MICROFABRICATION OF ELECTRODES AND SENSORS ON RECORDABLE COMPACT DISCS USING DESKTOP INKJET PRINTERS

by

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Abstract

This thesis describes a simple micro-patterning technique using a conventional desktop inkjet printer with no modifications. The technique demonstrates patterning of gold sputtered recordable compact discs (CD-Rs) and printing of phospholipid films on top of the patterned gold electrodes to configure an iodine vapour sensor.

Long-chain alkanethiols were used as masking layers, and they were applied to the gold-coated side of CD-Rs using an inkjet printer. This step was followed by wet-chemical etching to realize a set of interdigital gold electrode pair. Subsequently, a thin film of phospholipids was selectively deposited on top of each electrode pair, transforming it to serve as a conductometric chemical sensor unit. These units were then exposed to iodine vapour, and the electrical response was documented to successfully demonstrate the functionality of the sensor. This technique outlines a generic approach for producing disposable multiplex biosensor and portable electrochemical analyzer rapidly and economically.
To my parents,


Without their unconditional love, encouragement and blessings,

this work would not have been completed.

사랑하는 부모님께 이 논문을 바칩니다.

부모님의 조건없는 사랑과 격려와 축복이 없었다면

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List of Acronyms and Abbreviations

- μ-CP – Micro Contact Printing
- BMP – Bitmap
- CD – Compact Disc
- CD-R – Recordable Compact Disc
- CD-ROM – Compact Disc Read-Only Memory
- CE – Capillary Electrophoresis
- DNA – Deoxyribonucleic Acid
- DOD – Drop-On-Demand
- DVD – Digital Video Disc
- GIF – Graphics Interchange Format
- GIMP – GNU Image Manipulation Program
- GNU – GNU’s Not UNIX
- ITO – Indium Tin Oxide
- JPEG – Joint Photographic Experts Group
- LED – Light-Emitting Diode
- OLED – Organic Light-Emitting Diode
- PC – Polycarbonate
- PCB – Printed Circuit Board
- PDMS – Polydimethylsiloxane
- PLED – Polymer Light-Emitting Diode
- RFID – Radio Frequency Identification
- RNA – Ribonucleic Acid
- SAM – Self-Assemble Monolayer
- TFT – Thin Film Transistor
- THF – Tetrahydrofuran
- TIFF – Tagged Image File Format
- UPC – Universal Product Code
- UV – Ultraviolet
Chapter 1
Introduction

In this thesis, a rapid and reliable method is described to deliver nanoliter volumes of functional materials in order to pattern microstructures on gold CD-Rs by direct inkjet printing with a commercial desktop inkjet printer without any modification to either the hardware or software driver of the printer. Prior to covering detailed information about the procedures and results of this research, an introduction to various technologies related with the project and information about their non-standard applications is given in this section.

1.1 Compact Disc Technology

The basic principles of the compact disc technology are illustrated in this section.

1.1.1 Compact Disc, CD-ROM and CD-R

Compact discs (CDs) are a type of optical information storage media that have become one of today's most popular means of storing, retrieving and distributing digital information. The compact disc read-only memory (CD-ROM) and recordable compact disc (CD-R) are the two most known types of the CD.
The CD-ROM, best known media to distribute audio tracks and software programs, consists of three structural layers: (1) a polycarbonate (PC) substrate that forms the base of the CD-ROM, (2) a reflective metal layer sputtered on top of the PC substrate, and (3) a protective layer that protects the reflective layer from scratching and wearing out [1]. Most CD-ROMs come with pre-embedded data by the vendor. During the production, a master pattern stamps its pattern containing pits and plateaus, representing binary data, on the PC substrate via injection moulding [2]. During the reading operation in a CD drive, the depth of the pits stamped into the PC substrate cause destructive interference when a laser beam illuminates at the pits. Destructive interference disrupts the reading head from detecting the laser beam reflected back by the reflective metal layer. By detecting the presence or absence of the reflected laser beam by the reading head, a CD reader decodes the binary data stored in a CD-ROM [1, 2]. Because the data is permanently 'stamped' on the PC substrate, data stored in a CD-ROM cannot be easily erased and replaced with new data.

CD-Rs are blank CDs in which personal data can be recorded with a CD writer. Development of affordable CD writers and CD-Rs has further enhanced the versatility of CD technology. The CD-R has similar structural layers as the CD-ROM; however, it contains an extra layer of photochromic materials for writing purposes. Unlike a CD-ROM, no data is stamped and stored in the polycarbonate substrate in a CD-R; therefore, the PC substrate of a CD-R has no pits and plateaus which represent data. Instead, narrowly spaced (1.3μm) spiral tracks are embedded in the substrate to position and guide the laser beam during the reading and writing operation [1, 2]. In a CD-R, data is stored in the thermally sensitive dye layer which is chemically formulated to deform and
change its colour by the heat applied by a laser. For the thermally sensitive dye layer of CD-Rs, derivatives of cyanine, phthalocyanine and azo-based dyes are commonly used [3].

During the recording process, a laser beam is focused on the dye layer, and the heat generated at the location of a focusing point darkens the dye and creates an opaque spot. During the reading process, the reading laser beam penetrates from the bottom of the PC substrate through the unaffected dye layer. The reflective layer made of a thin metal film (i.e. silver, gold, or aluminium) reflects the beam back to a reading head. However, in contrast, opaque spots in the dye layer block the incident laser beam from reflecting back to the reading head [4]. This alternating circular pattern of opaque and transparent spots in the dye layer that either block the incident laser beam or allow it to reflect back to the reading head decodes the digital information stored in a CD-R.

1.1.2 Gold Recordable Compact Discs in Non-Storage Applications

Nowadays, abundance in electronic and computer hardware is fuelling interdisciplinary research. Particularly, research in chemical and biomedical sensor development toward health science and disease diagnostics is effectively exploiting these opportunities. One example of such novel research reported in the literature is the utilization of CD-Rs not for storage applications, but for modern materials and analytical chemistry [2, 4]. CD-Rs with gold reflective layers are well known for their data archiving capabilities because of gold’s excellent reflectivity, environmental stability, and long storage life expectancy.
Yu [5] discovered that the same sputtered gold layer serves as an inexpensive and convenient source of a metal substrate for the preparation of self-assembled monolayers. Angnes et al. pioneered the electroanalytical application of gold electrodes fabricated from CD-Rs (so-called "CDtrodes"), and compared their performance with gold electrodes fabricated on commercial gold substrates [6]. They also used CDtrodes to construct flow cells for electrochemical quantification of mercury in natural waters [6, 7]. Similar devices were developed from planar CD-R gold electrodes by Westbroek et al. for the amperometric determination of Ce(IV) [8]. More interestingly, CD-Rs can be employed as micro-patterned substrates for the preparation of micro/nanostructures [9-11]. For example, zirconia thin films with tunable topography can be deposited electrochemically on gold CD-R substrates [9]; polycarbonate substrates can be taken as polymeric stamps to fabricate metal nanostructures [10]; and blank CD substrates can be moulded to produce microfluidic devices [11]. By utilizing the CD-R reading mechanism, La Clair and Burkart were able to detect the binding of proteins to different ligands attached to a CD surface [12].

1.2 Surface Chemistry on Gold CD-Rs

Various surface chemistry experiments performed using gold CD-Rs as the experimental substrate is explained in this section.

1.2.1 Alkanethiolate Self-Assembled Monolayers on Gold CD-R

Self-assembly is considered one of the most fascinating phenomena occurring in various natural processes [5], and studies on self-assembled monolayers (SAMs) on solid substrates began more than 60 years ago [13]. Ulman’s extensive review [14, 15] shows
that SAMs have become more popular during the past two decades due to a better understanding of their structure and development of practical applications in science and technology [5].

Among many different self-assembly systems studied, SAMs of alkanethiols on gold substrates are the most actively and extensively investigated system. Long-chain alkanethiolate SAMs on gold have been used as model systems to examine kinetics of long-range electron transfer [16-18]. Several groups have shown potential applications of alkanethiolate SAMs for corrosion prevention, wear-out protection and bio-sensing applications [19-22].

Yu's experiment [5] characterizing of the gold reflective layer of a CD-R as a versatile and suitable substrate for the formation of SAMs is an important milestone for non-storage applications. Through various categories of characterizations such as wetting measurements, scanning tunnelling microscopy, electrochemistry, and infrared spectroscopy, Yu's experiments illustrated that SAMs of alkanethiols prepared on the gold substrates from CD-Rs exhibit no significant difference from those formed on commercial gold slides that are manufactured by the vacuum deposition. In regard to the pre-treatment of the gold substrates, which is a key issue for preparing high quality SAMs, Yu's preparation technique is much simpler and relatively safer than the conventional method [5]. The preparation of the gold substrate from gold CD-Rs is easily achieved by simply immersing the disc into concentrated nitric acid (HNO₃) for 3 – 5 minutes and peeling off the protective polymer layer, whereas the traditional method of
preparing commercial gold substrates involves cleaning in a dangerous bath of ‘piranha’ solution.

Because of these robust and versatile characteristics of gold CD-Rs and other technical reasons that will follow in later sections of this thesis, the gold substrates prepared from gold CD-Rs were used as the major substrate in these thesis experiments.

1.2.2 Patterning of Alkanethiolate Monolayers and Gold Films

Patterning SAMs into desired shapes or using patterned SAMs as templates to pattern their supporting substrate are also extensively and widely studied research topics. In the past decade, several methods (either lithographic or non-lithographic) have been reported for patterning gold films supported on solid substrates for potential applications such as the fabrication of electrode sets or microelectrode arrays [23]. Notably, one of these techniques uses micro-contact printing (μ-CP), a stamping technique that takes solutions of alkanethiols as “ink” to form SAMs on gold with designed patterns [24-28]. Closely packed organic films then act as etching resist (i.e. a mask) to protect the gold film against aqueous chemical etchants while unprotected regions are removed to produce the desired microstructures [28]. Elastometric stamps can be produced via standard lithographical protocols, after initial preparation of a master template or mould [26]. Once made, the elastometric stamps and its mould are difficult to modify. Recently, Daniel et al. have produced sub-millimetric tailored gold electrode sets via laser printing the electrode design on wax paper, heat-transferring it onto a gold CD-R, followed by the subsequent wet chemical etching [29, 30]. Such an easy method was also applied to construct gold microelectrodes (in single or twin sets) for amperometric

\[ ^\text{3:1 mixture of concentrated } \text{H}_2\text{SO}_4 \text{ and } 30\% \text{ H}_2\text{O}_2 \text{ heated to about } 90^\circ\text{C} \]
detection in capillary electrophoresis (CE) [31]. This technique is much simpler than the traditional protocols to prepare elastometric stamps, although it is still labor-intensive and cumbersome.

1.3 Inkjet Printing Technology

To satisfy the needs of different chemical and biological experiments, a better patterning method is required to pattern SAMs into desired shapes and sizes, as well as to easily and rapidly modify the pattern if needed. A suitable patterning procedure should avoid producing permanent masks or moulds that are difficult to modify and that often require access to expensive photolithography equipment and clean-rooms which ordinary chemical and biological laboratory environment often lack. A non-standard method of utilizing inkjet printing technology may provide a solution to this problem.

1.3.1 Various Inkjet Technologies

Two different operating modes divide major categories of inkjet printers: continuous mode and drop-on-demand (DOD) mode. In continuous mode, ink in a reservoir is pumped through a nozzle, forming a stream of ink. A periodic perturbation created by a piezoelectric crystal break the stream of ink and produces uniformly sized and spaced droplets. As ink droplets are directed to the printing substrate, they pass through an electrostatic field created by electrostatic deflection plates, which control the strength of the electrostatic field and deflect the direction of the flying droplets to the printing substrate or to an ink collection gutter where ink droplets are recycled.

Continuous mode inkjet printers are usually used in high-speed printing applications.

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* In this section, a review by B.-J. de Gans et al. [72] and references therein are referred to briefly introduce various inkjet technologies and their background information.
Depending on what kinds of the print heads are used, inkjet printers that operate in DOD mode are further divided into two different operation modes: thermal and piezoelectric print head. The thermal inkjet technology is the dominant technology in most consumer inkjet printers. The core part of thermal inkjet printers is the thermal print head that consists of several miniaturized electrically heated chambers. The thermal inkjet printers produce an image by passing pulses of current through the heating element in the print head. The heated ink in the chamber instantly creates a bubble, which propels a droplet of ink through the nozzle of the print head. Thermal print head requires that the ink must be water-based and the print head be replaced occasionally because of degradation to the heating element due to the thermal effect. Unlike thermal inkjet printers, piezoelectric inkjet printers use a piezoelectric crystal in their print head instead of a heating element. When current is applied across the piezoelectric crystal, a force is generated by the structural deformation of the piezoelectric crystal that propels a droplet of ink out of the nozzle.

1.3.2 Inkjet Technology in Non-Graphics Applications

Inkjet printing and drop-on-demand (DOD) technology are now not only popular for printing graphics and photographs, but also for other applications that require deposition of micro/nanoliter volumes of functional materials into desired locations. Inkjet printing technology has been effectively employed in creating microstructures such as microlens and ceramic pillar arrays [32, 33], manufacturing of polymer/organic light-emitting diodes (PLEDs and OLEDs) [34], multicolor flat-panel displays [35], flexible displays [36], and flexible thin-film transistors (TFTs) [37, 38]. Inkjet printing technology has the potential for delivering materials with specific chemical and
biological functionalities. Kido et al. have proposed to construct circular indexed protein microarrays with an inkjet printer on CDs [39]. Bietsch et al. have deposited alkanethiolate monolayers using an inkjet dispenser with a three-axis micropositioning system on gold surfaces. They have compared their resist qualities with those of μ-CP SAMs after selective wet-etching [13]. Pardo et al. have also created alkanethiolate SAMs and protein arrays on gold substrates with specially designed inkjet printers [40].

Stemming from the continued interest in the development of CD-based biosensing devices [2, 4], this research demonstrates an non-traditional way of using inkjet printers, for rapidly prototyping complex structures without requiring access to conventional clean-room and photolithographic facilities.
Chapter 2

Inkjet Patterning of Gold CD-Rs

This chapter focuses on explaining the overall process for fabricating various shapes and sizes of electrodes on gold CD-Rs by printing alkanethiols via an office inkjet printer, followed by subsequent chemical etching in aqueous solutions.

2.1 Overview of Inkjet Patterning Process on Gold CD-Rs

Fabricating gold microstructures using the gold substrate prepared from a CD-R is the essential goal of preparing microelectrode arrays for potential applications in electroanalytical chemistry. Figure 2.1 summarizes the overall inkjet patterning process on gold CD-Rs. Constructing microelectrodes on a regular, 4-layer structured gold CD-R starts with a simple surface treatment of a gold CD-R to remove the protective polymer film to expose the gold reflective layer (Figure 2.1(a) & (b)). This pre-treatment is followed by printing alkanethiol solutions into desired patterns on the gold film via an office inkjet printer to form a nanometer thick chemical resist (Figure 2.1(c)). The printed alkanethiol resist protects the gold film during the subsequent chemical etching (Figure 2.1(d)). After the etching process is completed, the alkanethiol resist is removed by UV exposure (Figure 2.1(e)), and the fabricated gold electrodes on the disc are washed
with ethanol and dried with a stream of nitrogen (Figure 2.1(f)). The following sections (Section 2.2 - Section 2.9) explain each process and its results in detail.

Figure 2.1 – Overall fabrication process of microelectrodes on gold CD-Rs via direct inkjet printing
2.2 Preparation of the Gold Substrate from CD-Rs

Prior to the inkjet printing of alkanethiol molecules, a clean and flawless gold substrate from a gold CD-R is required. In order to achieve the best result, the surface of a gold substrate must be prepared carefully so that alkanethiol molecules form a uniform resist layer when they are printed and self-assembled on the substrate. Any chip or crack on the surface of a gold substrate introduces non-uniformity in the alkanethiol resist layer, which results in construction of a low quality resist film that does not protect the gold substrate effectively during a subsequent chemical wet etching step. Therefore, although the instructions to prepare a gold substrate from a gold CD-R requires moderately simple procedures (as illustrated in the following paragraph), a great caution must be taken during the preparation.

On top of the metal reflective layer in a CD and CD-R, a protective polymer film protects the disc, allowing it to be more tolerant to scratches and chemical actions during normal usages. By simply removing the protective film of the disc, the gold substrate of a gold CD-R is exposed and is ready to be patterned. As shown in Figure 2.2(a), the protective film is removed by immersing the disc into concentrated HNO₃ [5]. The protective film swells after approximately two minutes (Figure 2.2(b)), and by repeatedly dipping the disc in and out of the acid, the polymer film gently slides away without other mechanical assistance, leaving the gold surface clean and scratch-free.
The disc is then rinsed with anhydrous ethanol and dried with nitrogen gas.

Figure 2.3(a) and (b) illustrate a gold CD-R before and after the removal of the protective film, respectively. Prolonged immersion in HNO$_3$ causes cracks on the surface of the gold substrate because HNO$_3$ may penetrate through tiny holes on the gold substrate causing damage to the layers underneath the gold substrate.
Because the density of concentrated HNO₃ is greater than a gold CD-R, the disc, when immersed, floats at the surface of the acid. Therefore, immersing the disc upside-down (facing the protective film of the disc to the liquid surface of the acid) ensures a full contact between the acid and the protective film, and thus swells the protective film uniformly and faster. This method not only shortens the preparation time, but also reduces the chances of the gold substrate being damaged during preparation. When the disc is immersed upside-down, the swollen protective film sinks to the bottom of the acid as soon as it separates from the disc. Otherwise, as shown in Figure 2.4(a), debris from the swollen protective film may remain on the surface of the gold substrate causing damage such as scratches and stains while cleaning off the material (Figure 2.4(b)).
(a) Debris of protective films on a gold CD-R

(b) Scratches and stains on a gold CD-R

Figure 2.4 – Damages on the gold substrate during the surface preparation
2.3 Selection of an Appropriate Inkjet Printer

Inkjet printing has been explored extensively [13, 32-40] as a versatile research tool in materials and bioanalytical chemistry. However, such experiments usually require either specialized inkjet dispensing devices that are often very expensive, or substantial modifications to commercial printers which are tedious and challenging to those individuals without sufficient technical background and hands-on skills.

The criteria for selecting the inkjet printer for this experiment requires that the inkjet printer

- be commercially available, reasonably affordable and desktop-sized,
- be able to print chemical solutions other than its original inks without losing its performance in maintaining both the resolution and precision,
- be able to take not only paper but also a rigid substrate
- require minor or no modifications to the printer and its operating software so that individuals can replicate the technique and use it for their own purpose without acquiring any extensive background knowledge or trainings.
After considering various commercially available inkjet printers, the Epson Stylus Photo R200, a popular office inkjet printer shown in Figure 2.5, was selected for the experiment.

![Epson Stylus Photo R200](image)

**Figure 2.5 – Epson Stylus Photo R200**

The choice for selecting the Epson Stylus Photo R200 was based on the following reasons and special features of the printer:

- The Epson Stylus Photo R200 is a photo printing desktop inkjet printer for home and office use for a very affordable price (approx. $100 CAD). Thus, most ordinary laboratories can afford to purchase this printer for various experiments and replace it if needed without too much burden.

  Unlike many other consumer inkjet printers, all Epson printers use a piezoelectric crystal as a printing mechanism in their print head. Because no
heating process is involved, the print head lasts longer. Moreover, the ink is not limited to water-based solutions. Therefore, the piezoelectric print head can be used to deposit temperature sensitive functional materials such as a mixture of biological molecules dissolved in an alcohol based solvent.

- The attached front-loading CD-print dock and labelling software of the Epson Photo Stylus R200 make creating the desired complex features directly on the surface of CDs and DVDs quick and easy; no modifications to either the printer hardware or the software driver are needed. As shown in Figure 2.5, a CD-R is placed on a special loading tray and positioned accurately for printing, enabling repeated delivery of different solutions at the same position (approx. ± 0.5 mm). Furthermore, blank CDs can be prepared with cutouts (3×1 inch) that hold a microscope glass slide, which permit the printing on glass or other solid substrates.

- This printer is ready to operate with refillable ink cartridges. Unlike the genuine cartridges that are designed by the printer manufacturer to be used only once and disposed of, the simple internal structures of refillable ink cartridges (Figure 2.6) makes them easy to clean and reuse. There cartridges are very suitable for multiplex, multistep printing experiments with different types of solutions.
2.4 Designing Patterns for Printing

The Epson Stylus Photo R200 comes with standard software known as "EPSON Print CD"\(^5\) (Figure 2.7) for designing and printing labels directly on CD-Rs with an inkjet printable surface. The white circular region in Figure 2.7 represents the printable area of a CD-R.

\(^5\) Version 1.20A, Copyright © SEIKO EPSON Corp. & Corpus Corp. 2003
The software allows users to add text, distort it into various shapes, and even specify the degree of arc of text that runs along the edge of the disc. One can also draw lines, rectangles, and circles with specific dimensions and a fill colour. Furthermore, the software can import and print photos and pre-drawn images in various file formats such as BMP, GIF, JPEG and TIFF on the disc. In the software, the length of the inner and outer radius of the disc can be also specified so that the standard 12cm in diameter CD-Rs or the smaller 8cm can be used. Initially, a variety of electrodes and labels were successfully designed and printed on gold CD-Rs using this software.

However, as the design of the electrodes became more complicated and the feature size of the design reduced, the software was difficult to use and unsuitable for designing microstructures because it was originally developed to design and print labels, which are generally bulky pictures and text. The research goal was to use an inkjet
printer to construct specially customized electrodes and microstructures useful for chemical and bio-sensing applications whose feature size is often in the sub-millimetre or micrometer range. Therefore, alternative software was needed for drawing micro-patterns, and EPSON Print CD was used only for importing and printing these patterns on the disc.

A freely distributed graphics editing software program called "GIMP"*** (the GNU** Image Manipulation Program) was selected for designing micro-patterns. Figure 2.8 illustrates a screenshot of "GIMP" with a design of a four-point probe.

![Figure 2.8 – Image of a 4-point probe using GIMP](image)

GIMP can be used to draw raster graphics as well as to retouch photographs.

Although GIMP is a freely distributed software program, GIMP includes basic and even

** GNU is a recursive acronym for "GNU's Not UNIX"
advanced graphics manipulating features similar to those offered in commercially available software programs such as painting, selection and masking tools, layers and special effects. However, the primary reason for selecting this software as the main design tool for the project is its ability to easily specify the dimension of one pixel in the metric unit and allow users to draw a pattern pixel by pixel. As shown in Figure 2.9, when a new image is created, the size of the overall image and each pixel can be specified. In the example, the size of one pixel is defined as 1μm by 1μm (1000 pixels/mm = 1 pixel/μm), and the overall size of the image is 1mm by 1mm (1000 pixels by 1000 pixels).

![Create a New Image](image)

*Figure 2.9 – Sample configuration for a new image in GIMP*

Figure 2.10 illustrates various patterns designed using GIMP. A complete list of testing patterns is available in Appendix A.1. Because the research goal is to prepare microelectrode arrays for potential applications in electroanalytical chemistry, most
testing patterns are 4-point probes and interdigitated electrodes for electrical measurements.

Figure 2.10 – Micrometre sized testing patterns
2.5 Preparation of Sample Ink Solutions

This section explains procedures for preparing alkanethiolate ink for inkjet printing.

2.5.1 Selection of a Base Solution for Alkanethiolate Ink

Initially, methanol and ethanol were chosen because they are good solvents for dissolving alkanethiols and various other molecules. However, as shown in Table 2.1, their viscosity is too low compared with the viscosity of the original Epson ink. Alkanethiol solutions prepared in methanol or ethanol are too thin causing too much fluid to print out and create bulky patterns. Finally, 2-propanol, which has approximately two times higher viscosity than ethanol, was chosen as the solvent for dissolving alkanethiol in this experiment. Although other types of alcohols are available with much higher viscosity and closely match that of normal inkjet printer inks, 2-propanol was chosen because it is less toxic, has a milder odour, and is safer to use. To study the concentration dependency, several different concentrations of alkanethiol solutions from 100μM to 2mM were prepared. These ink solutions were pumped into the refillable inkjet cartridge with a gas-tight syringe. Excess ink was wiped off using an absorbent cloth before the cartridge was installed into the printer. Once the refillable cartridge was prepared with the alkanethiol ink and installed in the printer, the printer was connected to a computer and ready for printing the pattern.
### Table 2.1 – Comparison of viscosity of various liquids.

<table>
<thead>
<tr>
<th>Liquids @ 25°C</th>
<th>Viscosity (mPa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.541</td>
</tr>
<tr>
<td>Water</td>
<td>0.890</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.074</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>1.945</td>
</tr>
<tr>
<td>Epson Inkjet Cartridge T048120</td>
<td>&lt; 5 $^{§§}$</td>
</tr>
</tbody>
</table>

#### 2.5.2 Using Organic Solutions as Solvents

The piezoelectric print head of Epson printers provides excellent inkjet delivery with very precise volume dispensation and high-resolution print quality. Because most body parts and pipes through which the ink flows from the cartridge outlet to the print head (Figure 2.11) are made of plastic, they are easily damaged by organic solvents. Although the refillable cartridge is robust against organic solvents, the adhesive bonds holding the rubber parts in the cartridge will corrode causing the parts to become loose. From the results of previous attempts to print water-insoluble polymers, even a tiny amount of organics such as THF or chloroform in the solvent damaged and clogged the print head and reduced the performance of the printer. Therefore, the choice of solvents is limited to water or alcohol based solutions to avoid damaging various components in

$^§$ CRC Handbook of Chemistry and Physics, 73rd edition, 1992-1993
$^{§§}$ Epson Inkjet Cartridge T048120 Product Information Sheet
the printer. When the printing of water-insoluble polymers is required, these polymers must be chemically modified so that they dissolve in aqueous or alcohol based solutions.

![Normal and damaged Epson Photo Stylus R200 print head](image)

(a) Normal print head  
(b) Damaged print head by organic solvents

Figure 2.11 – Normal and damaged Epson Photo Stylus R200 print head

2.6 Inkjet Printing Process on Gold CD-Rs

This section illustrates detailed procedures for inkjet printing of the alkanethiolate ink on a gold CD-R.

2.6.1 Importing Patterns into the EPSON Print CD

To print patterns on a disc, images prepared using GIMP are imported into the EPSON Print CD software and are rearranged to the desired location within the printable area of a disc. Figure 2.12 illustrates a screen shot of EPSON Print CD software loaded with various patterns of 4-point probes and interdigitated electrodes mentioned in Section 2.4.
2.6.2 Configuring the Epson Stylus Photo R200 for Printing Quality

Prior to actual printing, the printer was configured to achieve the best printing result. Figure 2.13 illustrates a sample printer configuration. For the ‘paper and quality options’, ‘CD/DVD’ and ‘Best Photo’ should be selected, respectively. Other options are available for different levels of printing quality; however, after conducting several sets of testing with different options, ‘Best Photo’ was determined to be the best choice for printing alkanethiol solutions. In the ‘print’ options, ‘Black Ink Only’ should be checked, assuming that the refillable cartridge containing alkanethiol ink is in the black ink cartridge slot of the printer and other cartridges were not used for printing. By selecting this option, an accidental deposition of inks from cartridges other than the black ink cartridge was prevented. Finally, ‘Edge Smoothing’ in the print option should be
unchecked because the printer tends to print bulky patterns or patterns slightly bigger than original patterns while smoothing out the outline of the patterns.

2.6.3 Loading a CD-R and Printing with the Epson Stylus Photo R200

As discussed in Section 2.3, the Epson Stylus Photo R200 has a special feature that allows direct printing of logos onto the surface of inkjet printable CDs and DVDs for labelling and identification. In this experiment, the feature is used to print alkanethiol ink on the gold surface of CD-Rs. As shown in Figure 2.14, the Epson Stylus Photo R200 has a drop-down front-load dock where a plastic tray loaded with an inkjet printable CD is loaded.
Before printing, the plastic tray and loaded gold CD-R must be clean and dust-free. Inside of the printer, several sets of pressing-rollers grab and rotate to control the movement of the plastic tray during printing. During this movement, the pressing rollers roll over the surface of the gold CD-R. These pressing rollers must be thoroughly cleaned because, when the printing starts, the plastic tray with the gold CD-R slides into the printer through the slot of the front-load dock. Actual printing starts as the plastic tray comes back out of the printer. While the tray exits the printer, patterns are drawn as the print head moves perpendicularly to the tray and deposits droplets of ink. When the printing is finished, the gold CD-R is removed from the tray and air-dried in a clean Petri Dish for at least 20 minutes.
2.7 Alkanethiols Printing Results

The dried alkanethiol pattern serves as a resist during the etching process. Before etching, the uniformity of the printed alkanethiol film was examined under an optical microscope. Figure 2.15(a) is the image of a dried alkanethiol pattern (the whitish powdery area) on a gold CD-R. The pattern serves as a resist to create a set of gold interdigitated electrodes, and Figure 2.15(b) illustrates a further magnified portion of the pattern.

![Image](image_url)

**(a) Interdigitated electrodes**  
**(b) A magnified view of the region indicated by dashed lines in (a)**

*Figure 2.15 – Alkanethiol Printing on Gold CD-R*

Generally, the printed alkanethiol patterns correspond to the original designs by ±20μm, which is normal considering that the viscosity of the alkanethiolate ink is much lower than the original ink and that the printing substrate is metal and not paper. A complete set of optical images of other alkanethiol patterns is presented in Appendix A.2.
2.8 Etching Process of the Gold Film on a CD-R

This section explains the principle and procedures for etching gold CD-Rs patterned with alkanethiol films.

2.8.1 Etching Solution Preparation

For etching a SAM covered gold film, Xia et al. [28] reported that the etching solution prepared with thiosulfate and ferricyanide as coordinating ligand and oxidant, respectively, was more rapid, selective, and less toxic than the aqueous KCN which is an ordinary free cyanide containing etchant for gold. In this experiment, we use an aqueous mixture of 0.1M $\text{K}_2\text{S}_2\text{O}_3$/1M KOH/0.01M $\text{K}_3\text{Fe(CN)}_6$ /0.001M $\text{K}_4\text{Fe(CN)}_6$ solution using H$_2$O of 18 MΩ quality [28].

2.8.2 Etching Mechanism

The principle of the gold etching mechanism is based on the electrochemical process with two primary steps as listed in Table 2.2. Similar to the dissolution of other metals, Au oxidizes to Au(I) while Fe(III) reduces to Fe(II).
2.9 Etching Results

From repeated experiments, approximately 10 to 15 minutes of etching was determined to be sufficient to effectively pattern the gold film with resolutions as low as 100μm; however, the etching time will vary with the concentration of the etchant as well as the thickness of the gold film on the CD-R. Figure 2.16 shows patterned gold electrodes and probes on a CD-R. After etching, the alkanethiol pattern protecting the gold layer was removed by exposing the CD-R to 254nm UV radiation for an hour. Subsequently, the substrate with decomposed alkanethiols was washed with ethanol and dried under N₂.
2.9.1 Interdigitated Electrodes and 4-Point Probes

Figure 2.17 illustrates a close-up micrograph of a set of interdigitated electrodes and 4-point probes. Fabricated gold structures on the CD-R closely resemble the actual shape and dimensions designed in the software program. Because inkjet printers draw lines by ejecting series of ink droplets, rough outlines of the structures are observed due to the spreading of these droplets. Additional images of other types of gold structures are provided in Appendix A.3.
2.9.2 Unsatisfactorily Etched Electrodes

After etching the gold CD, sometimes electrically shorted sets of 4-point probes and interdigitated electrodes are created.

Figure 2.17 – Gold electrodes fabricated on a CD-R by inkjet printing
In Figure 2.18, alkanethiol molecules that have not chemically bound to the gold substrate firmly spread out during the etching process to the nearby gold substrate that is supposed to be etched. These molecules then prevent this unwanted gold regions from being etched and produce electrically shorted probes and electrodes. Leaving the CD in the etching solution longer will not solve this problem because this is not due to the prematurely finished etching. Because other parts of electrodes are already etched, if one waits for those unwanted gold regions to be completely etched away, other electrodes may end up over-etched. Therefore, concentration effects of alkanethiol solutions (100µM to 2mM) on the formation of ideal gold patterns were examined and experiments determined that 0.5mM 1-octadecanethiol in 2-propanol is the most suitable solution. Higher concentrations resulted in bulky patterns with poor edge resolution, whereas lower concentrations resulted in non-uniform and low-quality alkanethiol films that were insufficient to protect the gold film effectively during the etching step.
In one occasion, the printer accidentally left a tiny droplet of alkanethiol solution between a set of adjacent electrodes during the printing process resulting in an electrical short of the interdigitated electrodes as shown in Figure 2.19. Unlike the previous problem, this electrical short is not a result of the alkanethiol solution spreading out. Fortunately, this type of printing error is not common.

![Image](image_url)

(a) Electrically shorted set of interdigitated electrodes  
(b) Magnified view of the region indicated by dashed lines

*Figure 2.19 – Short in electrodes due to a printing error*

### 2.9.3 Serpentine Gold Wires

The patterned gold electrodes must exhibit appropriate electrical characteristics for potential applications in conductometric sensors and electroanalytical chemistry. The resistance of each serpentine gold wire pattern (Figure 2.20(a)) was tested as a function of wire length with a pair of microelectronic probe electrodes (Figure 2.20(b)).
Figure 2.20 – Serpentine gold wire fabricated on a CD-R

Figure 2.21 illustrates the linear response of the resistance versus the length of gold wires indicating their ideal electrical performance for conduction measurements.

Figure 2.21 – Plot of the electrical resistance versus wire length and width of gold wires

The slopes of the three wires of different widths vary as expected; the calculated electrical resistivity of gold from Figure 2.21 is $9.4 \pm 1.6 \times 10^{8} \Omega \cdot \text{m}$, which is of the same
order of magnitude as the literature value \(2.2 \pm 0.2 \times 10^{-8} \Omega \cdot m\) [41]. The discrepancy may be caused by an inaccurate estimation of the gold film thickness, particularly due to chemical etching.
Chapter 3

Inkjet Printing of Phospholipids

In this chapter, phospholipids are used to demonstrate that microstructures of biological macromolecules (i.e. lipids, proteins, DNA, and peptides), which are of technological importance in the fabrication of microarray devices, can be prepared with standard inkjet printers.

3.1 Phospholipids

Phospholipids are the main components of cellular membranes (glyceryl esters) and consist of hydrophilic polar phosphate head groups and two hydrophobic carboxy-terminated alkyl chains. Figure 3.1 illustrates a symbol commonly used to represent a phospholipid molecule; the sphere symbolizes the hydrophilic polar head group and two thin rods indicate two hydrophobic chains.
Because of their ability to form bilayers (Figure 3.2(a)), micelles (Figure 3.2(b)&(c)), and liposomes (Figure 3.3) in aqueous solution, phospholipids often serve as models for the study of membrane interactions [42, 43] and as drug carriers [44, 45]. Phospholipids used in this experiment were 1,2-Dipalmitoyl-sn-Glycero-3-Phosphocholine (DPPC, C$_{40}$H$_{80}$NO$_{8}$P) from Avanti Polar Lipids (Alabaster, AL), and they were dissolved in 2-propanol for printing.
Figure 3.2 – Structure of a bilayer and micelle

Figure 3.3 – Structure of phospholipid liposome
3.2 Printing of Phospholipids on Gold CD-Rs

The inkjet printing results of various patterns using phospholipids on gold CD-Rs is illustrated in this section.

3.2.1 Printing on Gold CD-Rs

In order to examine the resolution and uniformity of inkjet-printed phospholipid films, different types of structures were designed including dots, lines and grids (Figure 3.4) with dimensions from 5μm to 200μm using phospholipid ink with concentrations from 1.0mM to 5.0mM. A complete set of the patterns designed and printed are provided in Appendix B.1 to Appendix B.7.

![Pattern Image](image)

(a) A pattern (1cm × 1cm) of 4 squares, each containing 50μm, 75μm, 100μm and 200μm wide grids

(b) Phospholipids printed on using the pattern shown in (a)

*Figure 3.4 Resolution testing and uniformity of inkjet-printed phospholipids films*

The clear borders and the contrast between the phospholipid film-covered and bare gold areas indicate that patterns with dimensions of 100μm are quite satisfactory. No clear dependence on the concentration was observed; however, when the dimension was below 50μm (higher resolution), the patterns were uneven and considerably
deformed (Figure 3.5). A resolution of 50µm is lower than the 17.6µm optimized resolution claimed by the manufacturer (5760dpi × 1440dpi). This poor result is probably due to spreading of the phospholipid solutions on the hydrophilic gold CD-R surface.

![Image](image.png)

(a) A pattern (1cm × 1cm) of 4 squares, each containing 5µm, 10µm, 20µm and 25µm wide grids

(b) Printing result of the phospholipid pattern

*Figure 3.5 – Uneven and deformed phospholipoid patterns*

In addition, the printer does not eject a single-drop (3 pL) at a time, rather multiple drops released even when a single pixel dot is specified. A close look at the printed phospholipid films in Figure 3.6 shows vesicle-like features, which may be the result of discrete individual drops. The resolution and quality of the printed microstructures could be improved by fine-tuning the technology and upgrading to a state-of-the-art printer design.
3.2.2 Printing on Patterned Gold CD-Rs

Just like the alkanethiol films, a similar resolution and uniformity can be achieved with phospholipid films printed on gold electrodes on CD-Rs that are fabricated using the method illustrated in Chapter 2. The inkjet-printed phospholipid films on the polycarbonate substrate of CD-Rs that was exposed after gold etching show no distinct difference from the one on the patterned gold electrodes or probes (Figure 3.7).

Figure 3.6 – Microphotograph of phospholipid films inkjet-printed on a gold CD-R
A list of microphotographs of phospholipid films printed on other types of gold structures are available in Appendix B.9 to Appendix B.10.

Figure 3.7 – Phospholipid films printed on gold electrodes patterned on gold CD-Rs

3.3 Preparation of Giant Liposomes

In this section, an application of inkjet-printed phospholipids film on a metal substrate is illustrated in conjunction with electroswelling, a popular technique for producing giant liposomes.
3.3.1 Liposome

As shown in Figure 3.3, liposomes, which are vesicles constructed from phospholipid bilayers and generally contain aqueous substances, have been used as excellent tools for analyzing and modeling membrane interactions [46]. Especially, giant liposomes are commonly used as drug and macromolecule carriers in cosmetics and pharmaceutical products [47].

3.3.2 Preparation of Phospholipid Ink

The phospholipid used in this experiment was 1,2-dipalmitoyl-sn-glycero-3-phosphocholine or DPPC ($C_{40}H_{80}NO_5P$), a white powdery substance commercially available from Sigma Aldrich™ (Figure 3.8(a)). Figure 3.8(b) illustrates the molecular structure of DPPC.

To prepare DPPC for electroswelling, it was first dissolved in a mixture of methanol and chloroform (10:1 V/V). Then, the dissolved DPPC was desiccated in a homemade vacuum chamber composed of a tupperware container and a plastic pipe for...
approximately 3 to 4 hours depending on the amount of the solvent used or until the solvent was completely evaporated (Figure 3.9).

After the desiccation for evaporating the mixture of methanol and chloroform, the residual DPPC had a white and gummy texture substance (Figure 3.10). This substance was dissolved again in 2-propanol to prepare an ink for printing.
3.3.3 Printing Phospholipids on a Metal Coated Glass Slide

Figure 3.11(a) shows a regular CD-R with two rectangular cut-outs used to hold titanium-coated glass slides for printing substrates. Three 1cm x 1cm square patches (shown in Figure 3.11(b)) are drawn for phospholipids printing on the glass slide.

![Image of regular CD-R with cut-outs](image1)

(a) Regular CD-R with two cut-outs for placing glass slides

![Image of squares drawn in EPSON Print CD](image2)

(b) Squares are drawn in EPSON Print CD to print phospholipids on a glass slide

*Figure 3.11 – Technique for printing phospholipid patches on a glass slide using a CD-R with cut-outs*

Before performing electroswelling, the glass slide printed with phospholipids printed was transferred into a vacuum chamber and desiccated for 30 minutes to completely evaporate 2-propanol (Figure 3.12) in the phospholipid film.
3.3.4 Electroswelling

Figure 3.13 to Figure 3.15 illustrates how electroswelling was performed. A nitrile o-ring is placed in the middle of the glass slide completely enclosing one of the phospholipid patches at the centre (Figure 3.13). Deionised water was filled into the shallow well created by the o-ring and the glass slide (Figure 3.14(a)). The amount of water added was just enough so that the surface of the water contacts with another glass slide when it is placed on top of the o-ring. On the glass slide, alternating current is applied across the two thin metal films (Figure 3.14(b)).
Figure 3.13 – Illustration of a simple electroswelling system model

(a) Filling with deionized water  
(b) Applying alternating current to the system

Figure 3.14 – Actual electroswelling experimental set-up
The electrical field generated from the alternating current across the two titanium thin films on the glass substrate slowly swells the phospholipids, and, as they detach from the substrate, they form liposomes (Figure 3.15).

Figure 3.15 – Illustration of the liposome formation during the electroswelling process (cross-sectional view)

3.3.5 Results of Electroswelling

After electroswelling, numerous liposomes were observed floating inside of the solution. The liposomes’ size ranges from approximately 1μm to 20μm in diameter. Figure 3.16 shows the images of liposomes at two different magnifications taken under the microscope.
glass substrates.

PMWS stamp with an array of identical micro-patterns (10μm × 10μm squares) with gaps between patterns (depicted by empty squares in Figure 3.17). This has been introduced to create monodisperse grain liposomes [48]. As shown in Figure 3.17, a combination of microcontact printing using PDMS stamps and electrospraying has been used to introduce liposomes with a mixture of substance via liposomes is essential. Recently, a precipitation technique based on a combination of microcontact printing and electrospraying has been used to introduce liposomes with a mixture of substance via liposomes is essential.

The result of the previous experiments produces polydisperse liposomes with a mixture of substance via liposomes is essential.

**Figure 3.16** A Potential Experimental Setup for Preparation of Monodisperse Liposomes.
Each micro-scale lipid patch on the glass substrate limits the size of a liposome created during the electroswelling process so that the liposomes have a relatively similar vesicle size. Figure 3.18 shows the glass substrates forming a similar configuration illustrated in Figure 3.15. The size of each liposome can be controlled by the size of the patches on the PDMS stamp, the spacing between them, and the duration of electroswelling [48].
Although this technique produces monodispersed liposomes, the method wastes phospholipids during the stamping process because phospholipids ink has to wet the entire surface of the PDMS stamp. Furthermore, every time the PDMS stamp needs modification, a new mould is required. By incorporating the inkjet printing technique into the procedure, instead of the PDMS stamping, expensive biochemical materials can be saved. Additionally, the process is simplified and can be rapidly modified if needed because no permanent moulds are required. As shown in Figure 3.19, an array of 100µm phospholipid dots printed on a gold substrate can be used in electroswelling. And, by controlling the dimension of the inkjet printed phospholipid patterns, liposomes with relatively similar sizes can be created (Figure 3.20). This experimental set-up will be much feasible if the inkjet printer can print patterns with a resolution of less than 50µm or a smaller resolution which the PDMS stamp can achieve.

*Figure 3.19 – Array of phospholipids dots printed on a gold CD-R*
Figure 3.20 – A potential experimental setup for producing monodispersed liposomes using electroswelling in conjunction with inkjet printing technology.
Chapter 4
Development of an Iodine Vapour Sensor on a CD-R by Inkjet Printing

To demonstrate the practical applications of the inkjet patterning technique on gold CD-Rs, this chapter introduces the development of a sensor that detects the presence of iodine vapour by measuring the change in conductance of phospholipid films printed on multiplex interdigitated electrodes fabricated on a gold CD-R.

4.1 Phospholipids as a Sensing Material

Recent studies show that the phospholipids are used as a sensing medium for detecting molecules such as glucose [49, 50] and xanthine [51]. By monitoring the change in their electrical properties, phospholipid films have also shown their sensing ability for detecting water [52] and various other ionic compounds [53, 54]. Specifically, the semiconductive properties of phospholipid films with iodine have been studied extensively by several groups because of the dramatic increase in the conductivity of phospholipid films when exposed to iodine vapour [55-57]. The experiment of Jendrasiak et al. suggests a possible use of the electrical response of phospholipid films as an iodine sensing medium [56], while Whitehouse et al. have reported that iodine can sense the presence of phospholipids [57]. To demonstrate the potential applications of inkjet patterning technique, a gold CD-R based, prototype iodine sensor was built via the
following three steps: design and patterning of gold electrode arrays on a gold CD-R; printing phospholipid films across the microelectrodes; and, finally, sealing and testing the device in a closed chamber.

4.2 Configuration of an Iodine Vapour Sensor

Various sensor designs developed for initial attempts and the final prototype are illustrated in this section.

4.2.1 Initial Designs and Results

To confirm the iodine vapour sensing ability of the phospholipids, mini chambers were constructed on top of four-probe electrodes fabricated on a gold CD as shown in Figure 4.1. Each chamber consists of a rubber o-ring that creates the sidewall of the chamber as well as a cover glass or a piece of scotch tape used for sealing the top. Prior to sealing the chamber, a piece of iodine crystal was placed inside of the chamber so that it sublimates, and encapsulated iodine vapour inside the chamber contacts with phospholipid film deposited on the electrodes.
Figure 4.1 – Mini chambers on four-probe electrode pattern fabricated on a gold CD-R

Figure 4.2 illustrates the inside view of a chamber through the cover glass after approximately 12 hours. The difference in colour between the region with only gold electrodes and the region covered with phospholipid films is clear. The phospholipid film covered region was darker because of the interaction between the iodine vapour and the phospholipids. However, the electrical measurements which recorded the change in the electrical resistance of the phospholipid films was difficult to perform and the consistency between the measurements of different chambers was poor due to the nature of the experimental configuration such as the uncontrolled ambient created by mini chambers.
As shown in Figure 4.3, another configuration was designed to provide more workable space for the experiment. Several sets of interdigitated electrodes were fabricated on a gold CD-R, and the phospholipid films were inkjet-printed on each set of the electrodes. After the phospholipid films were dried, wires were soldered to the electrodes for electrical connection (Figure 4.3(a)), and the entire disc was placed inside of an enclosable Petri dish that served as a chamber. The wires were accessible through holes drilled on the top cover of the Petri dish, and the edges of the dish were completely sealed with a silicone sealant (Figure 4.3(b)).
The graphs shown in Figure 4.4 illustrate the electrical response of the phospholipid films printed on two sets of interdigitated electrodes before and after the presence of iodine vapour in the Petri dish chamber. The two current–voltage (sweep the voltage from -5.0V to +5.0V) curves confirm that the conductance of the phospholipid films increases in the presence of iodine vapour. As for sensing applications, however, the magnitude of the electrical response in the phospholipid film is still too small (Approx. from -20nA to 20nA) from each set of interdigitated electrodes, and a higher signal-to-noise ratio is needed.
4.2.2 New Design: A Multiplex Electrical Sensor

With a simple four-probe arrangement or a set of interdigitated gold electrodes, the results obtained were not satisfactory because of the low conductivity of the phospholipid films [55], particularly when only thin films were inkjet printed. Therefore, a new pattern was developed that covered the entire surface of a gold CD-R with 84 sets of interdigitated gold microelectrodes configured in parallel (Figure 4.5). Using the inkjet printer technique, these electrodes were fabricated on a gold CD-R as described in Chapter 2. Each sensor unit had 84 sensing structures in parallel, which resulted in a much higher signal-to-noise ratio [58]. The inset of Figure 4.5 shows a magnified view of one set of the interdigitated electrodes: four pairs of 200-μm wide gold finger electrodes insulated from the electrical path at both ends. This configuration prevents potential breakdowns when any two electrodes are cross-linked due to unsatisfactory etching as explained in Section 2.9.2. The electrical connections are created by
depositing conducting polymer on the connection pads (the regions enclosed with solid lines in the inset of Figure 4.5), and a thin film of phospholipids is printed on top of the interdigitated electrodes to serve as the sensing area (the region enclosed with dashed lines in the inset of Figure 4.5).

Figure 4.5 – Design of a multiplex electrical sensor consisting of 84 sets of interdigital microelectrodes on a gold CD-R
4.3 Electrical Modelling of the Sensor Unit

Each sensor unit, consisting of a pair of gold electrodes with a phospholipid coating can be modeled as a simple resistor, and the entire sensor design can be converted into an equivalent electrical circuit model shown in Figure 4.6.

\[ R_{\text{total}} = \frac{1}{\frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + \ldots + \frac{1}{R_n}} = \frac{1}{\frac{n}{R_{\text{lipid}}}} \tag{Equation 1} \]

where \( R_1, R_2, \ldots, \) and \( R_n \) represent the resistance in the phospholipid films.

Using the sensing configuration, all sensing units were connected in parallel and a general formula, for 'n' sensing units is derived as [59]

This model assumes the capacitance and inductance are negligible, which is acceptable because the experiments for the sensor functionality used DC measurements over a relatively narrow voltage range [59].
4.4 Fabrication Results

The design shown in Figure 4.5 was successfully patterned onto a gold CD via inkjet printing of an alkanethiolate monolayer and subsequent chemical etching. Figure 4.7(a) shows a fabricated disc with all 84 multiplex sensor electrode arrays. For an optimum fabrication and testing result, a sensor fabricated using a design without any labelling as shown Figure 4.7(c) was used in the actual testing. After the etching step, the alkanethiol resist was removed by UV exposure, and the substrate with patterned gold electrodes was carefully cleaned with ethanol before deposition of conducting polymer and phospholipid films.
4.5 Electrical Integrity of the Patterned Gold Electrodes

Before printing the phospholipids and depositing conducting polymer films, the insulating properties of each set of the interdigitated electrodes was tested by monitoring the electrical resistance between the two ends using a multimeter. The measurements
showed, in most cases, the insulating properties were greater than 30 MΩ. Ideally, the resistance should be infinite: some electrically conducting impurities in the polycarbonate substrate and/or imperfect patterning may be responsible for the observed residual conduction. A few sets of electrodes exhibited a lower resistance and were discarded using a piece of Scotch tape similar to the adhesion test of metal thin-films (Figure 4.8).

![Disc with a few sets of sensing electrodes discarded due to their lower resistance](image)

4.6 Depositing Conducting Polymers

The initial plan was to inkjet-print conducting polymers on the connect pads (the regions enclosed with solid lines in the inset of Figure 4.5) for each set of sensing electrodes. Unfortunately, the amount and concentration of the inkjet-printed conducting polymer were not adequate to make a reliable electrical connection between the electrical path and the electrodes on the disc. Therefore, rather than using the inkjet printer, a
syringe is used to drop 5μL of the conducting polymer manually at each connecting spot.

Figure 4.9(a) and (b) are the images of the disc with droplets of conducting polymer before and after annealing at 65°C on a hot plate for approximately 2 hours, respectively. The resistances of the annealed conducting polymer films were less than 2kΩ.

(a) before annealing  (b) after annealing

*Figure 4.9 – Disc with conducting polymer before and after annealing*

### 4.7 Printing of Phospholipid Films

After the conducting polymer films are completely annealed and the integrity of the electrodes are confirmed once more, the surface of the disc is clean with nitrogen gas and loaded on the plastic tray for printing phospholipids on the interdigitated area of sensing electrodes. Figure 4.10 shows an example of a mask design loaded in *EPSON Print CD* for printing the phospholipids film on the interdigitated area of each sensing electrode. Each rectangular pattern (2mm × 4mm) represents the shape of the phospholipid film, and the position of each rectangle is located exactly above the interdigitated area of a corresponding sensing electrode. Rectangular patterns are missing
from some locations because, at these locations as previously explained in Section 4.5, sensing electrodes were discarded due to unsatisfactory etching.

Figure 4.10 – Pattern loaded in Epson Print CD for printing phospholipids films on sensing electrodes

Figure 4.11 shows the printing results of phospholipid films on the sensing electrodes using 5mM of phospholipid solution prepared in 2-propanol. In Figure 4.11(a), four sets of sensing electrodes are shown; the black spots are annealed conducting polymer films and the broad whitish lines at the centre of the interdigitated electrodes are the printed phospholipids films. Figure 4.11(b) illustrates a zoom-in image of the phospholipid film covered region.
4.8 Packaging of the Sensor Unit

Because the fabricated device needs testing as a chemical vapour sensor, a controlled ambient was created. In order to create a controlled ambient, electrical wires were first soldered to the connection pads on the CD-R substrate, and the entire unit was then placed inside an enclosable Petri dish with port-holes through which gas/vapour and electrical wires could pass through. The edges of the dish were completely sealed with a silicone sealant. Figure 4.12 shows the prototype multiplex sensor for I₂ vapour that was sealed in a Petri dish.
This arrangement was allowed to dry for 24 hours inside a vacuum chamber (Figure 4.13), which removed all gas bubbles in the sealant and at the same time desiccated the phospholipid films.
4.9 Sensor Testing and Evaluation

In order to test the constructed iodine vapour sensor, diluted iodine solutions in diethylene glycol (C₄H₁₀O₃) were prepared. Diethylene glycol was used as it is inert to phospholipid films and does not produce an electrical response in the sensor unit [56].

![Iodine solutions at 10 different concentration levels](image1)

![Sealed chamber (Petri dish) enclosing the sensor into which the iodine solution is injected](image2)

Figure 4.14 – Preparation and injection of iodine solution into the Petri dish chamber containing the sensor

This experiment was carried out with 10 different concentrations as shown in Figure 4.14(a). The I-V characteristics were measured after a 5 µL of each solution was injected into the device (Figure 4.14(b)). Electrical measurements were performed with an Autolab electrochemical analyzer*** from -5.0 V to 5.0 V at a scan rate of 0.1 V/s with a step potential of 2.6 mV/step.

Figure 4.15(a) shows the sensor’s current-voltage response to different concentrations of iodine vapour. A full list of the electrical response of the sensor is available in Appendix C. Except at the beginning of the measurement (from -5.0V to

***Model: PGSTAT30, Eco Chemie B.V., Utrecht, The Netherlands
approx. -4.5V), the curves are generally linear, indicating ohmic conduction behaviour in phospholipid films (Figure 4.15(a)). This result supports the assumption of Equation 1 that only resistance needs to be considered in the phospholipid model. Measurement of the slopes of the current-voltage curves was used to calculate the correlation between the conductance of the device and the iodine concentration. The conductivity change of this sensor device is significant (Figure 4.15(b)) when the concentration of I₂ increases from zero to saturation (this, in turn, corresponds to an increase in the vapour pressure of I₂ in the chamber). The simplest explanation of the conductivity change in phospholipid films is that I₂ or I⁻ accumulates in the head-head group region of the lipid bilayer [55-57]. This interpretation deserves further investigation, as it is critical for optimising the sensitivity of the prototype I₂ sensor.
(a) Current-voltage curves of the multiplex sensing CD when iodine solutions of different concentrations are added.

(b) Plot of electrical conductance versus iodine concentration.

Figure 4.15 – Electrical responses of the phospholipids film in the sensor.
Chapter 5

Other Explorations and Future Work

This chapter illustrates other potential applications and future work, which may benefit from the inkjet patterning technology illustrated in this thesis.

5.1 DNA Micro Arrays

Scientists are trying to understand the function of genes, proteins, RNAs and the interactions between them. Due to its high throughput, DNA micro arrays allow scientists to understand not only the function of a single gene, but also the series of interactions between genes and its products [60]. The inkjet patterning technique illustrated in this thesis can be used to fabricate an electrochemical biochip on gold CD-Rs used for the detection of DNA sequences. A reaction site constructed on a gold CD-R is shown in Figure 5.1(a), where each site consists of nine electrodes for reference, working and counter electrodes (Figure 5.1(b)).
5.2 Antennas for RFID Tags

The most popular identification technology currently in use is the Universal Product Code (UPC) or commonly known as the barcode. Objects with a barcode are identified by reading the barcode with a laser barcode reader and retrieving their information remotely from a central database. However, the barcode technology requires a line-of-sight between the barcode and the laser barcode reader. Furthermore, items can only be processed one at a time. Recently, the radio frequency identification (RFID) is changing the way people identify objects [61, 62]. RFID uses radio waves for communication between the ID tags, consist of a microchip, an antenna, and the ID tag reader. Upon request from the RFID reader, the microchip in the ID tag broadcasts the object’s information such as a simple serial number or detailed information about the product through the antenna. Upon receiving the object’s information, the RFID reader can display the information or use it to access the central database in order to retrieve further information. Because RFID technology uses radio frequencies for
communication, a line-of-sight between the tag and the reader is not required. Moreover, RFID technology can simultaneously process multiple objects.

Despite RFID’s numerous advantages over the barcode, its technology has a major disadvantage: the manufacturing cost. Barcode tags are produced by simply drawing several sets of straight lines, whereas RFID tags require microchips and antennas. RFID manufacturers are investigating inkjet printing technology for constructing inexpensive antennas and even microchips using metal colloids and semiconducting polymers [63]. The roll-to-roll manufacturing process with the aid of inkjet printing will greatly reduce the manufacturing cost of RFID tags.

The inkjet patterning technique demonstrated in this thesis can be used to produce RFID antennas. Figure 5.2(a) illustrates several coiled antennas fabricated on a gold CD-R having similar designs to RFID antennas currently use in the market. As an example, Figure 5.2(b) demonstrates coiled antennas transferred to the back of business cards.

(a) Gold antennas fabricated on a CD-R  
(b) Gold antennas embedded on the back of business cards

Figure 5.2 – Coiled antennas fabricated on a gold CD-R for RFID tags
5.3 Metal Cathodes for Organic Light-Emitting Diode

An organic light-emitting diode (OLED) is one kind of thin-film light-emitting diode (LED) and is different from other LEDs in that its emissive layer consists of organic compounds. The operational principle of an OLED is electroluminescence [64, 65]. A typical OLED has a transparent anode, a metal cathode and an electroluminescence layer sandwiched in between the anode and cathode. When a voltage is applied across the anode and cathode, holes and electrons are injected from the anode and cathode, respectively, into the electroluminescence layer. A photon, a light quantum, is emitted when a hole and an electron combine in the electroluminescence layer. Potentially, a gold CD-R, using the same inkjet printing technique discussed, may serve as a metal cathode that can be patterned into various shapes for producing OLEDs. Figure 5.3 shows an image of four 7-segment display patterns and an image of a fabricated gold CD-R using the same patterns. Each segment can be individually addressed electrically.

Figure 5.3 – The original design and metal cathode and fabricated metal cathode on a gold CD-R
As shown in Figure 5.4, the OLED construction, using a gold CD-R and the inkjet printing technique, is completed by placing a transparent PC disc coated with a thin indium-tin-oxide (ITO) film and an organic electroluminescence layer on top of the patterned gold CD-R. Applying a voltage across the ITO film and the patterned gold substrate will generate photons in the electroluminescence layer, and the light will illuminate through the transparent ITO anode.

![Diagram](image)

(a) A transparent polycarbonate CD coated with an indium tin oxide layer and organic electroluminescence layer (top) and an inkjet patterned gold CD-R as a metal cathode (bottom)

(b) A cross-sectional view of the sandwiched structure of the polycarbonate CD and the patterned gold CD-R

Figure 5.4 - Potential OLED device constructed using the inkjet patterned gold CD-R as a metal cathode

5.4 Future Work

In this thesis, phospholipid films are used to detect the relative iodine vapour pressure in a controlled ambient by monitoring the change in the conductance of the films. Conversely, a future project may involve developing a sensor to determine the concentration of phospholipid films that are printed using phospholipid inks with unknown concentration by injecting iodine vapour with known vapour pressure and
observing the electrical response of the phospholipid films. In addition, as presented in this thesis, other popular sensing media that change their electrical response in the presence of certain chemicals or biological molecules can be also used.

One of future projects is to improve the resolution of the inkjet printer. Reverse-engineering the printer’s hardware and software will allow direct control of the voltage to the piezoelectric print head. This modification will allow the size of ink droplets to be controlled, which will improve the resolution of the printing patterns. Additionally, the resolution may be improved by modifying the alkanethiol ink solution to have characteristics similar to the manufacturer’s original ink solutions.

Using inkjet drop-on-demand technology, stereolithography and printed electronics are one of the most rapidly growing research and commercial fields. The inkjet based stereolithography, or commonly known as the 3D printing, is a rapid prototyping technology that creates solid 3D models by first dividing a computer model into multiple layers of thin films and then, with curable plastic polymers, inkjet-printing these layers on top of each other to reconstruct the 3D model [66-68]. Printed electronics are manufactured by inkjet-printing semiconductive inks and metal colloids for transistors and electrical connections, respectively, in order to produce complete electrical circuits that are functionally identical to the conventional electrical circuits built on PCB boards [69-71]. Inkjet printing enables the roll-to-roll process for mass production of printed electronics, which results in lower manufacturing costs. Furthermore, flexible and soft materials can be used as a main building substrate for printed electronics so that the devices are much more durable and robust.
By combining stereolithography and printed electronics technology, complete electronic devices that include fully functional electronics as well as the package of the device may be produced using only an inkjet printer. Research on the modification of the inkjet printer used in this thesis into a preliminary testing bench suitable for developing stereolithography technology and printed electronics will be a follow-up of the work presented in this thesis.
Chapter 6
Conclusion

In this thesis, a simple and reliable technique was demonstrated for patterning biomaterials and creating microelectrode arrays by the inkjet printing technology using an office desktop inkjet printer without any modification to either the hardware or software. The gold film on a commercially available CD-R can be patterned into multiplex electrode sets by printing alkanethiol solutions to form SAMs as an etching-resist layer, followed by a wet chemical etching protocol. Phospholipids can be deposited with unprecedented flexibility into different features and locations on a gold CD-R or a metal-sputtered glass slide with a lateral resolution up to 50 μm. The quality of functional material printed on a substrate was also reasonably sufficient to carry out a post-processing such as electroswelling for producing liposomes. The fabrication and testing of a CD-based prototype iodine vapor sensor was also demonstrated by using phospholipid films on top of interdigitated electrodes as sensing entities.

In contrast to conventional lithographic techniques, the inkjet printing technology does not require extensive instrumentation and/or clean rooms. The inkjet printing technique in conjunction with the gold CD-R patterning technique provides rapid fabrication of sensing devices for research, and it can be effectively used for commercial production of low-cost sensors.
Appendix A
Patterning of Gold CD-Rs

A.1. Complete List of Testing Patterns for Alkanethiol Printing

(a) 4-point probes (straight)

(b) 4-point probes (bend)

(c) Interdigitated electrodes
A.2. Inkjet Printed Alkanethiol Films on Gold CD-Rs

(a) Interdigitated electrodes

(b) A magnified view of the region indicated by dashed lines in (a)

(c) 4-point probes (200μm width, 800μm spacing between probes)

(d) A magnified view of the region indicated by dashed lines in (c)

(e) 4-point probes (500μm width, 500μm spacing between probes)

(f) A magnified view of the region indicated by dashed lines in (e)
A.3. Fabricated Electodes on Gold CD-Rs

(g) 4-point probes
(500μm width, 100μm spacing between probes)

(h) A magnified view of the region indicated by
dashed lines in (g)

(a) A set of interdigitated electrodes
(200μm width electrodes, 400μm spacing)

(b) A magnified view of the region indicated by
dashed lines in (a)

(c) A set of 4-point probe
(200μm width electrodes, 400μm spacing)

(d) A magnified view of the region indicated by
dashed lines in (c)
(e) A set of 4-point probe (500μm width electrodes)

(f) A magnified view of the region indicated by dashed lines in (e)

(g) A set of 4-point probe (1mm width electrodes)

(h) A magnified view of the region indicated by dashed lines in (g)

(i) Micrograph at the boundary of a gold electrode and polycarbonate (PC) substrate exposed after the gold etching
A.4. Unsatisfactorily Etched Electrodes

(a) A set of shorted electrodes due to printing error

(b) A magnified view of the region indicated by dashed lines in (a)

(c) A set of shorted electrodes due to spread of alkanethiolate inks

(d) A magnified view of the region indicated by dashed lines in (c)

(e) Unsatisfactorily etched probes

(f) Unsatisfactorily etched probes
A.5. Serpentine Gold Wires

(a) Serpentine gold wires fabricated using a gold CD-R with various sizes of length and width
(b) 100μm width, 200μm spacing between two parallel wires, loops at every 8mm
(c) 100μm width, 300μm spacing between two parallel wires, loops at every 8mm
(d) 150μm width, 150μm spacing between two parallel wires, loops at every 8mm
(e) 150μm width, 300μm spacing between two parallel wires, loops at every 8mm
(f) 200μm width, 200μm spacing between two parallel wires, loops at every 8mm
(g) 200μm width, 400μm spacing between two parallel wires, loops at every 8mm
Appendix B

Inkjet Printing of Phospholipids

B.1. Patterns Used to Examine Printed Phospholipid Films

(a) Patterns (1cm × 1cm) containing 5, 10, 20, 25, 50, 75, 100, 200μm dots

(b) Patterns (1cm × 1cm) containing 5, 10, 20, 25, 50, 75, 100, 200μm (width) lines

(c) Patterns (1cm × 1cm) containing 5, 10, 20, 25, 50, 75, 100, 200μm (width of lines) grids
B.2. Array of Phospholipid Dots (5\(\mu\)m, 10\(\mu\)m, 20\(\mu\)m and 25\(\mu\)m) on Gold CD-R

(a) A pattern (1cm \(\times\) 1cm) of 4 squares, each containing 5\(\mu\)m, 10\(\mu\)m, 20\(\mu\)m and 25\(\mu\)m dots

(b) Phospholipids printing result of the pattern

(c) 5\(\mu\)m \(\times\) 5\(\mu\)m dots

(d) 10\(\mu\)m \(\times\) 10\(\mu\)m dots

(e) 20\(\mu\)m \(\times\) 20\(\mu\)m dots

(f) 25\(\mu\)m \(\times\) 25\(\mu\)m dots
B.3. Array of Phospholipid Dots (50µm, 75µm, 100µm and 200µm) on Gold CD-R

(a) A pattern (1cm x 1cm) of 4 squares, each containing 50µm, 75µm, 100µm and 200µm dots

(b) Phospholipids printing result of the pattern

(c) 50µm x 50µm dots

(d) 75µm x 75µm dots

(e) 100µm x 100µm dots

(f) 200µm x 200µm dots
B.4. Array of Phospholipid Lines (5μm, 10μm, 20μm and 25μm) on Gold CD-R

(a) A pattern (1cm x 1cm) of 4 squares, each containing 5μm, 10μm, 20μm and 25μm wide lines

(b) Phospholipids printing result of the pattern

(c) 5μm wide (width) lines

(d) 10μm wide (width) lines

(e) 20μm wide (width) lines

(f) 25μm wide (width) lines
B.5. Array of Phospholipid Lines (50μm, 75μm, 100μm and 200μm) on Gold CD-R

(a) A pattern (1cm x 1cm) of 4 squares, each containing 50μm, 75μm, 100μm and 200μm wide lines

(b) Phospholipids printing result of the pattern

(c) 50μm wide (width) lines

(d) 75μm wide (width) lines

(e) 100μm wide (width) lines

(f) 200μm wide (width) lines
B.6. Array of Phospholipid Grids (5μm, 10μm, 20μm and 25μm) on Gold CD-R

(a) A pattern (1cm x 1cm) of 4 squares, each containing 5μm, 10μm, 20μm and 25μm wide grids

(b) Phospholipids printing result of the pattern

(c) 5μm wide (width) grids

(d) 10μm wide (width) grids

(e) 20μm wide (width) grids

(f) 25μm wide (width) grids
B.7. Array of Phospholipid Grids (50µm, 75µm, 100µm and 200µm) on Gold CD-R

(a) A pattern (1cm x 1cm) of 4 squares, each containing 50µm, 75µm, 100µm and 200µm wide grids

(b) Phospholipids printing result of the pattern

(c) 50µm wide (width) grids

(d) 75µm wide (width) grids

(e) 100µm wide (width) grids

(f) 200µm wide (width) grids
B.8. Micrograph of Inkjet Printed Phospholipid Films on a Gold CD-R
B.9. Phospholipid Films Printed on Patterned Gold Electrodes

(a) 4-point probes (1mm width probes)

(b) A magnified view at the dashed lined region in (a)

(c) 4-point probes (1mm width probes)

(d) A magnified view at the dashed lined region in (c)

(e) Interdigitated electrode (100μm width, 100μm spacing between electrodes)

(f) A magnified view at the dashed lined region in (e)
(a) 4-point pad (1mm x 1mm)

(b) A magnified view of the region indicated by dashed lines in (a)

(c) 4-point pad (500μm x 500μm)

(d) A magnified view of the region indicated by dashed lines in (c)

(e) 4-point pad (100μm x 100μm)

(f) A magnified view of the region indicated by dashed lines in (e)
B.10. Micrograph of Inkjet Printed Phospholipid Films on a Patterned Gold CD-R

(a) Phospholipids on interdigitated electrodes
(b) Phospholipids on polycarbonate substrate
(c) Phospholipids printed on one of 4-point pads (100 μm x 100 μm)
(d) A magnified view of the gold pad in (c)
(e) Phospholipids printed on one of 4-point pads (200 μm x 200 μm)
(f) Phospholipids printed on one of 4-point pads (500 μm x 500 μm)
(g) Micrograph of phospholipid droplets printed at the boundary of fabricated gold substrate and polycarbonate substrate.
Appendix C

Electrical Response of I₂ Sensor

As illustrated in Chapter 4, the sensor's current-voltage (I-V) response was collected using Autolab electrochemical analyzer while injecting different concentration levels of iodine solutions into the chamber containing the sensor. Four measurements were taken for each Relative Iodine Vapour Pressure (RIVP) levels except when the RIVP was 0%. The analyzer was configured to have the following setup: Scan Range: ±5V, Step Potential: 2.59mV, Scan Rate: 100mV/sec.

C.1. Relative Iodine Vapour Pressure at 0%

![Graph showing the electrical response of I₂ sensor at 0% RIVP](image)
C.2. Relative Iodine Vapour Pressure at 10%

[Graphs showing relative iodine vapor pressure measurements at 10% relative humidity, including voltage (V) on the x-axis and current (A) on the y-axis, with measurements labeled as #1, #2, #3, #4, and an average.]
C.3. Relative Iodine Vapour Pressure at 20%
C.4. Relative Iodine Vapour Pressure at 30%
C.5. Relative Iodine Vapour Pressure at 40%
C.6. Relative Iodine Vapour Pressure at 50%

![Graphs showing relative iodine vapour pressure measurements at 50% for different voltage levels.](image-url)
C.7. Relative Iodine Vapour Pressure at 60%

1. Relative Iodine Vapor Pressure @ 60%
   - Measurement #1
   - Voltage (V)

2. Relative Iodine Vapor Pressure @ 60%
   - Measurement #2
   - Voltage (V)

3. Relative Iodine Vapor Pressure @ 60%
   - Measurement #3
   - Voltage (V)

4. Relative Iodine Vapor Pressure @ 60%
   - Measurement #4
   - Voltage (V)

5. Relative Iodine Vapor Pressure @ 60%
   - All Measurements
   - Voltage (V)

6. Relative Iodine Vapor Pressure @ 60%
   - Average
   - Voltage (V)
C.8. Relative Iodine Vapour Pressure at 70%
C.9. Relative Iodine Vapour Pressure at 80%
C.10. Relative Iodine Vapour Pressure at 90%
C.11. Relative Iodine Vapour Pressure at 100%
C.12. Summary of the Sensor’s Electrical Response

I-V Response of Phospholipids Sensor on CD-R.
(Relative Iodine Vapour Pressure: 0% - 100%)
Scan Range: -5V-+5V, Step Potential: 2.5mV, Scan Rate: 100mV/s

A Conductance of Phospholipid Films (Ω⁻¹) in respect to the Relative Iodine Vapour Pressure (%)

Δ Conductance of Phospholipid Films (Ω⁻¹) in respect to the Δ Relative Iodine Vapour Pressure (%)

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Appendix D
Potential Applications

D.1. DNA Micro Array

(a) DNA micro array constructed on a gold CD-R
(b) One of four reaction sites of the CD-R shown in (a)

(c) Another design of DNA micro array on a CD-R
(d) A magnified view at a reaction site of the CD-R shown in (c)

(e) Micrograph of a reaction site

(f) Micrograph of a reaction site
D.2. Patterns Used to Fabricate Coiled Antennas for RFID Tags

(a) 1cm × 4 cm

(b) 2 cm × 2 cm

(c) Business card size
D.3. Metal Cathode in Organic Light-Emitting Diode (OLED)

(a) 4 sets of 7-segment digits fabricated on a gold CD-R

(b) A magnified view of the top portion of the CD-R
Reference List


[24] A. Kumar and G. M. Whitesides, "Features of gold having micrometer to centimeter dimensions can be formed through a combination of stamping with an elastomeric


