a flow rate of 100 sccm. The operation pressure was set at 0.05 Torr. After oxygen plasma treatment for 10 minutes, at a power of 300 W, the flex substrates were immediately put into a dry box to minimize potential contamination. The bottom cladding was then spin-coated onto the flexible substrate.

For the purpose of depth profiling, a minimum coating thickness of the optical cladding layer was desired. The polymeric cladding was deposited by spin-coating at 5000 rpm for 60 s onto the flexible substrates. After spin-coating, the cladding layers were soft-baked on a hot plate at 90 - 120 °C for 5 minutes in order to remove casting solvent. The curing was accomplished by photo-generating a strong acid to catalyze the crosslinking process of silanol (Si-OH) groups forming a highly stable Si-O-Si chain. The photo-curing was performed to form an insoluble thermoset
polymer using 60 W ultra-violet lamps at 5 mW/ cm². A post exposure bake step was conducted at 90 °C for 5 minutes to drive the condensation reaction. Lastly, a final bake was applied at 150 °C for 60 minutes in a convection oven.

For ToF-SIMS depth profiling as illustrated in Figure 5.5, a 5 kV Cs⁺ primary ion source was used to sputter away the surface of the sample using a raster size of 300 × 300 µm². The sputtered species contain elements in various excited states, ions with positive or negative charges and clusters of the particles. The central 100 × 100 µm² area of the resulting flat-bottomed crater was analyzed using Bi₃⁺ primary ions at intervals of 100 seconds of sputtering. The sputtered negative ions are extracted and analyzed by a mass analyzer. The relative ratios of the sputtered ions provide a direct measure of the composition of the layer that had been removed. As sputtering proceeds, a depth profile of the elements of interest is obtained. The sputtering time can be converted to sputtering depth by determining the crater depth using a Zygo SWLI. All data analysis is carried out using IonSpec and IonImage (version 4.0) software that are included with the ToF-SIMS IV instrument.

Figure 5.5 Principle of depth profiling using ToF-SIMS.

5.2.2 Interface depth profiling

For depth profiling, a characteristic marker of secondary ions in each material was considered. In this experiment, the secondary ions CN⁻ and CNO⁻ were selected as characteristic ions of polyimide KaptonHN™. Benzene rings and the organic
fragments were used as characteristic markers for the LCP Vecstar™ substrate. For the polysiloxane Lightlink™ material, Si was selected as marker being unique compared to the substrate materials. Variations in the intensity of these peaks could therefore be used to locate the transition and interface between the two materials.

As shown in Figure 5.6, the relative abundance of the sputtered secondary ions provides a direct measure of the composition of the elements of interest. ToF-SIMS analysis of the polysiloxane yields a low intensity of CN as nitrogen is only present in the surfactant used in the optical polymer. Conversely, a very intense CN peak is observed when analyzing the KaptonHN™ surface, owing to the presence of imide rings. The intensity of the Si ions generated from the KaptonHN™ material is relatively low as silicon is only found within the filler materials used or contamination from the air during processing. In the polysiloxane material the peak intensity is much higher as silicon is located throughout the polymer backbone. Figure 5.7 shows the high intensity of the CN and Si ions relative to each material and illustrates the distribution of these ions as being homogeneous in both materials.
Figure 5.6 Negative ToF-SIMS spectra indicate the relative intensity of the characteristic markers as measured in both KaptonHN™ and Lightlink™.

<table>
<thead>
<tr>
<th>Sample Parameter</th>
<th>Spectrum Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample:</td>
<td>Polarity: negative</td>
</tr>
<tr>
<td>Kapton 0.5 x 0.5 mm</td>
<td>Area / μm²: 0.502 mm</td>
</tr>
<tr>
<td>Kapton 0.2 x 0.2 mm</td>
<td>Time / s: 264 scans</td>
</tr>
<tr>
<td>Lightlink 0.5 x 0.5 mm</td>
<td>PI dose: Limit</td>
</tr>
<tr>
<td>Lightlink 0.2 x 0.2 mm</td>
<td></td>
</tr>
</tbody>
</table>

[Graphs showing CN⁻, CNO⁻, and Si⁺ peaks]
To maintain the recommended processing and curing recipe of the Lightlink™ material, the spin-coated thickness of polysiloxane material was limited to the minimum of 4 µm. Therefore, a longer time was required to sputter through the thick coating of optical cladding layer. The sputtering rate of the cured polysiloxane material using a 5 kV Cs⁺ sputtering source was calculated as 0.4 nm/s. The optical images of the depth profiling process of the polysiloxane deposited onto untreated KaptonHN™ substrate are shown in Figure 5.8. The initial smooth surface was observed as the removal of the polysiloxane coating until a sharp interface transition occurs at $t = 10687$ s. The substrate surface containing filler materials was observed from $t = 11325$ s onwards.
The initial depth profiles obtained from ToF-SIMS contain secondary ion counts per unit time as a function of sputtering time. The sputtered depth was determined using a Zygo scanning white light interferometer. As shown in Figure 5.9, the final sputtered depth was determined to be less than 7 µm, for which the upper 4 µm is believed to be the spin-coated polysiloxane (up to \( t = 10687 \) s) and the remaining 3 µm is the substrate material. The depth measured was used to convert the D-SIMS data unit of time to a sputter depth. This depth calibration assumes that the primary
current remained stable during the course of the profile and that the erosion rate remained constant.

*Figure 5.9 The line scan depth profile of the crater measured by Zygo scanning white light interferometer, the inset image shows the depth contour of the 100 x 100 µm² crater.*

5.2.3 *Interfacial width*

The depth profiles of polysiloxane waveguide material deposited on both flexible substrates are shown in *Figure 5.10* and *Figure 5.11* respectively. Significant increase of interpenetration has been observed in the plasma-treated KaptonHN™ samples. However, no measureable difference was observed in Veestar™ samples. Interfacial width has been proposed as the indicator for the interpenetration of two immiscible polymers [85, 86]. There are several proposals in literature on the definition to determine interfacial width. Brown et al. adopted the definition of interfacial width as the distance from the interface at which the concentration of the component had dropped to 8% [83]. Xu et al. applied the derivative of the depth profile as an error function corresponding to 84 and 16% of maximum intensity [85]. Because the machine error also contributes to the interface width, the value of a true interface width is usually smaller than the calculated value using an error function.
Figure 5.10 ToF-SIMS depth profiling of polysiloxane Lightlink\textsuperscript{TM} spin-coated on (a) pristine and (b) oxygen plasma treated KaptonHN\textsuperscript{TM} surfaces.
The interface width between the polysiloxane cladding layer spin-coated onto pristine and plasma treated KaptonHN™ surface were determined in this manner, as shown in Figure 5.12. The latter was found to be thrice the former, indicating a more diffused interface between polysiloxane and plasma-treated KaptonHN™. The interface width of the pristine interface was determined to be < 92 nm while the plasma modified interface was determined to be < 310 nm, where both indicators are based on the Si⁺ signal. As the interface width measured is larger than the roughness,
it would be due to the diffusion and not only the topography of the KaptonHN™
surface. Beside the increase of \(CN^-\) indicating the interphase region, the exponential
decay indicating a diffusive mechanism of \(Si^-\) was observed in the interphase region
of both samples. The large interfacial width value can be explained by the presence
of “solvent-swelled” polysiloxane solution that was provided for the waveguide-on-
flex application as well as the plasma treatment. In addition, the plasma-modified
surface of KaptonHN™ with uniform micro roughness provides an easy pathway for
interpenetration. The interphase region between the optical cladding and polyimide
has increased after oxygen plasma treatment.

It is believed that Lightlink™ polymer diffuses into the surface modified polyimide
during polymerization. Diffusion usually takes place in the first few minutes where
the activated polyimide imidizes and solvent evaporates. With plasma treatment
providing etch pits, micro roughness and short molecular chain surface, its diffusive
mobility increases rapidly. As a result, plasma treatment enhances the bondability of
the spin-coated polysiloxane on the flexible substrate at a temperature below the
polymer melting point through interfacial interaction and micro-diffusion. Further
degrees of interdiffusion can be controlled by choice of the curing temperature of the
underlying polysiloxane cladding film.

Contrarily, Figure 5.11 shows the mixed result of the depth profiling between the
polysiloxane cladding layer spin-coated onto pristine and plasma-treated LCP
Vecstar™ surface. Such a result is not unexpected due to the large surface roughness
of LCP substrate. The decaying of the \(Si^-\) signal from the two samples indicated
interpenetration of < 230 nm and < 242 nm respectively. The large interpenetration
between the two immiscible polymers was made possible with the microfibril-like
structures and the surface etched pits after plasma treatment. However, without the
surface activation by plasma treatment and introduction of functional species, the
contribution to the practical adhesion is believed to be minimal. The modified
surface chemistry with more active polar end groups promotes interfacial covalent
bonding with increased molecular mobility. Therefore, the adhesive strength can be
enhanced through interfacial interaction and micro-diffusion, resulting in an increase
of the interfacial transition zone.
Figure 5.12 The transition of the Lightlink\textsuperscript{TM} markers to KaptonHN\textsuperscript{TM} markers indicates the interfacial width. Enlarged interfacial width as shown on the plasma treated sample is a measure of enhanced interfacial strength.

The interfacial width values obtained from ToF-SIMS depth profiling approach are summarized and listed in Table 5.1. Knowing that plasma treatment has successfully increased the surface roughness and introduced functional group, an adhesion test is required to investigate the effect of interfacial interpenetration.
Table 5.1 Summary of interfacial width quantification from ToF-SIMS depth profiling experiment.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Interfacial width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lightlink\textsuperscript{TM} - pristine KaptonHN\textsuperscript{TM}</td>
<td>&lt; 92</td>
</tr>
<tr>
<td>Lightlink\textsuperscript{TM} - plasma-modified KaptonHN\textsuperscript{TM}</td>
<td>&lt; 310</td>
</tr>
<tr>
<td>Lightlink\textsuperscript{TM} - pristine Vecstar\textsuperscript{TM}</td>
<td>&lt; 230</td>
</tr>
<tr>
<td>Lightlink\textsuperscript{TM} - plasma-modified Vecstar\textsuperscript{TM}</td>
<td>&lt; 242</td>
</tr>
</tbody>
</table>

5.2.4 Further application of depth profiling

The ToF-SIMS depth profiles reported in the previous section are an indication of interfacial interpenetration. The interfacial width obtained from the transition of characteristic markers can be correlated with the interfacial strength characterisation. The information extracted from the depth profiling work can apply further to the following:

- **Characterisation and correlation with the interfacial strength**: Polymer chain entanglements and diffusion are two interface formation mechanisms which enhance the interfacial strength. Further characterisation of interfacial strength is required to understand the correlation between interfacial width and interfacial strength. As shown in Figure 5.12, the enlarged interfacial width of the plasma treated KaptonHN\textsuperscript{TM} sample indicates enhanced interpenetration which can be used as indicator for improved interfacial strength.

- **Characterisation of interfacial chemical properties**: Beside physical chain entanglement, the interfacial crosslinking of the appropriate functional groups is critical for enhanced adhesion. The interfacial depth profiling describes the intensity of the important chemical species at the interface.
- **Optimization of surface treatment and material curing recipes**: With the understanding of interfacial strength and chemical species present at the interface, both surface treatment and material curing processes can be optimized to obtain a desired interfacial strength.

- **Investigation of core-cladding interface optical absorption characteristic**: The depth profiling technique can be applied to investigate the chemical species which are present at the core-cladding interface to identify absorption groups and optimize the interface formation and curing recipe.

### 5.3 Adhesion and interfacial strength characterisation

There are many established methods reported in the literature to quantify the adhesion and interfacial strength of two polymeric materials. In order to correlate the effect of plasma treatment with the depth-profiled interfacial width, an experiment is required to characterize the adhesion strength of the liquid polymer deposited on both pristine and plasma-treated flexible substrates. Unlike ToF-SIMS approach, these tests are usually destructive, where a controlled load is applied to the specimen to initiate damage to the interface. Several tests have been considered, e.g. 90° T peeling test [87], tape peel test, pull test, blister test, indentation debonding test [88, 89] and beam bending test [90]. Tight control over test parameters must be maintained in order for these tests to be repeatable. A double beam test is suitable to test the adhesion of two polymeric films. The modified beam bending test, namely the double cantilever beam (DCB) test, is preferred due to the ease of sample preparation and controllable approach for obtaining adhesive failure at the interface.

#### 5.3.1 Double cantilever beam test

A double cantilever beam testing was established based on the description in [81, 91]. The DCB approach is useful to determine the interfacial fracture energy, $G_c$. 

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Based on the linear elastic fracture mechanics (LEFM), the fracture energy deduced using the displacement method can be expressed as [91],

$$G_c = \frac{3P\delta}{2Ba}$$

where load, $P$, and displacement, $\delta$, interaction is assumed to be linear at any certain crack length, $a$. The specimen width, $B$, is fixed for all the samples.

For sample preparation, the spin-coated polysiloxane material on the flexible substrate was fully cured before being transferred to the L-shape beam using cyanoacrylate adhesive. As illustrated in Figure 5.13, a pre-crack was initiated at the edge of the coating, separating the flexible substrate from the liquid polymer.

*Figure 5.13 Pre-crack introduced to the specimen before the application of peeling load.*

The specimen was then attached onto an Instron 5848 machine as shown in *Figure 5.14*. In order to measure the crack length, a method of “dye and pry” was adopted. Upon peeling, the samples were dipped into a container filled with acrylic paint. The
dipped sample was then removed and allowed to dry. The painted area left by the
dry paint is considered as the crack length. The critical peeling load, \( P \) was
determined based on the stabilization of the load-displacement curve, as shown in
Figure 5.15.

Figure 5.14 Specimen attached onto L-shape beam was clamped onto Instron for
separation (left). After crack propagation, the specimen was dyed before being
peeled completely for crack length measurement (right).

Figure 5.15 Load-displacement curve of a DCB test indicating the stabilization of
the peeling load, signalling crack propagation.
5.3.2 Results and Discussion

It was noted that not all specimens successfully induced crack propagation with stabilized peeling load as shown in Figure 5.1. The tests were repeated until three load-displacement curves were obtained for each surface finish. Both pristine and oxygen plasma treated KaptonHN™ and Vecstar™ substrates were compared. The results are summarized in Table 5.2 and the calculated fracture energy, \( G_c \), is plotted for comparison in Figure 5.16.

Table 5.2 The DCB experimental values of extension \( \delta \), peeling load \( P \) and crack length \( a \).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Surface treatment</th>
<th>Extension, ( \delta ) (m)</th>
<th>Peeling load, ( P ) (N)</th>
<th>Crack length, ( a ) (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KaptonHN™</td>
<td>Pristine</td>
<td>0.001</td>
<td>29.5</td>
<td>0.012</td>
</tr>
<tr>
<td>KaptonHN™</td>
<td>Pristine</td>
<td>0.001</td>
<td>25.6</td>
<td>0.010</td>
</tr>
<tr>
<td>KaptonHN™</td>
<td>Pristine</td>
<td>0.001</td>
<td>14.5</td>
<td>0.006</td>
</tr>
<tr>
<td>KaptonHN™</td>
<td>Oxygen plasma treated</td>
<td>0.005</td>
<td>27.2</td>
<td>0.003</td>
</tr>
<tr>
<td>KaptonHN™</td>
<td>Oxygen plasma treated</td>
<td>0.005</td>
<td>27.3</td>
<td>0.004</td>
</tr>
<tr>
<td>KaptonHN™</td>
<td>Oxygen plasma treated</td>
<td>0.005</td>
<td>43.0</td>
<td>0.006</td>
</tr>
<tr>
<td>Vecstar™</td>
<td>Pristine</td>
<td>0.001</td>
<td>6.9</td>
<td>0.003</td>
</tr>
<tr>
<td>Vecstar™</td>
<td>Pristine</td>
<td>0.001</td>
<td>19.3</td>
<td>0.009</td>
</tr>
<tr>
<td>Vecstar™</td>
<td>Pristine</td>
<td>0.001</td>
<td>16.1</td>
<td>0.009</td>
</tr>
<tr>
<td>Vecstar™</td>
<td>Oxygen plasma treated</td>
<td>0.005</td>
<td>20.5</td>
<td>0.004</td>
</tr>
<tr>
<td>Vecstar™</td>
<td>Oxygen plasma treated</td>
<td>0.005</td>
<td>11.0</td>
<td>0.002</td>
</tr>
<tr>
<td>Vecstar™</td>
<td>Oxygen plasma treated</td>
<td>0.005</td>
<td>22.6</td>
<td>0.004</td>
</tr>
</tbody>
</table>
The average fracture toughness values, $G_c$, measured for Lightlink$^\text{TM}$ deposited on pristine KaptonHN$^\text{TM}$ and Vecstar$^\text{TM}$ are 148 J/m$^2$ and 123 J/m$^2$ respectively. These values are comparable to the reported polyimide-epoxy $G_c$ values range that from 21 – 179 J/m$^2$ from Hoontrakul et al. [81]. The measured average fracture toughness values of oxygen plasma modified KaptonHN$^\text{TM}$ and Vecstar$^\text{TM}$ samples increased to 2228 J/m$^2$ and 1781 J/m$^2$. The reported higher $G_c$ is correlated with the increase in interfacial width observed in the Lightlink$^\text{TM}$ and KaptonHN$^\text{TM}$ interface. The increase of $G_c$ measured from the plasma-treated samples is mainly due to the increase of peeling load, $P$, and extension, $\delta$, required for a shorter crack length, $a$. For the plasma-modified interface, there is evidence that both polyimide/ LCP and polysiloxane are present at both sides of the fracture surface. Hence, it can be concluded that the crack propagates through the newly created interpenetrating polyimide/LCP-polysiloxane interphase. The fracture surfaces of the untreated interfaces are very smooth. It is clear that the crack growth does not propagate through the bulk polysiloxane coating or the substrate material. Hence, it is concluded that the crack propagates along the weakly formed interface between the unmodified substrate and polysiloxane.

*Figure 5.16 Calculated fracture toughness, $G_c$ of the polymeric interface with and without oxygen plasma treatment on flexible substrates.*
From the DCB test result, plasma treatment has successfully enhanced the adhesion between the spin-coated polysiloxane on the flexible substrate. As discussed in the previous chapter, both surface roughness and surface chemistry of the substrate surface have been modified as well as the improved wettability. This has resulted in the increased of fracture energy measured at the interface. The increased surface roughness has significant effect on the polyimide surface with the increased interfacial interpenetration of both materials. This has resulted in promoting more covalent bonding at the functionalized surface. However, the large interfacial interpenetration of LCP material with and without plasma treatment maybe due to the solvent-related surface swelling. This can be concluded from the large interfacial width measured at untreated (<230 nm) and treated (<242 nm) interface. However, the untreated interface reported lower fracture energy compared to the treated LCP, indicating the effect of plasma treatment on the adhesion performance.

Table 5.3 Summary of the effect of plasma treatment on surface properties, interfacial width and fracture energy.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Surface roughness</th>
<th>Surface chemistry</th>
<th>Interfacial width</th>
<th>Fracture energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>KaptonHN™</td>
<td>Increased</td>
<td>Functionalized</td>
<td>Increased</td>
<td>Increased</td>
</tr>
<tr>
<td>Vecstar™</td>
<td>Increased</td>
<td>Functionalized</td>
<td>No change</td>
<td>Increased</td>
</tr>
</tbody>
</table>
5.4 Summary

This chapter describes a ToF-SIMS depth profiling approach to characterizing the interface of waveguide-on-flex technology which is critical in understanding the effect of plasma treatment to the de-wetting and poor adhesion issues in waveguide-on-flex applications. It is reported in chapter 4 that plasma pre-treatment activates the substrate’s surface for a possible interpenetration mechanism, thus strengthening the interface with depositing polysiloxane. ToF-SIMS depth profile has demonstrated an increase in the interfacial width between polysiloxane and KaptonHN™. Interpenetration of the polysiloxane into the plasma-activated polyimide layer enhances the entanglements between the polymer chains, therefore promotes the number of primary covalent bonds across the final interface. Using the intensity of the $CN$ ion as a function of depth, the interfacial width has been observed to increase from $< 92$ nm for the pristine interface to $< 310$ nm following 10 minutes of oxygen plasma treatment. The insignificant difference observed in the interfacial width between polysiloxane and LCP Vecstar™ substrate is thought to be due to the contamination of LCP surface morphology. However, the LCP surface has been activated with functional groups, e.g. $COOH$, $CNOH$, for primary covalent bonding. As a result, the adhesion characterisation using the DCB approach has shown an increase of fracture toughness as a result of the plasma modified interface. The fracture energies of both the polysiloxane-polyimide and polysiloxane-LCP interfaces have increased from very low values of 148 J/m$^2$ and 123 J/m$^2$ to 2228 J/m$^2$ and 1781 J/m$^2$ respectively.
Chapter 6
POLYMERIC WAVEGUIDE PATTERNING TRIALS USING SCREEN PRINTING AND ELECTROSTATIC INDUCED LITHOGRAPHY

Conventional polymeric optical waveguide materials have been developed for photolithography application. In the last decade, several novel approaches investigated by researchers looked at ways to reduce the cost of fabrication, enabling flexibility in manufacturing and improvements in the optical and mechanical performance. This chapter briefly reviews the patterning techniques used in polymeric waveguide fabrication before presenting the investigation of selected approaches. In the early part of this research, the screen printing technique was selected to assess the feasibility of adopting an additive printing approach to waveguide fabrication. As the research progressed, a new micro-patterning approach for polymer, i.e. electrostatic-induced lithography was found to be an exciting approach capable of producing a micro-patterned structure with smooth surfaces. Compared with existing waveguide fabrication, which produces a rough surface as a result of material etching, the electrostatic-induced lithography is found to be attractive in producing a low loss polymeric waveguide.

6.1 Review on polymeric waveguide patterning approaches

Common techniques for depositing optical cladding layers are similar to those used for polymeric films in microelectronic packaging. The major concerns when fabricating polymer films by spin-coating, doctor blading or lamination are the homogeneity of the film and the adhesion with the substrate. It has been suggested that in order to keep optical losses to a minimum, polymer optical films should exhibit surface roughness of no more than 1/20$^{th}$ of the operating wavelength [60]. The key to achieving smooth surfaces in polymeric films includes allowing
sufficient time for levelling and avoiding evaporation rates that are high enough to produce blistering and cracking.

Beside the cladding layer, the formation of a high quality waveguide depends on the formation of an optical core. A low surface roughness on the interfaces of both core-cladding and cladding-substrate is crucial for low loss waveguides. The general requirements for the manufacturing of polymer optical waveguides are as following:

1. A low temperature process, <200 °C, compatible with established PCB production.
2. Low sidewall roughness and surface contamination to minimize optical loss due to impurities, Rayleigh scattering and interface roughness.
3. The waveguide formation process must be high speed to achieve low cost production.

As shown in Figure 6.1, the techniques that have been used for patterning optical waveguides in polymer films are categorized into photo-patterning, subtractive lithography, soft lithography, direct lithography and a few notable distinctive techniques. Table 6.1 summarizes the key advantages and disadvantages for each technique while the fabricated optical core’s size and the measured propagation loss are listed in Table 6.2.

**Figure 6.1 List of optical waveguide patterning techniques.**

<table>
<thead>
<tr>
<th>Photo-patterning</th>
<th>Subtractive lithography</th>
<th>Soft-lithography</th>
<th>Direct lithography</th>
<th>Distinctive techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photo-Lithography</td>
<td>Plasma etching</td>
<td>Moulding</td>
<td>Direct writing</td>
<td>Ion exchange*</td>
</tr>
<tr>
<td>UV direct writing</td>
<td>Reactive Ion etching</td>
<td>Embossing</td>
<td>Dispensing</td>
<td>Light-induced self-written</td>
</tr>
<tr>
<td>Photo-bleaching</td>
<td>Laser ablation</td>
<td>Screen print/doctor blading</td>
<td>Inkjet printing</td>
<td>Electrostatically self assembly**</td>
</tr>
</tbody>
</table>

* Application in glass sheet.
** New technique demonstrated in this thesis.
Photolithography and plasma etching are two standard and mature processes in the microelectronics industry. Very significant efforts have been made to optimize the conventional planar processing for waveguide patterning using photolithography \([31, 34, 36, 39, 80, 92, 93]\), plasma and reactive ion etching (RIE) \([92, 94]\) to achieve deep and smooth vertical sidewalls. Photo-exposure is a fast process with a couple of seconds to minutes for sufficient exposure. However, the etch rate for plasma and RIE processes are in the range of 60 to 240 nm/ min, translating into hours of material removal process for 50 \(\mu\)m structures. Higher etch rates also result in higher surface roughness values. A further limitation of plasma etching is the chamber size that is generally not big enough to handle large area substrate processing. The techniques of UV direct write \([12, 31, 34, 39]\) and photo-bleaching \([25]\) have the advantage of being high speed. These processes also have the advantage of fabricating waveguides without chemical etching by changing the refractive index of optical polymer. The UV direct write approach is very popular in research due to its design flexibility and is maskless process. Another material removal approach is through laser ablation \([19, 34, 95, 96]\). Laser ablation is used to remove core and cladding polymer materials on either side and forms the waveguide. Excimer laser is preferred since no debris is observed upon the ablation process. However, the “yellowing” effect contributes to the increased loss at shorter wavelengths \([95]\).

Alternately, the fabrication of micro channels using soft lithography approaches, such as moulding \([13, 15, 27, 43, 45, 97]\) and embossing \([14, 18, 42, 98-100]\), has been actively pursued. Such techniques involve generating a pre-patterned electroformed/ electroplated nickel master or a mould made of SU-8 or polydimethylsiloxane (PDMS), before the pattern is replicated in the polymeric films and cured. The difference between moulding and embossing is that moulding is the core-filling process into a pre-patterned mould; while a pre-patterned master is used to imprint/ emboss into polymeric films to form waveguide patterns via elevated pressure and temperature. Beside UV direct writing, a proton-beam writing technique has been demonstrated to fabricate a 5 \(\mu\)m x 5 \(\mu\)m waveguide in SU-8 material \([101]\). Other direct lithographic techniques have seen significant development, such as direct dispensing \([44]\) and inkjet printing \([34, 102, 103]\) due to the apparent advantages in flexibility, additive processing and the possibility of 3D
fabrication. These additive methods only deposit material where it is needed. This translates into minimum material wastage. However, these techniques need to overcome the critical challenges, which are, forming a deep vertical side wall optical core and production of printable materials.

Table 6.1 Advantages and disadvantages of waveguide patterning approaches.

<table>
<thead>
<tr>
<th>Approaches</th>
<th>Advantages</th>
<th>Disadvantages/ Challenges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolithography</td>
<td>Standard microelectronics process.</td>
<td>Surface roughness.</td>
</tr>
<tr>
<td>Photo-bleaching</td>
<td>Fast speed; no chemical etching.</td>
<td>Shape control and unevenness of core.</td>
</tr>
<tr>
<td>UV direct writing</td>
<td>Maskless; inexpensive; rapid prototyping; large area processing.</td>
<td>Core size and resolution limited by the laser spot; slow writing speed.</td>
</tr>
<tr>
<td>Plasma, RIE</td>
<td>Conventional microelectronics process; used in single mode &lt;10 μm waveguide</td>
<td>Etch rate correlates with surface roughness; long etching time; chamber size limitation.</td>
</tr>
<tr>
<td>Laser ablation</td>
<td>Controlled removal of materials; optimized excimer laser ablation.</td>
<td>Surface roughness and debris; yellowing effect.</td>
</tr>
<tr>
<td>Moulding</td>
<td>Large area replication; non-photosensitive material.</td>
<td>Expensive mould fabrication.</td>
</tr>
<tr>
<td>Embossing</td>
<td>Effective for large core processing; large replication; suitable for complex patterns.</td>
<td>Expensive master fabrication; precision at large area processing.</td>
</tr>
<tr>
<td>Dispensing, inkjet printing</td>
<td>Additive process; low temperature, flexible, maskless process.</td>
<td>Inkjet-able inks; discontinuous structure and bad aspect ratio.</td>
</tr>
<tr>
<td>Light/laser induced self written</td>
<td>Automation in waveguide-fiber coupling; 3D waveguide</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.2 Summary of demonstrated optical core microstructures and propagation losses of the waveguide fabricated with various techniques.

<table>
<thead>
<tr>
<th>Approaches</th>
<th>Optical core sizes/ pitches (µm) [ref]</th>
<th>Propagation loss measurement (dB/cm) [ref]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolithography</td>
<td>10 x 40/ - [36]</td>
<td>0.5 @850 nm [36]</td>
</tr>
<tr>
<td></td>
<td>35/ 62.5 [39]</td>
<td>0.7 @1320 nm [36]</td>
</tr>
<tr>
<td></td>
<td>60 x 45/ 250 [80]</td>
<td>0.037 @850 nm [39]</td>
</tr>
<tr>
<td></td>
<td>50/ 250 [93]</td>
<td>0.04 @850 nm [80]</td>
</tr>
<tr>
<td>Photo-bleaching</td>
<td>50, 55, 60/ 250 [25]</td>
<td></td>
</tr>
<tr>
<td>UV direct writing</td>
<td>50/ 125 [39]</td>
<td>0.05 @850 nm [39]</td>
</tr>
<tr>
<td></td>
<td>50 x 10/ 250 [12]</td>
<td>0.58 @632.8 nm [12]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.21 @850 nm [12]</td>
</tr>
<tr>
<td>Proton beam writing</td>
<td>5 x 5/ - [101]</td>
<td>0.19 @632.8 nm [101]</td>
</tr>
<tr>
<td>Plasma, RIE</td>
<td>3-5/- [94]</td>
<td>-</td>
</tr>
<tr>
<td>Laser ablation</td>
<td>70/ 330 [34]</td>
<td>0.13 @850 nm [95, 96]</td>
</tr>
<tr>
<td></td>
<td>50/ 125 [19, 95, 96]</td>
<td></td>
</tr>
<tr>
<td>Moulding</td>
<td>70/ 250 [27]</td>
<td>0.03 @850 nm [27]</td>
</tr>
<tr>
<td></td>
<td>50/- [13]</td>
<td>0.6 @850 nm [13]</td>
</tr>
<tr>
<td></td>
<td>70/- [97]</td>
<td>0.3 @850 nm [97]</td>
</tr>
<tr>
<td></td>
<td>7.8 x 5/- [45]</td>
<td>0.28 @1.3 µm [45]</td>
</tr>
<tr>
<td></td>
<td>200/- [43]</td>
<td>0.26 @1.55 µm [45]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2 @850nm [43]</td>
</tr>
<tr>
<td>Embossing</td>
<td>60 x 40-80/- [14]</td>
<td>0.22 @850 nm [100]</td>
</tr>
<tr>
<td></td>
<td>56 x 50/ 250 [100]</td>
<td>0.07 @850 nm [18]</td>
</tr>
<tr>
<td></td>
<td>40/- [18]</td>
<td>0.3 @850 nm [42]</td>
</tr>
<tr>
<td></td>
<td>6.8 x 7.5/- [42]</td>
<td></td>
</tr>
<tr>
<td>Dispensing</td>
<td>250 x 16/- [44]</td>
<td>0.4 @633 nm [44]</td>
</tr>
<tr>
<td>Inkjet printing</td>
<td>80 x 10/- [102]</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>100/- [103]</td>
<td></td>
</tr>
<tr>
<td>Light/ laser induce self written</td>
<td>80 – 120/- [104]</td>
<td>1.0 @800-1000 nm [104]</td>
</tr>
</tbody>
</table>
Other distinctive approaches demonstrated in the literature are ion exchange [16] and light induced self writing [104]. The ion exchange technique was demonstrated in a thin glass layer waveguide structure. The desired refractive index difference between core and cladding zone of the waveguide was achieved in the exchange of glass and salt melt ions causing a density difference in the glass matrix. Light induced self written technique grows the optical core portion by selective photo-polymerization of the resin mixture caused by multimode optical fiber irradiation. This allows automation of the optical interconnection coupling between the waveguide and the optical fiber during the waveguide formation process. This technique is further advanced with a modified femtosecond laser-assisted self writing approach reported by Cai et al. for 3D waveguide fabrication [105].

6.2 Screen printing

The polymer waveguide fabrication was first approached using screen printing. Screen printing was selected for trial as a commercial model of a DEK 265 printer was available in Loughborough University, so it was appropriate to first test the optical materials using screen printing. It is also a mature process widely used in the microelectronics industry, low cost and is suitable for large area printing of polymeric materials. Screen printing, also known as a doctor blading process, is used with a specific screen design to print the liquid core material through the screen pattern onto the cured cladding layer. The disadvantage of screen printing is that the thickness of each deposition step is limited to a range of 5 - 10 µm thick, depending on the material. Hence, for large multimode core sizes ranging from 30 µm to 70 µm, several prints are required for height stacking. This leads to both material and process challenges in order to achieve desired print-to-print alignment. In addition, it is recommended to equip the DEK printer with an internal UV lamp for an immediate and enclosed curing process. The trial of polymeric optical waveguide fabricated by screen printing was conducted using a low cost prototyping UV curable material of Norland Optical Adhesive (NOA), as discussed in Chapter 2. Subsequent paragraphs describe the work conducted to investigate the planar 2D
processing in forming large optical core microstructures by stacking liquid polymer while curing.

6.2.1 Experiment

The screen printing trial was a collaboration work with DEK R&D center in Weymouth, England. Two different polyester screens were designed for optical core and cladding deposition respectively. The screen design for the cladding was a rectangular 250 x 80 mm large area pattern. The screen design for the various optical core sizes deposition is shown in Figure 6.2.

Figure 6.2 Mechanical drawing for the waveguide optical core pattern designed for screen fabrication.

The design of the screen consisted of four different core geometries, as listed in Table 6.3, with ten channels of waveguides on each design. The screen was designed to scale the limit in micro-scale level stack printing accuracy of optical core. Each print of polymer layer was expected at ~10 µm thickness. Hence, the alignment
accuracy in forming the printing, curing and stacking of core material was the critical process control. Low cost NOA material was used as an evaluation optical polymer and was spin-coated on 125 \( \mu \)m thick Kapton\textsuperscript{TM} substrate. NOA63 with viscosity at 2500 cP was used as the core material while NOA65 with viscosity at 1500 cP was used as cladding material.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Design & Core width (\( \mu \)m) & Core pitch (\( \mu \)m) \\
\hline
I & 200 & 400 \\
\hline
II & 100 & 250 \\
\hline
III & 75 & 250 \\
\hline
IV & 50 & 250 \\
\hline
\end{tabular}
\caption{Waveguide dimension designed for screen printing.}
\end{table}

The size of the Kapton\textsuperscript{TM} substrate was cut to 100 x 300 mm sheet. Prior to the optical polymer deposition, the substrate’s surface was cleaned with methanol in an ultrasonic bath before drying. This is followed by oxygen plasma treatment for surface activation. NOA65 was then screen printed onto the substrate’s surface and formed a 10 \( \mu \)m thick bottom cladding layer. The printed bottom cladding layer was cured with a 100 W UV lamp for 10 minutes before the deposition of the core material. NOA63, which is of higher viscosity than NOA65, was used as core material. The first layer of screen printed core material was UV cured before applying the over cladding step to complete the fabrication process. For the core stacking process, the screen printed core structure was UV cured prior to the repeating print to form stacked core layers. Each print of core material was measured as 10 \( \mu \)m thick. The screen printing process is illustrated in Figure 6.3.
6.2.2 Results and discussion

The screen printed waveguides as shown in Figure 6.4, were observed under a microscope and analyzed by using a Zygo SWLI profilometer. A cross-section of the sample was used to evaluate the profile and thickness of the screen printed UV curable optical polymer. Figure 6.5 shows the cross-sectioned optical image of Design I sample with 200 µm core width and 400 µm core pitch while Figure 6.6 shows the screen-printed waveguide array profile as measured by Zygo SWLI profilometer. It was observed that the UV cured core screen printed onto cladding materials spread substantially, leading to a broad and shallow structure. The low height-width aspect ratio microstructure was not ideal for optical core design. The good wetting between the core and cladding was expected, as both materials are made of the same NOA epoxy grade. The screen-printed core was immediately UV cured to prevent further spreading of the core width. Therefore, multiple printings to form stacking core layers were required to achieve desired core height of 30 - 50 µm.
Figure 6.5 Cross-sectioned optical image of the screen printed core on bottom cladding based on Design I screen (core width = 200 µm; core pitch = 400 µm).
Further experiments to print multilayer stacking core structures were conducted on all four designs of waveguide dimensions. The optical images of the stack-printing core layers are shown in Figure 6.7. Two major issues were found in this experiment:

(1) **The alignment accuracy of the stacking core layers**: Although the screen printing process was aligned using the optical marker recognized by the DEK printer, stacked printing misalignment was observed under the microscope, as shown in Figure 6.7. The misalignment was observed consistently in all four designs. However, a DEK representative was confident this issue would be overcome with a proper vacuum substrate holder to fix the position of the flexible substrate during screen printing process.

(2) **The side wall edges were rough and formed a wavy line along each edge**: The wavy edge was particularly obvious towards the smaller screen printed core’s width. This can be explained by the surface tension effect. Some of the printed waveguide tracks were merged and joined due to surface tension of the liquid polymer. The wavy lines were due to the separation between the meshing of the polyester screen and the surface tension of liquid polymer.
Optimization of both the screen printing process and screen-printable material formulation are required in order to obtain improved alignment and reduce the material’s stickiness to the polyester mesh during screen snap off. The wavy core structures will increase the optical scattering loss of the waveguide. The finding in this screen printing experiment is compared to the observation reported in dispensing [44] and inkjet-printing approach [102]. The spreading of the core material on the cladding surface is a major obstacle to achieving a desired waveguide’s core structure at a 1:1 height-width aspect ratio. The symmetrical core structure is also critical in reducing polarization dependent loss [8]. Several methods are recommended to improve the spreading characteristics by deploying a low energy, hydrophobic surface and controlling the substrate temperature.
6.3 Electrostatic induced lithography

A new method has been adopted in this research to fabricate polymeric waveguide-on-flex based on electrostatic induced lithography and pattern formation. A spin-coated liquid optical polymer placed in between two conductive plates experiences an electrostatic force in an applied electric field gradient across the plates. The surface electrohydrodynamic instability is exploited for the replication of optical core microstructures using a pre-patterned conductive plate. Initial results show good pattern transfer in physical shape. A very smooth sidewall surface is observed upon the growth process induced by an electrostriction phenomenon. An initial feasibility study was carried out using viscous UV curable NOA optical polymer and then followed by trials with Lightlink™ commercial optical polymer. Multimode waveguides with 50 µm x 50 µm cross section and 250 µm pitch were demonstrated on a 10 mm x 10 mm flexible substrate. The whole fabrication process is found to be fast, cost effective without using resists, exposures, developers and etching. Compared to a conventional photolithography approach, the electrostatic induced lithography is also applicable to non-photosensitive polymers.

6.3.1 Literature review

Over the last decade, there has been much research on the formation of self-assembled or ordered structures in polymer thin films due to surface instabilities induced by both electrostatic forces[106-108] and heat flux across the field [109, 110]. A review of the recent developments in electrostatic layer-by-layer thin film assembly was given in [111] where the fundamental understanding of surface level adsorption is addressed. Efforts have been undertaken to extend the application of surface electrohydrodynamic instability to the fabrication of nano- and micro-structures in polymer films [112-114]. This method is based on dielectric media experiencing a force in an electric field gradient. Strong field gradients can produce forces that induce instability, and overcome gravity and surface tension in thin liquid films. The imposed field also moves the liquid from the regions of low field to high field, thus allowing a precise control of pattern. If the top electrode is replaced by a topographically patterned electrode, the instability occurs first at the locations where
the distance between the electrodes is smallest. Notably, a modified approach has been reported by Salac et al. using an in-plane electric field patterning of polymeric thin film [115].

The concept of the electrostatic induced lithography is illustrated schematically in Figure 6.8. The polymer microstructures are formed by disturbing the dynamical surface stabilities of the spin-coated liquid core layer between two conductive plates. The growth of the liquid core structure is induced by an applied electric field, which overcomes the surface tension into a pattern pre-designed on a metal electrode. Depending on the voltage $U$, the electrode spacing $d$, the initial film thickness $h_0$, the dielectric constant $\varepsilon$, and the surface tension $\gamma$, a characteristic wavelength of $\lambda$ is amplified.

Figure 6.8 A schematic illustration of a liquid polymer film destabilized by an electrostatic pressure induced by the applied electric field through a pre-patterned top electrode and flat bottom electrode.
The characteristic wavelength $\lambda$, is given by a balance of force between the destabilizing pressure gradient, $p$ of the local film thickness, and surface tension $\gamma$ [116],

$$\lambda = 2\pi \sqrt{\frac{2\gamma}{-\frac{\partial p}{\partial h}}}$$  \hspace{1cm} (1)

For an applied voltage, $U$ in (3), the destabilizing pressure (2) scales with the square of the electric field strength in the polymer layer $E_p$ [116],

$$p = -\varepsilon_0 \varepsilon_p (\varepsilon_p - 1)E_p^2$$  \hspace{1cm} (2)

where

$$E_p = \frac{U}{\varepsilon_p d - (\varepsilon_p - 1)h}$$  \hspace{1cm} (3)

and $\varepsilon_0$ is the dielectric permittivity in vacuum. For a high enough field where $E_p$ is at $10^7$ V/m, the electrostatic force overcomes gravity and other interfacial pressures, such as van der Waals disjoining pressure or the Laplace pressure [107]. Undulations start developing towards a liquid morphology spanning between the two electrodes as shown in Figure 6.9. Temporally, the amplitude of the fluctuations increases to a point where it induces a localized growth of a polymer structure. For larger applied bias voltage, the size of the surface feature $\lambda$ is smaller in accordance with the equation given above. The presence of a pattern on one of the master electrode enables the creation of a non-uniform electrical field strength which locally enhances this instability pattern.
In the 3D-Mintegration project, Heriot-Watt University evaluated the electrostatic induced micro-patterning technique in the fabrication of 3D polymer microstructure for micro-fluidic devices [114]; while the author evaluated this approach for polymer waveguide fabrication. The potential advantage of this process in patterning the waveguide core pattern relies on its ability to obtain smooth surfaces, minimizing the side-wall roughness for low-light scattering. Feasibility study was subsequently conducted to investigate the possibility of employing this technique with both NOA epoxy and polysiloxane Lightlink™ for waveguide fabrication.

### 6.3.2 Experiment

An initial trial was conducted using the experimental set up in Heriot-Watt University as shown in Figure 6.10. The viscous UV curable NOA optical polymer was chosen as the trial material. The material was spin-coated onto a KaptonHN™ substrate prior to the electrostatic induced lithography process. As shown schematically in Figure 6.11, this approach is fundamentally different from soft lithography, where a mould is pressed into a polymer melt, and mechanically deformed into the shape of a mould. A nickel based plate with waveguide arrays pattern fabricated by an electroplating process was used as a master. The grounded
bottom electrode was a simple flat sheet metal to provide rigid support for the flexible substrate. The initial gap between the master and the top surface of optical polymer was maintained by the spacer to provide a path for surface evolution. It has been predicted that the applied electric fields required across this capacitor like arrangement to induce polymeric microstructure growth are of the order of $10^7$ Vm$^{-1}$ [107]. In this experiment, a voltage in the range 0.5 – 1.0 kV was applied with a gap of 50 µm translating into $1 - 2 \times 10^7$ Vm$^{-1}$. The liquid polymer becomes attracted by the extruded pattern on the master electrode and tends, over time, to replicate the pattern. The sample was immediately UV cured upon removal of the electric field.

*Figure 6.10 Experimental set up of electrostatic-induced patterning method in Heriot-watt University.*

*Figure 6.11 Schematic of the experimental setup used for the electrostatic induced lithography patterning of optical polymer.*
In this initial experiment, a nickel master was electroplated with a test pattern as shown in Figure 6.12. The substrate size was cut to 5 cm x 5 cm and three different waveguide patterns were designed, i.e. straight, 90° radial turn and 180° radial turn. The core size (the width of the pattern) was designed at 50 µm, core pitch at 250 µm and bend radius at 0.5, 1.0, 1.5, 2.0 or 2.5 mm.

*Figure 6.12 Illustration of the waveguide test pattern designed for the initial electrostatic induced lithography experiment.*
6.3.3 Feasibility investigation

Figure 6.13 shows a SEM image of the arrays of NOA waveguide structures replicated from a nickel master. The spacing between the master and the spin-coated core layers was 50 µm. As the electrodes were subjected to a voltage potential of 0.8 kV DC, the pattern formation took place over a time period of 15 minutes resulting in microstructures of 50 µm height at 250 µm pitch. The sidewalls of the microstructures are relatively smooth. The steep vertical sidewall with a height-width aspect ratio close to 1:1 is ideal for waveguide fabrication compared to the spread and bad aspect ratio observed in techniques such as screen printing, dispensing and inkjet printing.

Figure 6.13 SEM image of NOA-based polymeric waveguide patterns replicated from the initial electrostatic induced lithography feasibility study (0.8 kV for 15 minutes with estimated 50 µm gap). The inset shows an optical microscope image of the electroformed nickel master as a topographically structured electrode.
Throughout the feasibility study, three scenarios were explored during the electrostatic-induced lithography of the liquid polymer, demonstrating the possibility in controlling the growth of the morphology in the polymerised domain. In the first scenario, the Lightlink™ core polymer was subjected directly to an applied voltage of 0.8 kV without the pre-bake step. Figure 6.14 shows the resulting weakly formed structures. The lower viscosity Lightlink™ polysiloxane, led to the spreading of the liquid on the deposited surface over time.

Figure 6.14 SEM image of the fabricated Lightlink™ waveguide structures with DC voltage of 0.8 kV. Pre-bake is excluded, $h_0 = 10 \, \mu m$, $d = 50 \, \mu m$.

With the soft bake step included and an initial film thickness, $h_0$ at 10 \, \mu m, Figure 6.15(a)-(b) shows the next scenario obtained by limiting the polymer volume and time for growth. The surface tension of the more viscous NOA optical polymer upon electrostatic-induced lithography resulted in semi-spherical structures. Such structures may be advantageous for optical interface coupling with circular fibre facets. The defect observed on the sample was possibly because of insufficient initial
film thickness coated for the electrostatic-induced lithography process, resulted in discontinuity and broken waveguide arrays.

The third scenario was an array of steep sidewall waveguide structures as shown in Figure 6.15(c)-(d) with the initial film thickness, \( h_0 \) of 15 \( \mu \text{m} \). Indeed, the polymer was seen to have reached the top electrodes. The undulation of the sidewall occurred during the separation of the master surface from the polymer. However, the release of the waveguide structures from the master can be improved by using a surface release agent on the master surface.

*Figure 6.15 SEM images of the fabricated NOA waveguide structures with DC voltage of 0.8 kV. Pre-bake included, \( d = 50 \mu \text{m} \). (a-b) \( h_0 \) at 10 \( \mu \text{m} \); (c-d) \( h_0 \) at 15 \( \mu \text{m} \).*

From the feasibility study, the electrostatic induced lithography has proven to be capable to grow steep and vertical sidewall optical core microstructures using both NOA and Lightlink\textsuperscript{TM} optical polymers. The NOA optical polymer was successfully
grown to 40 - 50 µm in height as measured by profilometer and presented in Figure 6.16.

*Figure 6.16 Zygo image of electrostatic induced growth height of optical polymer.*

From the current processable form factor of 10 x 10 mm², there are several issues that need further investigation prior to successfully introducing this method in waveguide fabrication:

- Polymeric growth characteristics, core formation mechanisms, growth rate and optical polymer curing recipes that will determine the fabrication of waveguide using this approach.
- A specially formulated material for electrostatic-induced lithography with characteristics such as viscous and low solvent-solids ratio optical polymer for thick coating deposition and avoiding an unnecessary pre-bake step.
- The possibility of a parallel curing step with the electrostatic pressure maintained on the microstructures formed. The microstructures can either be cured using UV exposure via a transparent conductive top electrode or via elevated temperature using a hotplate.
- The coplanarity and field variation may prove a substantial challenge when considering large area processing in the future.
• The possibility of molecular re-orientation and packing density changes as a result of the field-induced growth and its effect to the optical properties.

6.4 Summary

Many different approaches have been demonstrated by researchers in the fabrication of multimode polymeric optical waveguide. While the industry may prefer mature manufacturing processes i.e. photolithography and plasma etching, several new approaches have introduced advantages such as direct, low cost processing and flexibility into the fabrication techniques. Initial trials with NOA materials using a DEK screen printer present fundamental challenges in producing optical core structures with a 1:1 height-width aspect ratio on a flat cladding layer. Repeating prints were conducted to form stacking layers of core material, but alignment and spreading of the liquid polymer during curing were two issues in this process. An electrostatic-induced lithography was found to be a promising technique capable to fabricate smooth surfaces with steep vertical sidewall microstructures. A feasibility study of the electrostatic induced lithography was conducted using NOA epoxy and Lightlink™ polysiloxane. Initial results included the successful fabrication of 50 µm x 50 µm optical core structures. Further characterisation activities have been identified to fully understand the application of the process in waveguide fabrication.
Chapter 7
CHARACTERISATION OF POLYMERIC WAVEGUIDE-ON-FLEX FABRICATION USING ELECTROSTATIC INDUCED LITHOGRAPHY

Polymer optical waveguides will play a key role in several rapidly developing optical networking and optical backplane applications due to their low cost processibility and flexible integration approach into optoelectronic devices. The keys to an optically low loss waveguide fabrication are ultra-smooth, defect free coatings of optical layers and well-defined optical core micro structure with low sidewall roughness. It is with this motivation that the electrostatic induced lithography is adopted to replicate the polymer waveguide arrays. Using this process, an array of multimode waveguide was fabricated on flexible substrate for integration with electrical circuitry. This chapter recommends the process flow of electrostatic induced lithography waveguide fabrication, considers various process recipes and reports the pattern formation of the polymeric optical core. By adjusting the spin-coated liquid core thickness, pre-bake condition and applied voltage, the surface morphology, aspect ratio and profile of the optical core microstructure were investigated.

The set up of the electrostatic induced lithography in Loughborough University is described in section 7.1. Experiments were designed to characterize and understand the optical material response to the electric-field induced growth. While no specific material has been developed for electric-field induced waveguide patterning, there are existing optical polymers designed for photodefinable, moulding, laser ablation, and inkjettable applications. The characterisation results are discussed in section 7.2 and help to define a new set of material requirements, useful in future formulation of electrostatic-induced lithography optical polymer. As a result of the work, section 7.3 proposes a new electrostatic induced lithography set up utilizing the transparent planar electrode for further investigation.
7.1 Experiment

7.1.1 Electrostatic induced lithography set up

A safety box was constructed for the application, as shown in Figure 7.1. As a very high voltage application of 0.1 – 3 kV is involved, the safety box is equipped with a safety interlock to automatically cut-off the power supply when the door is opened.

Figure 7.1 The electrostatic induced lithography set up.

Figure 7.2 illustrates the electrostatic induced lithography set up for the patterning of the optical core material for a waveguide-on-flex application. As a strong electric field as high as $10^{-7}$ V/m is required [107], the process is not directly applicable to patterning of liquid polymer on a thick printed circuit board (PCB). The thin flexible substrates at 50 – 125 µm are ideal for a strong field across the gap created by the spacer placed between the electrodes. A design alteration is required if the optical waveguides are to be fabricated on a PCB made of FR4 materials using the electrostatic induced lithography. A PCB is usually made with thick FR4 dielectric materials coupled with several copper layers for interconnection. Such a material structure has rendered the process almost impossible for waveguide-on-PCB fabrication.
A nickel based plate with waveguide arrays pattern as depicted in Figure 7.3 was fabricated using an electroforming process by MicroStencil Limited. The electroformed extrusion height and the track width were 50 µm. The waveguide patterns were designed in straight lines, U bend, X crossing and Y splitter. The grounded bottom electrode was a simple flat sheet metal to provide rigid support for the flexible substrate to be attached. The initial gap between the master and the top surface of optical polymer was determined by the spacer to provide a path for surface evolution.
7.1.2 Process recipes and critical variables

As shown in Figure 7.4, the recommended processing and curing protocols of the Lightlink™ optical polymer using a photolithography process were purposely altered to suit the electrostatic induced lithography technique. Before applying the bottom cladding layers, the surface of the flexible substrate KaptonHN™ used in this experiment was plasma-treated. The cladding layer was applied by spin-coating and cured. This was followed by the micro-patterning of the optical cores using the electrostatic induced lithography. Compared to the conventional photolithography process, the development process to drive smooth dissolution in the unexposed regions of the core’s film was omitted in the electrostatic induced lithography. The patterned optical core microstructures were fully cured with UV exposure and a final bake before the subsequent over cladding process.

Figure 7.4 Schematic diagram of the Lightlink™ waveguide fabricated on flexible substrate using (a) conventional photolithography process; and (b) the proposed electrostatic-induced lithography approach.
The process flow of the electrostatic-induced lithography of optical core patterning is illustrated in Figure 7.5. Firstly, the liquid Lightlink\textsuperscript{TM} XP6701A core material is spin-coated onto the cured cladding layer to achieve the initial coating thickness in the range of 10 – 15 µm. The coating is then put on a hot plate for soft baking, to reduce the solvent content. A soft exposure is included prior to the application of the electrostatic induced growth process. With the coating material fine-tuned to a more viscous state, the electrostatic-induced lithography process begins with an electrical potential applied in a controlled temperature environment. Upon the completion of microstructure growth, the final UV exposure and baking process are included to fully crosslink the material and remove all unnecessary solvent.

**Figure 7.5 Characterisation of process recipes.**

![Diagram](image)

In this experiment, several process variables in the electrostatic-induced lithography have been identified for process characterisation:

1. The spin coating variables of speed (RPM) and time (second) were varied to investigate the effect of different initial spin-coated core thickness. The initial coating thickness determines the final volume available for the electrostatic-induced lithography process.

2. The soft bake temperature (°C) and time (minutes) reduced the solvent content, therefore increasing the viscosity of the coating.

3. The pre-exposure step (second) was included to introduce partial crosslinking of the material, thus controlling excessive flow of material.

4. The electric potential (voltage) was varied to achieve high enough field for adsorption to occur and overcome surface tension, thus forming 3D
microstructures. The temperature (°C) and time (minutes) of the applied field to the specimen were varied to investigate the material response to electrostriction effect.

7.2 Results and discussion

Several experiments were designed to investigate the effect of process variables identified in the electrostatic-induced lithography. These variables are critical to understanding the material response to the electrostatic effect. A modelling tool was used to simulate the electrostatic field distribution within the gap between two electrodes. Then, the effect of UV exposure, electric potential, soft bake temperature and time are discussed respectively. The initial coating thickness was used to control the waveguide shape formation. From these characterisation activities, a new set of material requirements for electrostatic-induced lithography material set is presented and discussed.

7.2.1 Electrostatic field modelling

The dynamic behaviour of lithographically induced self assembly at the nano-scale has been proposed by Deshpande et al. [117] and Wu et al. [113]. However, the growth mechanism at the micro level is yet to be ascertained. The growth mechanism of the electrostatic-induced lithography optical waveguide could be considered as follows: when a high enough electrostatic field is sustained, the thinly coated Lightlink\textsuperscript{TM} core layer can be destabilized by a strong field between the electrodes [106]. The instability leads to the undulation observed on the surface morphology. With the variation of electrostatic field caused by the pre-patterned master, the electrostriction force overcomes the surface tension and deformation of the polymer coating occurs. A high enough field can be assisted by elevated temperature processing to further promote the electrostatic-induced lithography of the liquid polymer, and grows into patterned microstructures [112].
In order to understand the electrostatic field distribution between the two electrodes, a simple model has been constructed using COMSOL© Multiphysics software. The software package has an electrostatic analysis module which allows simulation of the electrostatic field between two electrodes. A simple single protrusion model was created with symmetrical boundary conditions. Both the protrusion height and air gap are modelled at 50 µm. The top edge of the model is applied with 1000 V while the bottom edge is grounded. Side edges are assigned as symmetrical boundary condition with no charge. The result is plotted in Figure 7.6 showing the contour distribution of electrostatic field in the air gap.

Figure 7.6 Electrostatic field distribution between the two electrodes simulated by COMSOL.

From the contour plot, concentrated fields occur at the two edges of the protrusion, signalling high electrostatic field strength at the corners. By plotting the field strength horizontally across the air gap, the field strength variation across the depth of air gap, d is shown in Figure 7.7. The “edge effect” is not expected until the air
gap reduces to <10 µm. This finding explains the initial observation of “sharp edges”, as shown in the inset image of Figure 7.7, which appeared across a flat top waveguide structure when electrostatic-induced lithography process was completed. A further step can be taken to eliminate the sharp edges phenomenon by controlling the air gap, such that it does not become lower than 10 µm. Alternatively, this can be achieved by allowing additional time for the material’s surface tension to take over after the electrostatic-induced lithography process is completed.

Figure 7.7 “Edge effect” as observed in the experiment, supported by the modelling result. The “edge effect” becomes significant at <10 µm.

Field strength across depth, d

Edge effect occurs at 10 micron and below.
7.2.2 Characterisation of process recipes

Subsequent experiments were set up to investigate the effect of each process parameters and their relationship with the material response in waveguide fabrication.

Figure 7.8 compares the electrostatic-induced surface morphology with and without including a soft-UV exposure prior to the electrostatic-induced lithography process. UV exposure on Lightlink™ core material generates photo-acids to catalyze crosslinking of Si-OH to form rigid and symmetrical Si-O-Si chains. Knowing that a fully cured core material requires exposure of 2000 mJ/cm², the minimum exposure time of a UV radiation of 5 mW/cm² system required to achieve a fully cured state is 400 s. Therefore, a pre-UV exposure time of 100 s was conducted to allow partial-crosslinking of the material. Besides producing more rigid chains in the material, UV exposure is also expected to have caused the liquid polymer to be in a more viscous state. Hence, the flow of the material can be restricted upon the completion of the electrostatic-induced lithography process. Based on the observation in Figure 7.8, it is recommended that a soft-UV exposure step be introduced prior to the electrostatic-induced lithography process. The solution with pre-exposure shows improved surface morphology and better controlled growth.

Figure 7.8 Comparison of Lightlink™ surface morphology (a) with and (b) without pre-exposure prior to electrostatic-induced lithography. [Coating of 12 µm; pre-bake 40 °C at 10 mins; **pre-UV exposure at 5 mW/cm² for 100 s**; electrostatic-induced lithography of 0.9 kV at 30 mins].
Knowing that pre-exposure assisted in the electrostatic-induced lithography growth of optical core, Figure 7.9 compares the soft exposure time at 100 s, 200 s and 300 s. At 200 s of soft exposure time, the optimum growth of Lightlink™ was observed. The thin white line in the middle of the track observed in $t = 200 \text{ s}$ sample, indicates that the growth has reached the master’s surface prior to separation. The waveguide track formed in the $t = 100 \text{ s}$ sample was weakly formed and widely spread, with a track width larger than 100 $\mu$m from a 50 $\mu$m pattern. In contrast, the $t = 300 \text{ s}$ sample indicates a cured state and insufficient growth of polymer occurred to form waveguide track.

*Figure 7.9 Comparison of Lightlink™ optical core’s growth at different pre-exposure time. [Coating of 12 $\mu$m; pre-bake 40 °C at 10 mins; pre-UV exposure at 5 $mW/cm^2$ for t s; electrostatic-induced lithography of 0.9 kV at 30 mins].*

Sufficient solvent content is required to maintain the viscous state of the liquid optical polymer. However, a more viscous growth is desired so that improved height-width aspect ratio for optical core structure can be achieved. The soft bake step is included to reduce the solvent content and promote viscous growth. Figure 7.10 compares the growth characteristic of different soft bake temperature and time. The soft bake temperature is recommended to be lower than 50 °C to prevent excessive drying out as the solvent is removed. Hence, the soft bake time is varied to achieve different viscosities. Generally, a smooth 50 $\mu$m waveguide track is achieved with the soft bake conditions at $T = 45 \text{ °C}$ and $t = 15 \text{ mins}$. 
As the material has been fine-tuned to a desired state prior to the electrostatic-induced lithography process, the effect of electric potential is investigated to compare the effect of the electrostatic field’s strength in optical core formation. While maintaining the initial process condition as listed in Figure 7.11, the electrostatic-induced lithography process is conducted by applying three different electric potentials, i.e. 0.5, 0.9 and 1.5 kV. A high enough field strength is required for surface adsorption to overcome surface tension, and forms 3D microstructures. At $1 \times 10^7$ V/m, little evidence or insufficient growth of polymeric structure is observed. At $1.8 \times 10^7$ V/m and $3 \times 10^7$ V/m, a substantial growth of polymeric structure occurs. The growth of the polymer has reached a height of 40 µm, contacting the master surface. Knowing that the destabilizing pressure scales with the square of the electric field strength [116], the existing electrostatic field strength of $1.8 – 3.0 \times 10^7$ V/m is sufficient for electrostatic-induced lithography process at the micro scale level.
Figure 7.11 Comparison of Lightlink™ optical core’s growth at different electric potential. [Coating of 12 µm; pre-bake 40 °C at 10 mins; pre-UV exposure at 5 mW/cm² for 100 s; electrostatic-induced lithography of 0.5, 0.9, 1.5 kV at 30 mins].

Based on the process recipes obtained in the above characterisation, the electrostatic-induced lithography has successfully fabricated waveguide microstructures made of Lightlink™ optical polymer. However, as shown in Figure 7.12, the separation of the nickel master from the optical core material upon completion of electrostatic-induced lithography process induced peeling or uncured residue trailing off the microstructures. This has resulted the loss of part of a waveguide track after the separation. To aid the separation, a surface release agent (Buehler 1,1-dichloro-1-fluorethane tri-methylated silica) was applied on the master surface prior to the electrostatic-induced lithography process. The end result is shown in Figure 7.12 (b).
Figure 7.12 Comparison of Lightlink\textsuperscript{TM} optical core’s surface morphology after master separation (a) without and (b) with surface release agent. [Coating of 12 µm; pre-bake 45 °C at 15 mins; pre-UV exposure at 5 mW/ cm\textsuperscript{2} for 200 s; electrostatic-induced lithography of 0.9 kV at 30 mins].

7.2.3 Waveguide shape control

With the understanding of material responses to the process variables, the waveguide shape fabricated by the electrostatic-induced lithography process can be controlled by varying the initial coating thickness of Lightlink\textsuperscript{TM} core on the cured cladding. By changing the spin-coating speed, the coating thickness is varied. The coating thickness translates into the volume of material available for polymer growth process induced by the electrostatic-induced lithography. Therefore, the correlation between spin-coating speed (RPM) and the measured coating thickness of Lightlink\textsuperscript{TM} material was characterized and plotted in Figure 7.13.
In the experiments, three different spin-coating speeds were employed. As a result of different coating thickness, the electrostatic-induced lithography process successfully demonstrated different shapes of waveguide structures based on Lightlink™ material. For a thick coating (600 rpm) deposition, the growth of liquid polymer induced by the electrostatic-induced lithography process resulted in flat top and rectangular-section (50 µm x 50 µm) waveguides. At an intermediate spinning speed of 1000 rpm, the hemispherical waveguide shape (30 µm x 80 µm) was observed while the highest speed at 1500 rpm resulted in the lowest volume of material, sufficient to form the oval structures (10 µm x 200 µm) only. The optical images of the waveguide control experiment are shown in Figure 7.14 together with the profile measurements obtained from Zygo profilometer.

Figure 7.13 Correlation of spin-coating speed (RPM) and the measured coating thickness of Lightlink™.
Figure 7.14 Electrostatic-induced lithography optical core profile control of (a) rectangular, (b) hemisphere and (c) oval by varying the coating thickness.

7.2.4 Desired properties for electrostatic-induced lithography

The characterisation of electrostatic-induced lithography recipes has resulted in further understanding in the material properties critical for electrostatically induced growth. As discussed before, the electrostatic-induced lithography is compatible with both photosensitive and non-photosensitive materials. The material response to the electrostatic-induced lithography technique can be characterized by investigating the following properties of the material in question: (1) viscosity and (2) electrostriction.

The surface electrohydrodynamic instability is considered to be opposed by the viscous dissipation in the liquid [118]. As shown in previous process characterisation, soft-baking increases the coating’s viscosity by reducing the solvent/ solid ratio. From these experiments, the NOA epoxy used in the initial investigation was at 2000 – 3500 cP; while the Lightlink™ core material was prepared at 250 cP. As the UV curable NOA optical polymer formed steep vertical microstructures without prior modification to the material state, it can be concluded that a more viscous liquid optical polymer solution suits the electrostatic-induced lithography process. The addition of a pre-UV exposure step of Lightlink™
improves the process by reducing the solvent. Furthermore, a soft UV exposure initiates partial crosslinking of Si-OH chain to a rigid Si-O-Si. By reducing the viscosity of the coating, the material viscous growth characteristic has also improved.

Throughout the experiment, the electrostatically-induced growth of polymer microstructures is found to be related to the electrostrictive behaviour of a material. Electrostriction is explained as the generation of stresses or strains in response to an electric field, leading to deformation. In the case of the electrostatic-induced lithography process, there are two possible sources of strain generation, i.e. (i) strain results from the external forces caused by the electrostatic pressure from two electrodes; and (ii) internal intermolecular forces due to lattice deformation [119]. The electrostrictive property can be characterized by measuring the material’s strain response to an electric field. Although the electrostrictive behaviour of polymer films is investigated mostly for application in actuators [120], the strain deformation induced by electrostatic field characteristic fulfils the physical phenomenon observed in the electrostatic-induced lithography process. When an electrical potential is applied across the electrodes, the polymer film is compressed by the resulting electrostatic forces. The force per unit area that squeeze the film is,

\[ f_{\text{film}} = \varepsilon_r \varepsilon_0 E^2 = \varepsilon_r \varepsilon_0 \frac{v^2}{h^2} \]

where \( f_{\text{film}} \) is the force per unit film area, \( \varepsilon_r \) is the relative dielectric constant of the polymer film, \( \varepsilon_0 \) is the dielectric constant of free space, \( v \) is the applied voltage, \( E \) is the electric field and \( h \) is the film thickness. As the film is unconstrained and unloaded, the strain in thickness, \( s \) resulting from the squeeze pressure is,

\[ s = \frac{f_{\text{film}}}{\text{Modulus}} = -\frac{\varepsilon_r \varepsilon_0 v^2}{h^2 \cdot \text{Modulus}} \]

From the equation, the electrostriction response is proportional to the square of the electric field. The experimental set up to measure electrostrictive behaviour of polymer films were described and reported by Pelrine et al. [120]. Coincidentally,
silicone is reported to have a high electrostrictive response, making it ideal for the electrostatic-induced lithography process. The silicone material has given the highest strain performance of 32% as listed in Table 7.1.

Table 7.1 Measured electrostrictive performance of various polymer dielectrics in the actuator application [120].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Strain</th>
<th>Actuation pressure</th>
<th>Young’s modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyurethane</td>
<td>11</td>
<td>1.9</td>
<td>17</td>
</tr>
<tr>
<td>Silicone</td>
<td>32</td>
<td>0.21</td>
<td>0.7</td>
</tr>
<tr>
<td>Fluorosilicone</td>
<td>28</td>
<td>0.14</td>
<td>0.5</td>
</tr>
<tr>
<td>Ethylene propylene</td>
<td>12</td>
<td>0.022</td>
<td>1.8</td>
</tr>
<tr>
<td>Polybutadiene</td>
<td>12</td>
<td>0.19</td>
<td>1.7</td>
</tr>
<tr>
<td>Isoprene</td>
<td>11</td>
<td>0.094</td>
<td>0.85</td>
</tr>
</tbody>
</table>
7.3 Summary

This chapter focused on the process characterization of electrostatic-induced lithography fabricated polymeric waveguide. The electrostatic-induced lithography set up in the Loughborough University was presented. Several critical process variables were identified for process characterisation using the Lightlink™ material. A model of the electrostatic-induced lithography growth mechanism has been proposed based on the electrohydrodynamics of surface instabilities induced by an electric field. The edge effect observed in both experimental work and electrostatic field modelling was limited to the growth condition when the gap is less than 10 µm. The state of the polymeric coating prior to the electrostatic-induced lithography growth was modified using a pre-bake and pre-UV exposure. A sufficiently high electric field (>0.5 kV at 40 µm gap) was required to achieve the desired height-width aspect ratio of the microstructures. This work has further suggested a method of controlling waveguide shape by varying initial coating thickness. As a result, a process recipe of electrostatic-induced lithography fabricated optical core (50 µm x 50 µm) using Lightlink™ core XP-6701A is proposed as the following:

- Initial coating thickness of 15 µm.
- Pre-bake at 45 °C for 15 mins.
- Pre-UV exposure at 5 mW/ cm² for 200 s.
- Electrostatic-induced lithography at 0.9 kV for 30 mins with a gap of 40 µm.
- Cured for 500 s at 5 mW/cm².
- Final bake at 130 °C for 10 minutes on hot plate.

For further material development in electrostatic-induced lithography, a set of desired material properties is defined based on the solvent/ solids ratio, viscosity and electrostrictive response.
Chapter 8
WAVEGUIDE OPTICAL CHARACTERISATION

The optical characterisation of the polymeric waveguide-on-flex involves measuring the optical properties and optical losses. In optical communication, the behaviour of optical structures is wavelength-dependent. Therefore, it is critical that the optical efficiency of the fabricated waveguides is characterized at the wavelength of interest. In this case the predominant application will be in datacom architectures which transmit light at 850 nm. In this chapter, the key optical properties and the optical budget for a waveguide-on-flex application are discussed. It is followed by the investigation of electrostatic effects on the optical properties of Lightlink™ material before the measured propagation loss of the fabricated waveguide is presented and discussed.

8.1 Optical properties and budget

Two main materials are required in the optical waveguide design, the optical core material and the cladding material. The refractive index of the core material must be greater than the cladding material for light confinement. The selection of the refractive index will also determine the acceptance angle for the light to be coupled into the waveguide. Using Snell’s Law, and \( n_3 = n_{\text{air}} \sim 1 \), the acceptance angle \( \theta \), can be derived as follows:

\[
\sin \theta = \sqrt{n_1^2 - n_2^2}
\]

The term \( \sqrt{n_1^2 - n_2^2} \) is equal to the numerical aperture, \( NA \). As shown in Figure 8.1, if the sine of the angle of incidence of the coupling light source is lower than the \( NA \), then the light will be guided along the waveguide due to the satisfied conditions of total internal reflection. A typical polymeric waveguide is designed with
core/cladding contrast at 2% for light confinement purpose. The Lightlink™ materials used in this experiment have refractive index of 1.51 and 1.48 for core and clad respectively. This has resulted in a $NA$ of 0.30, translating to a critical angle of incidence at $17.5^\circ$.

Figure 8.1 Illustration of critical angle incidence and the total internal reflection.

The refractive index of a material is related to the free volume, molecular packing density and polarizability of the material [8]. In the context of electrostatic-induced lithography, the possibility of electrostatic field effect on the material’s refractive index is the subject of interest. In general, aromatic polymers possess higher refractive indices than aliphatic ones due to better packing density and electronic polarization [8].

One of the most crucial challenges to the application and fabrication of polymeric waveguides is the optical budget. Optical budget depends on integration of an optoelectronics system such as the efficiency of the optical device, coupling design and transmission losses. The factors contributing to optical loss in polymer waveguides can be divided into intrinsic loss (due to material’s absorption) and extrinsic loss (propagation loss due to fabrication impurities, dust, micro cavities and inhomogeneity) [31]. The absorption is usually measured on slab waveguides where fabrication imperfections can be avoided. In the case of channel waveguides, propagation loss measurement is usually measured with the cutback method.
Optical loss can be defined as [36]:

\[ L = 10 \log \frac{P}{P_0} \]

with \( P_0 \) as the power of the incident light and \( P \) as the power of transmitted light. Given the known loss, \( L \), the parameter for a particular waveguide design, the intensity \( I \) at a distance \( z \) from the input is numerically related to the input intensity \( I_0 \), as:

\[ I = I_0 e^{-lz} \]

This exponential relationship implies that the optical throughput of a waveguide will be a critical function of \( L \). Figure 8.2 depicts numerically the range of waveguide losses which will be significant to the design. For a waveguide designed for on-board application, a waveguide length of 5 – 10 cm will require performance of < 0.1 dB/cm propagation loss in order to have a minimum of 40 % power transmitted.

Figure 8.2 Numerical prediction of waveguide efficiency with known loses, \( L \).
8.2 Effect of electrostatic field on optical properties of polymer

The basic optical requirements for polymeric waveguide materials are high transparency at the working wavelengths and maintaining the 2\% refractive index difference of core and cladding for wave guiding purpose. Unlike the conventional approaches in optical core patterning, a high electric field at approximately $1 \times 10^7$ V/m is applied to the optical material throughout the electrostatic-induced lithography process. The effects of such strong field on optical properties were investigated.

8.2.1 Refractive index

Under the influence of electric field, the change in the polymer’s refractive index may occur due to the molecular re-orientation and change in the packing density. As discussed in chapter 2, the polysiloxane Lightlink™ used in the electrostatic-induced lithography waveguide fabrication process is made of highly amorphous and a flexible aliphatic chains structure of Si and side groups. Nevertheless, the refractive index of the material is fine-tuned by the contents of the rigid phenyl groups, which have large molecular refraction. In the liquid phase, large molecular force must be overcome in order for molecular structure re-orientation to occur. Furthermore, the electrostrictive response of the material in the electrostatic-induced lithography process is believed to be due to the external electrostatic pressure, rather than the intermolecular forces. Direct measurement of refractive index changes due to electric field in optical fibers have been reported [121]. A control of refractive index by a similar electrostatic self-assembled method to organize the physical order of the multiple monolayers thin film materials was demonstrated by Arregui et al. [122] and Shibru et al [123]. Chuang and co-workers have reported the use of low electric field ($V/\mu m$) in fine-tuning the 1\% of an epoxy’s refractive index used in polymer waveguide fabrication [46]. The 400 \( \mu m \) thick epoxy layer was UV cured together with a low 10 – 70 V electric field to lower the refractive index. The change in the refractive index is suggested as the change of polymer molecular orientation due to the electric field where epoxy is known to consist of rigid phenyl groups.
To confirm the several hypotheses discussed above, the refractive indices of the polysiloxane Lightlink™ core were measured. According to the material specification, the refractive index of a fully cured Lightlink™ material is $n = 1.51$ at 850 nm. Two samples were prepared in the condition as described in Table 8.1 to compare the effect of electrostatic field. The refractive indices of the samples were measured with a prism coupler (a Metricon unit) at a wavelength of 847 nm and the result is listed in Table 8.2.

**Table 8.1 Sample preparation steps for the refractive index measurement.**

<table>
<thead>
<tr>
<th>Normal procedure: Unexposed</th>
<th>Electrostatic-induced lithography: Exposed to electrostatic field</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin-coating: 12 µm core thickness.</td>
<td>Repeat.</td>
</tr>
<tr>
<td>Pre-bake at 45 °C for 15 minutes on hot plate.</td>
<td>Repeat.</td>
</tr>
<tr>
<td>Pre-UV exposure at 5 mW/cm² for 200 s.</td>
<td>Repeat.</td>
</tr>
<tr>
<td>Skipped.</td>
<td>Electrostatic-induced lithography of 0.9 kV at 30 mins (40 µm gap).</td>
</tr>
<tr>
<td>Cured with 500 s at 5 mW/cm².</td>
<td>Repeat.</td>
</tr>
<tr>
<td>Final bake at 130 °C for 10 minutes on hot plate.</td>
<td>Repeat.</td>
</tr>
</tbody>
</table>

The refractive indices of the samples were measured first on the substrate, before the coatings were removed and measured separately for comparison. The result shows a slightly higher refractive index (0.5 %) on the free standing film. However, there is no significant change of refractive index measured from the two samples. The measured refractive indices of the electric-field exposed and cured optical core materials at the range of 1.5150 and 1.5163 are in accordance with the material specification. The slight change observed at less than 0.02 % is of no critical interest to the waveguide design which has 2% difference between core and clad layers. Furthermore, the measurement has not taken into account the machine tolerances and sample variations. The result supports the hypothesis as the following:
The polysiloxane material is made of highly amorphous material with flexible aliphatic-chains structure. Therefore, limited re-ordering of molecular orientation occurs in the thickly coated polymer film when exposed to electric field, as opposed to the report by Chuang et al. in the application of an epoxy [46].

The electrostatic-induced lithography growth of polymer microstructures is due to the external electrostatic pressure as a result of the electrostrictive behaviour. The process generates minimal or no molecular orientation in the thick coating >10 $\mu$m. The adsorption process of positively and negatively charged molecules may occur only at the surface layers of a thick coating [111].

Table 8.2 The refractive index of Lightlink$^\text{TM}$ core material exposed to electrostatic field in electrostatic-induced lithography process. Measurement is the courtesy of Dow Chemical using Metricon unit at 847 nm.

<table>
<thead>
<tr>
<th></th>
<th>On KaptonHN$^\text{TM}$</th>
<th>Free standing film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal procedure: Unexposed</td>
<td>1.5152</td>
<td>1.5161</td>
</tr>
<tr>
<td></td>
<td>1.5156</td>
<td>1.5160</td>
</tr>
<tr>
<td>Average</td>
<td>1.5154</td>
<td>1.5161</td>
</tr>
<tr>
<td>Exposed to electrostatic field</td>
<td>1.5150</td>
<td>1.5162</td>
</tr>
<tr>
<td></td>
<td>1.5150</td>
<td>1.5163</td>
</tr>
<tr>
<td>Average</td>
<td>1.5150</td>
<td>1.5163</td>
</tr>
</tbody>
</table>

8.2.2 Absorption

Beside refractive index, the effect of electrostatic field on the material’s intrinsic loss was also investigated. Lightlink$^\text{TM}$ polymer is known to be highly transparent in the visible region of the spectrum [38]. Absorption effects are expected to be more prominent at 1300 – 1550 nm region due to the presence of aliphatic and hydroxyl...
group in the material. Figure 8.3 compared the optical property of the processed samples with and without electrostatic field exposure.

Figure 8.3 UV-visible absorbance spectra of Lightlink™ optical core material exposed to electrostatic field in electrostatic-induced lithography process. Measurement was conducted using UV-visible double beam spectrometer.

The samples were spin-coated onto a transparent glass at 1000 RPM for 30 s. It was followed by the soft bake process at 45 °C for 15 minutes on a hot plate. One sample was exposed to an electric field of 0.9 kV at a 50 µm gap with temperature maintained at 35 °C for 15 minutes. All the samples were then exposed with UV curing before subjected to a final bake at 130 °C for 10 minutes on a hot plate. Two UV cure times were prepared (200 s and 1000 s) using spin-coated core material. The ultraviolet-visible absorption spectra (180 – 1100 nm) of cured Lightlink™ core material were evaluated using an ultra violet-visible double-beam spectrometer. An absorption spectrometer measures the way that the light absorbed by a compound varies across the UV and visible spectrum. As shown in the Figure 8.3, it is concluded that no unwanted intrinsic absorption was induced by the electric field at temperature below 35 °C. The processed material maintains optically transparency in the wavelength range of 350 nm to 1100 nm.
8.3 Optical loss measurement

8.3.1 Cutback approach

Figure 8.4 schematically illustrates the typical set up of an optical platform used to characterize the optical performance of a fabricated waveguide [42, 97]. The sample is placed on a work stage, with light source butt-coupled into the waveguide before collection by the fibre at the other end. The propagation loss of the fabricated waveguides was determined by detecting the transmission of light beam from a stable 850 nm light source, which travel down the waveguide and was coupled out into the fiber and photo-detector. The butt-coupled fibre architecture, aligned a 50/125 µm multimode fibre to the 50 µm x 50 µm optical core waveguide placed on the sample stage. The coupled light was then measured by photo-detector (PD). The power measured by the PD was compared directly to the power output from the laser source. Such a measurement is termed as insertion loss, and is expressed in dB, as $10 \times \log_{10}(P_1/P_0)$ where $P_0$ is the reference measurement in mW and $P_1$ is the measurement of coupled light propagating through the waveguide and collected by PD.

Although the set up was simple, such measurement included both the fiber-waveguide coupling loss as well as the propagation losses along the waveguide. In order to be certain of measuring only the loss caused by the attenuation, the cutback approach was adopted [97]. The attenuation of the waveguide, $A$, in dB/ cm, is calculated as [97]:

\[ A = 10 \times \log_{10}(P_1/P_0)/L \]

where $L$ is the length of the waveguide.
\[
A = 10 \times \log \left( \frac{P_1}{P_0} \right) \text{ dB/cm}
\]

### 8.3.2 Optical measurement equipment

The Tempo Optical Platform, commissioned and used by Misselbrook [124] was used in order to test the electrostatic-induced lithography fabricated waveguide. The optical platform was procured with an 850 nm vertical cavity surface emitting laser (VCSEL) transmitter module and a PD receiver module. A Melles Griot optical table was used to ensure that the optical measurements were isolated from external vibrations. All the process equipment was therefore mounted on the optical table. Detail of the components and parts of the platform were reported in [124]. However, several alterations of the setup were made to meet the requirements identified and illustrated in Figure 8.4. As shown in Figure 8.5, 3 charge-coupled device (CCD) cameras were positioned at three different axes for visual alignment. Although 850 nm light is not visible by the human eye, the CCD cameras are capable to detect light well into the infra red spectrum. The alignment stages were arranged at either side of the sample stage. Each of the two Nanotrack alignment stages were used to hold both optical fibers fast to the stages and aligned to the both ends of the waveguide. When in use, the alignment stages were used to move the fibers in x, y and z orientations relative to the facet of the waveguide sample. The fibers carrying the light source were aligned visually using the three CCD cameras. The first alignment stage was manoeuvred until the light coupled out from the waveguide was detected by the opposite camera. The top and side cameras ensured that the fibers were coupling to the correct waveguides. The key components and equipments used in the measurement are listed in Table 8.3.
Figure 8.5 Picture of Tempo Optical Platform set up in Loughborough University used to characterize the propagation loss of the electrostatic-induced lithography fabricated waveguide.

Table 8.3 List of components and equipments used in the optical loss measurement.

<table>
<thead>
<tr>
<th>Components/ Equipments</th>
<th>Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCSEL transmitter</td>
<td>Light source</td>
</tr>
<tr>
<td>PD module 770 series optical power meter</td>
<td>Transmitted light receiver</td>
</tr>
<tr>
<td>700R Controller Module</td>
<td>Operates module selection; display measurement data and calibrated wavelengths.</td>
</tr>
<tr>
<td>Melles Griot 3-axis Nanotrack positioning table</td>
<td>Alignment stages for first and second fibres positioning.</td>
</tr>
<tr>
<td>Sample stage</td>
<td>Fixture for sample placement</td>
</tr>
<tr>
<td>CCD cameras</td>
<td>Used to find first light in the sample and visual alignment.</td>
</tr>
</tbody>
</table>
8.4 Results and discussion

8.4.1 Sample preparation

To estimate the loss quickly, three electrostatic-induced lithography fabricated waveguide-on-flex samples were prepared. The cutback approach with butt-coupling measured the insertion loss of the samples at different lengths of 2.0, 1.5 and 1.0 cm each. Both ends of the waveguide samples were carefully polished so that minimum light is scattered away. The samples were attached to a rigid carrier for measurement purposes. For rigidity purposes, the carrier was then glued with epoxy adhesive onto the sample stage. The first light was visually aligned to the first fiber to the waveguide using CCD camera. The loss measurement was taken by scanning the second fiber in nano-scale movements across the other end of waveguide facet. The measurement of insertion loss was taken at the lowest possible reading during the scanning process. At this stage of work, the measurement process was manually controlled.

8.4.2 Propagation loss

The insertion losses measured for different length are shown in Table 8.4. Based on the table shown, the insertion losses for 3 lots of samples are increased with the increased of waveguide length. As the light coupled into the waveguide, light travels along the path and loses energy due to material absorption and scattering losses. The average insertion loss is 17.1 dB for 2 cm, 15.7 dB for 1.5 cm and 15.1 dB for 1.0 cm.

Table 8.4 Insertion loss measurements for electrostatic-induced lithography fabricated waveguides at different lengths.

<table>
<thead>
<tr>
<th></th>
<th>Insertion Loss (dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L₀</td>
</tr>
<tr>
<td>Sample 1</td>
<td>-17.1</td>
</tr>
<tr>
<td>Sample 2</td>
<td>-18.9</td>
</tr>
<tr>
<td>Sample 3</td>
<td>-15.2</td>
</tr>
</tbody>
</table>
However, the measurement process could be improved in many aspects. The coupling loss could have been reduced with the use of index matching fluid knowing that the refractive index of polysiloxane material and optical fibers are in the range of 1.49 – 1.51 and 1.46 – 1.48 respectively. For a reference, the measurement of fiber-to-fiber coupling loss itself reported a -4.0 dB loss, signalling a large amount of light scattering in the coupling stage. Furthermore, the large coupling loss was not unexpected with the 50 µm core of the fiber used in coupling in and out of the waveguide. The core’s size of the waveguide was expected to be only in the range of 30 - 50 µm.

Based on the cutback approach, the propagation loss was calculated in Table 8.5. Figure 8.6 plots the insertion loss values of the three samples, where the slope of the mean line represents the average propagation loss measured in this experiment. Consequently, the excessive propagation loss of -1.97 dB/ cm indicates that manually fabricated waveguides are not ready for industrial application. Inevitably, the waveguide propagation loss can be improved through process optimization.

Table 8.5 Calculated propagation loss of electrostatic-induced lithography fabricated waveguides using cutback approach.

<table>
<thead>
<tr>
<th></th>
<th>Propagation Loss (dB/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L_0$</td>
</tr>
<tr>
<td>Length</td>
<td>0.5</td>
</tr>
<tr>
<td>Sample 1</td>
<td>-2.4</td>
</tr>
<tr>
<td>Sample 2</td>
<td>-2.8</td>
</tr>
<tr>
<td>Sample 3</td>
<td>-3.0</td>
</tr>
</tbody>
</table>

The propagation losses of waveguide maybe due to defects such as contaminants, voids, micro cracks and material shrinkage. These defects directly affect the light propagation inside the waveguide and scattering at the interfaces. Optical performance improvements may be realized through the optimization of the fabrication process for channel waveguides. To meet the performance specification
of polymer waveguide for optical interconnect with low loss, it requires a cleaner environment, strict process control and more precision handling than the current set up is capable to produce.

*Figure 8.6 Measured propagation loss of the fabricated waveguide is -1.97 dB/cm at 850 nm wavelength.*
8.5 Summary

The optical budget of an optical system is numerically presented. The model is based on waveguide’s efficiency which scales exponentially with the known propagation loss against the distance of light travels. Two key optical properties of the electrostatic-induced lithography fabricated waveguide were investigated. The effect of electrostatic field on the material’s refractive index and intrinsic absorption were measured. The results support the hypothesis that insignificant molecular re-orientation occurs in the polysiloxane material. In addition, it also suggested the electrostatic-induced lithography growth is possibly generated by the external electrostatic pressure as a result of electrostrictive behaviour. To further characterize the propagation loss of the electrostatic-induced lithography fabricated waveguides, an optical test platform was set up to perform cut back measurement. The results show an average insertion loss of -16 dB and propagation loss of -1.97 dB/cm. Several process and equipment related factors have been identified to further improve the measurement technique as well as the optical performance of the waveguides.
Chapter 9
CONCLUSIONS

This chapter presents in three sections, the conclusions from the work completed in the thesis. The first section concludes the surface properties characterisation of both flexible substrate candidates, and the effects of plasma surface treatment as well as sonochemical surface treatment. The results from the experimental work allow substantial information on the surface properties to be investigated, before the deposition of optical polymer materials. In the second section, the finding from ToF-SIMS depth profiling technique is introduced in characterising the polymeric interface interpenetration. The interfacial width of the interface is quantified and correlated with the adhesion measured by double cantilever beam approach. In the third section, in comparison with the screen printing option, the new waveguide patterning approach based on electrostatic-induced lithography technique is introduced.

9.1 Surface modification and characterisation of flexible substrates

Both polyimide KaptonHN™ and LCP Vecstar™ were identified as candidates in the investigation of the waveguide-on-flex application. While KaptonHN™ has been widely used in various applications, LCP films are recently introduced with the advantage of lower dielectric constant and better resistance to moisture absorption. The pristine surface properties of both substrates were investigated and presented. Plasma treatment, a process widely used in the industry for surface cleaning and preparation, was carried out on the substrates. In addition, a newly developed sonochemical treatment was also adopted to investigate the effects on the flexible substrates. The summary of the results is as follows:
1. Plasma treatment is found to successfully remove local surface inhomogeneity found on the samples i.e. slip additives on KaptonHN™ and microfibrils on Vecstar™ surfaces. Plasma treatment successfully introduces etch pits onto both KaptonHN™ and Vecstar™, and prolonged plasma treatment generates uniform micro roughness for improved adhesion.

2. Based on the Owens-Wendt method of surface energy estimation, the pristine surface free energies of KaptonHN™ and Vecstar™ are 49.8 mN/m² and 35.8 mN/m² respectively. 5 minutes of oxygen plasma treatment successfully increases the surface energy of the substrates to 65.0 mN/m² and 64.3 mN/m² respectively. The increases are due to the increase of polar components upon plasma treatment.

3. Surface chemistry analysis reveals that the surfaces of both substrates primarily consist of carbon-rich skins and lack functional groups for interfacial bonding. Functional species such as COOH and CNOH are introduced onto the substrates surface upon oxygen plasma treatment. The chemically active surface will promote covalent bonding and crosslinking at the interface with the depositing material.

4. The sonochemical treatment using a horizontally agitated 20 kHz ultrasonic horn in de-ionised water does not generate sufficient energy for surface etching of KaptonHN™. As a result, insignificant changes are introduced to the surface chemistry. However, aggressive surface damage was found on the LCP Vecstar™ surface with significant amounts of functional species i.e. CNOH and COOH being introduced to the surface chemistry. However, the practical adhesion of such aggressive surface physical damage is recommended for future work to further investigate the effects of sonochemistry approach to the substrates.
9.2 Sampling depth analysis of polymer interface

Conventional adhesion characterisation techniques such as peel test, do not provide an insight into the interfacial width due to the material interactions. A depth profiling approach using ToF-SIMS is therefore adopted to characterise the interface of waveguide-on-flex technology where the polymeric chain entanglement and interpenetration is critical in ensuring good adhesion. The summary of the findings is as follows:

1. Depth profiling has found an increase in the interfacial width between polysiloxane Lightlink™ materials coated on polyimide KaptonHN™. The interpenetration of the polysiloxane into the plasma-activated polyimide layer enhances the entanglements between the polymer chains.

2. Using the intensity of the \( CN^- \) ion as a function of depth, the interfacial width between Lightlink™ and KaptonHN™ has been observed to increase from < 92 nm for the pristine interface to < 310 nm following 10 minutes of oxygen plasma treatment.

3. The insignificant difference observed in the interfacial width between polysiloxane Lightlink™ materials coated on LCP Vecstar™ substrate is due to the subdivided micro fibrils of the surface morphology. However, plasma treatment has introduced the LCP surfaces with functional groups e.g. \( COOH, CNOH \), to covalent bonding.

4. The adhesion characterisation using the DCB approach has shown an increased of fracture toughness as a result of the plasma modified interface. Both the polysiloxane-polyimide and polysiloxane-LCP interfaces have increased from very low fracture energy, \( G_c \) of 148 J/m\(^2\) and 123 J/m\(^2\) to 2228 J/m\(^2\) and 1781 J/m\(^2\) respectively. The increase of fracture energy at the polysiloxane-polyimide interface is found to be correlated with the increase of interfacial width as well as chemically prepared surface to promote covalent bonds across the final interface.
9.3 Waveguide-on-flex fabrication and optical characterisation

Initial trials with NOA materials using a DEK screen printer presented fundamental challenges in producing optical core structures with a 1:1 height-width aspect ratio on a flat cladding layer. Repeating prints were conducted to form stacking layers of core material, but alignment and spreading of the liquid polymer during curing were two issues in this process.

An electrostatically-induced lithography approach was found to be a promising technique to fabricate smooth surfaces with steep vertical sidewall microstructures. A feasibility study of the electrostatic-induced lithography was followed by a detailed process characterisation using polysiloxane Lightlink™ material. As a result, a process recipe for a 50 µm x 50 µm optical core waveguide fabricated using Lightlink™ core XP-6701A is proposed as follows:

1. Initial coating thickness of 15 µm.
2. Pre-bake at 45 °C for 15 mins.
3. Pre-UV exposure at 5 mW/cm² for 200 s.
4. Electrostatic-induced lithography at 0.9 kV for 30 mins with a gap of 40 µm.
5. Cure for 500 s at 5 mW/cm².
6. Final bake at 130 °C for 10 minutes on hot plate.

The effect of electrostatic field on the material’s refractive index and intrinsic absorption were measured. The results support the hypothesis that insignificant molecular re-orientation occurs in the polysiloxane material. An optical test platform was set up to perform cut back optical measurement. The results show an average insertion loss of -16 dB and propagation loss of -1.97 dB/cm. Several process and equipment related factors have been identified to further improve the optical performance of the waveguides.
Chapter 10

FURTHER WORK

From the results achieved by this thesis, it has been revealed that plasma treatment does provide sufficient surface modification to both polyimide and LCP substrate. Both surface properties and fracture energy characterisation indicate improved of adhesion at the interface. Depth profiling approach at the interface provides insight into the interfacial interpenetration of two materials. However, effort has to be made to correlate the interfacial width to the interfacial strength. Electrostatic-induced lithography has successfully demonstrated fabrication of smooth surface microstructures for optical waveguide application. Yet, more efforts are required to improve the fabrication process to reduce optical losses due to the fabrication. Recommendations for further work are presented for each area in the respective following sections.

10.1 Surface modification and characterisation of flexible substrates

While there is no physical modification observed on the KaptonHN™ surface after sonochemical treatment, it is believed that collapse of the microjetting bubbles has not generated sufficient energy to initiate an etching reaction of the smooth surface. Several variables can be further investigated to produce sufficient energy for an etching mechanism to occur including ultrasonic frequency, vibration mode of the ultrasonic horn and the choice of sonification liquid. However, aggressive surface physical damage is observed on the Vecstar™ substrate. The effect of sonochemical treatment further reveals the fibrils-like structure of the LCP substrate. Further experiment is required to assess the adhesion strength of such aggressive surface physical modification in order to translate into practical purpose.
The development of sonochemical surface treatment is at its early stage of research and application. As the observation from the aforementioned work, the current ultrasonic horn produces a few localized spots of modified surface. For practical application purposes, further work is recommended to include large area and better uniformity in the modified surface.

10.2 Sampling depth analysis of polymer interface

Through the depth profiling experiment at the polymeric interface of waveguide-on-flex, the interfacial width of two polymers has been quantified from the transition of characteristic markers. It is believed that interfacial width indicates the material interphase interpenetration and polymer chain entanglements. Initial adhesion characterisation using the double cantilever beam approach indicated that increased interpenetration of polysiloxane-polyimide interface as a result of plasma treatment has contributed to the increased fracture toughness, $G_c$. This hypothesis is inconclusive for polysiloxane-LCP interface due to the insignificant difference of interfacial width measured.

Beside surface treatment, the curing recipes of the deposited material can be characterized and optimized to achieve a strengthened interface. The soft bake temperature and duration, which allow solvent evaporation and interpenetration of polymer chains prior to UV exposure, determine the state of the diffused interface formation.

10.3 Waveguide-on-flex fabrication and optical characterisation

From the above characterisation experiments, further research can be conducted using a recommended set up as illustrated in Figure 10.1. Based on the experimental set up as discussed section 7.1, an improved version of an electrostatic-induced lithography waveguide fabrication set up is proposed. The laboratory scale set up employs the 2D planar glass electrode patterned with conductive indium tin
oxide (ITO) for waveguide patterning. The top electrode made of transparent glass and ITO materials allowed the direct UV curing process during the electrostatic-induced lithography growth process. A bottom electrode works as hot plate to control the temperature of the specimen. The installation of a microscopic camera enables the in-situ monitoring of growth mechanisms, characterisation of growth rate and aspect ratio of polymeric microstructures.

To further investigate the research work of electrostatic-induced lithography fabricated polymeric waveguides, it is recommended that the electrostrictive behaviour of several selected optical polymers are characterised for comparison. The viscous growth characteristic of a candidate material can be characterized through the strain response of the material when exposed to an electric field.

*Figure 10.1 Schematic illustration of the proposed set up based on a transparent electrode with in-situ UV curing, temperature control and microscope monitoring capabilities.*

In order to further characterizing the optical performance of the electrostatic-induced lithography fabricated waveguide, it is recommended that the fabrication process is aided by more precision handling control, cleaner environment and the identified changes to the measurement set up. This will allow accurate, repeatable and
reproducible experiments to be conducted. With the modifications made, an
investigation into the bending losses of waveguide-on-flex is suggested to complete
the study. The bending loss characterisation can be compared with the measurement
conducted by Anzures et al. [39] and Bosman et al. [19]. Subsequently, the
waveguide can be subjected to reliability testing based on common industrial
standard of Telecordia GR-1221 and GR-1209 [30, 39].
REFERENCES


