PRINTED MICROSCALE INORGANIC LIGHT EMITTING DIODES ON FLEXIBLE SUBSTRATES FOR DISPLAY, BIOMEDICAL, AND ROBOTIC APPLICATIONS

BY

RAK HWAN KIM

DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Materials Science and Engineering in the Graduate College of the University of Illinois at Urbana-Champaign

Urbana, Illinois

Doctoral Committee:

Professor John A. Rogers, Chair
Professor Paul V. Braun
Professor Xiuling Li
Professor Shen Dillon
Flexible electronics can offer various advantages such as intimate, conformal contacts to curvilinear surfaces and a high level of tolerance to an external strain over the conventional devices integrated on rigid platforms. With suitable choices of materials, design, and integrating strategies, inorganic semiconductor materials can be utilized as active components, integrated with flexible platforms. The deterministic transfer printing technique can generate this outcome where the single-crystalline semiconductor active components retain its original properties, thereby offering flexible electronic system with higher performance compared to organic materials based counterparts. In this dissertation, inorganic III-IV materials were explored to realize the high performance inorganic light emitting diodes (LEDs) on flexible substrate, ranging from bendable, to foldable, and to stretchable formats. In particular, advanced methods in materials growth, processing, mechanics, thermal design, and system manufacturing combine to enable unusual modes of use for inorganic LEDs. Using the type of LED systems, various applications for bio medicine and robotics such as photo-activation of drugs, in situ spectroscopy, or even optical ablation are possible, in minimally invasive modes. Overall, the outcomes have the potential to lead to applications that can complement new emerging areas as well as those already well addressed by conventional forms of inorganic LEDs or organic LEDs.
# TABLE OF CONTENTS

## CHAPTER 1 INTRODUCTION

1.1 Research Motivation .................................................................................1  
1.2 Transfer Printing Technique ..................................................................3  
1.3 Flexible Electronics ................................................................................4  
1.4 Overview of Thesis .................................................................................5  
1.5 References ..............................................................................................5  

## CHAPTER 2 FLEXIBLE MICROSCALE INORGANIC LIGHT EMITTING DIODES FOR LARGE AREA LIGHTINGS AND DISPLAYS

2.1 Introduction ............................................................................................8  
2.2 Experiment ..............................................................................................9  
2.2.1 Basic Epitaxial Design ......................................................................9  
2.2.2 Fabrication Procedures .....................................................................10  
2.2.3 Measurement of Emission Spectra ....................................................10  
2.2.4 Fatigue Test .....................................................................................10  
2.3 Results and Discussion ........................................................................11  
2.3.1 Heterogeneous Anchor ...................................................................11  
2.3.2 Characterizations of Transfer Printed μ-ILEDs .................................11  
2.3.3 Bendable, Addressable μ-ILEDs Arrays ..........................................13  
2.3.4 Large Area Display .........................................................................14  
2.4 Conclusion .........................................................................................15  
2.5 References ............................................................................................15  
2.6 Figures ..................................................................................................17  

## CHAPTER 3 INORGANIC LIGHT EMITTING DIODES WITH VERTICAL METAL ELECTRODE STRUCTURES

3.1 Introduction ...........................................................................................28  
3.2 Experiment ............................................................................................29  
3.3 Results and Discussion ........................................................................31  
3.4 Conclusion ............................................................................................35  
3.5 References ............................................................................................36  
3.6 Figures ..................................................................................................37  

## CHAPTER 4 STRETCHABLE INORGANIC LIGHT EMITTING DIODES ARRAY

4.1 Introduction ............................................................................................47  
4.2 Experiment ............................................................................................48  
4.2.1 Fabricating Arrays of μ-ILEDs with Serpentine Interconnects ..........48  
4.2.2 Transfer Printing of Stretchable Arrays ..........................................49
4.2.3 Stretching Tests and Electrical Characterization ........................................... 50
4.3 Results and Discussion ......................................................................................... 50
  4.3.1 Design Consideration for Stretchable Arrays ................................................. 50
  4.3.2 Various Deformation Modes with Stretchable Arrays .................................... 52
  4.3.3 Stacked, Laminated Layouts for High Area Fill Factors ................................. 54
  4.3.4 Integration with Various Substrates .............................................................. 55
4.4 Conclusion ............................................................................................................ 56
4.5 References ............................................................................................................ 56
4.6 Figures .................................................................................................................. 58

CHAPTER 5 STRETCHABLE, TRANSPARENT GRAPHENE INTERCONNECTS
FOR MICROSCALE INORGANIC LIGHT EMITTING DIODES ................................. 74

5.1 Introduction .......................................................................................................... 74
5.2 Experiment ........................................................................................................... 75
  5.2.1 Preparation of CVD-Grown Graphene ......................................................... 75
  5.2.2 Preparation of Isolated μ-ILEDs and Integration with Graphene ................. 75
5.3 Results and Discussion ......................................................................................... 76
  5.3.1 Characterization of Graphene ...................................................................... 76
  5.3.2 Sagging Down Mechanism of Graphene ....................................................... 77
  5.3.3 Electrical Characterization of Graphene ....................................................... 79
  5.3.4 Electrical and Optical Characterization ......................................................... 80
  5.3.5 Stretchable Arrays with Graphene Interconnects ........................................... 81
5.4 Conclusion ............................................................................................................ 83
5.5 References ............................................................................................................ 83
5.6 Figures .................................................................................................................. 85

CHAPTER 6 BIOMEDICAL AND ROBOTICS APPLICATIONS WITH
STRETCHABLE ARRAYS ...................................................................................... 102

6.1 Introduction .......................................................................................................... 102
6.2 Experiment ........................................................................................................... 102
  6.2.1 Fabrication of thin plasmonic crystals on plastic substrates ....................... 103
  6.2.2 Spectroscopic measurement of the plasmonic crystals ............................... 103
  6.2.3 Fabrication of flexible, illuminated plasmonic crystal sensors .................... 103
  6.2.4 Animal experiment ....................................................................................... 104
6.3 Results and Discussion ......................................................................................... 105
  6.3.1 Stretchable Array Integrated on Unconventional Substrates ....................... 105
  6.3.2 Photonic Suture Thread and Implanted Array .............................................. 106
  6.3.3 Plasmonic Sensors ....................................................................................... 107
  6.3.4 Short Range Proximity Sensors .................................................................. 108
6.4 Conclusion ............................................................................................................ 109
6.5 References ............................................................................................................ 110
6.6 Figures .................................................................................................................. 112
CHAPTER 7 MATERIALS AND DESIGNS FOR WIRELESSLY POWERED IMPLANTABLE LIGHT EMITTING SYSTEMS

7.1 Introduction .......................... 123
7.2 Experiment .................................. 124
  7.2.1 Fabrication of InGaN μ-ILEDs in Releasable Geometries ........ 124
  7.2.2 Preparation of Wireless Systems .......................... 125
  7.2.3 Thermal Analysis: FEA .................................. 126
  7.2.4 Animal Model Evaluations .......................... 126
7.3 Results and Discussion .................... 127
  7.3.1 Inductive Coils Design and Characterizations ........ 127
  7.3.2 Integration into Flexible System .................... 128
  7.3.3 Integration into Multi-Pixels, Stretchable, Stacked System .... 129
  7.3.4 Thermal Analysis and In-vivo Demonstrations ........ 131
7.4 Methods .................................. 133
  7.4.1 Mechanical Analyses of Stretchable System: FEA ........ 133
  7.4.2 Thermal Analysis: Analytical Modeling ........ 134
7.5 Conclusion .................................. 136
7.6 References .................................. 136
7.7 Figures .................................. 138

CHAPTER 8 SUMMARY AND OUTLOOK .................. 157

8.1 Summary .................................. 157
8.2 Outlook .................................. 158
This chapter introduces an overview of my doctoral research about printed microscale inorganic light emitting diodes on flexible substrates for display, biomedical, and robotic applications. Section 1.1 introduces the research motivation behind my doctoral research, and Section 1.2 and 1.3 provide related overview for transfer printing technique and stretchable electronics for relevant bio-medical applications, respectively. Section 1.4 in brief describes the overview of thesis. Significant components of this chapter were published as T.-I. Kim, R.-H. Kim and J.A. Rogers, "Microscale Inorganic Light-Emitting Diodes on Flexible and Stretchable Substrates," *IEEE Photonics Journal* **2012**, 4(2), 607-612.

### 1.1 Research Motivation

Light emitting diodes (LEDs) is a future light source with low energy consumption, high emission intensity and efficiency, and its future business applications range from display, to lighting industry, to bio-medicine, and to robotics, and for various emerging applications are growing very rapidly [1]. Inorganic III-IV materials for this light emitting diode are at the center of various material choices since they provide much more reliable and stable performance over long period of time even under harsh environment than other materials, such as organic LED materials [2, 3]. Therefore, single crystal III-IV inorganic materials become a natural choice for high performance LEDs. Using this high efficiency inorganic light source, in other aspects, various new concepts in biomedical and sensing applications has been generated [4-10]. Optical energy transfer, for example, can stimulate bio-systems to
promote cell growing and nervous signal transmission. Also, optoelectronic sensing functionality on human body parts can generate new potentials in robotics as well as biomedical applications. However, many of these new applications require unconventional non-flat format, such as the LEDs array interacting with and/or integrated on soft and curvilinear surfaces of body parts, which are incompatible with conventional LEDs technologies [11-14]. The commercially available forms of inorganic LEDs (ILEDs) normally incorporate rigid and brittle III-IV semiconductor wafers into a mounted format onto bulky bottom electrodes and then encapsulate them with epoxy lens, thereby restricting the ways that these devices can be used. On the contrary, organic materials are well adaptable because they are believed to be flexible in nature and the associated fabrication process is well matched with the established thin film technology [15, 16]. Therefore, research in organic LED (OLED) materials is motivated by virtue of simple integration of thin film devices on flexible substrates. However, critical weaknesses of OLED are that the electrical properties, such as the effective mobility, on/off ratio, the power consumption, and reliability are much worse than those that are achievable with inorganic materials even if there are many researches in enhancing device performance.

In that sense, there is growing interest in the use of inorganic micro/nanomaterials and devices in ultrathin geometry, otherwise brittle and rigid, in similarly unusual forms on curved, non-flat substrates. The fundamental concept for those efforts is that the brittle and rigid inorganic materials can be flexible by the thin geometry such as thin film nano-ribbon, which can be easily generated by selective removal of a sacrificial layer and subsequent release of an active layer [17]. In such a way, while using the highly efficient ILEDs system and conventional thin film processes, an extremely deformable ILEDs array, whose level of
deformation is far beyond simple bending deformation, is desirable. Complex, multi-directional, and out-of-plane modes of deformations, which are indispensable for bio-medical applications, can be achieved by stretchable electronics [18]. In case of stretchable electronic systems, high levels of strain (»1%) should be absorbed without fracture of active components or significant degradation in their electronic properties. Such a capability can be achieved by isolations of brittle, rigid inorganic materials from the applied strains where stretchable conductors as electrical interconnects between other elements where the isolated active components are in isolated configurations can correspond to the external strain.

By those considerations, the overall theme of my doctoral research is to propose materials and design strategies to construct microscale inorganic light emitting diodes (µ-ILEDs) system on various flexible substrates such as plastic, elastomer, human tissue, and other related materials. Based on developed design and materials strategies, one of main goal is to implement those systems to stretchable optoelectronics, which is the most favorable format for various bio-medical and robotic applications. Additionally, my second goal is to develop other related techniques to yield high performance devices with wireless operation capabilities for practical uses of this system.

1.2 Transfer Printing Technique

Deterministic assembly techniques that use elastomeric stamps to manipulate µ-ILEDs represent versatile, high throughput manufacturing strategies. The underlying method, known as transfer printing, can be considered as a massively parallel ‘pick-and-place’ technology that is compatible with extremely thin, fragile device components, originally developed for manipulating individual silicon transistors [19-21]. In this process, thin active layers or fully
integrated devices formed on a growth wafer are released, retrieved with a polymeric stamp and then delivered to a foreign substrate. The key to successful operation is an engineered mechanism to modulate the adhesion to the stamp, from a strong state, for retrieval, to a weak one, for printing. Several approaches are available, ranging from those that use peel-rate dependent viscoelastic behaviors in the stamps [22], to pressure-modulated contact areas [19], to interfacial shear loading [23], each of which can be used for efficient transfer of released inorganic pixels even without separate adhesive layers on the target substrate. The concepts of transfer printing technique can yield advanced systems that offer not only the mechanics of a flexible plastic sheet but also a stretchable rubber band. This latter capability is important because it enables integration of μ-ILED technologies directly and intimately with the soft, curvilinear surfaces of the human body, in a non-invasive fashion [24]. Potential applications range from health monitors, to oximeters and highly functional surgical tools.

1.3 Flexible Electronics

Flexible lighting and display systems follow simply from the use of thin inorganic semiconductor membranes on thin, plastic substrates, sometimes in neutral mechanical plane layouts to enhance further the degree of bendability. Stretchable characteristics demand additional attention to the mechanics in order to avoid fracture of brittle, inorganic materials during large-scale deformations, where overall strains can, in certain cases, exceed 100%. The most powerful schemes incorporate layouts in which metal interconnects absorb the applied strain, in a way that mechanically isolates the inorganic materials. Interconnects with non-coplanar geometries in straight or serpentine shapes [25], on either flat or structured elastomer supports, are effective. In these cases, controlled buckling and associated out-of-plane motions
accommodate in-plane deformations, such that the strains in all of the constituent materials, except the elastomeric substrate, are small (e.g. <0.25%; far below the fracture strain). Optimized designs, guided by quantitative mechanics modeling, enable stretching to 150% or more, without inducing fracture in any of the functional layers. The use of structured elastomers [26] enables this type of mechanics, even in systems that involve high areal coverage of active devices. In most cases, the interconnections consist of tri-layer stacks of polymer/metal/polymer. Stretchable arrays can be readily integrated into platforms that are suitable for natural, ‘soft’ interfaces to the human body. For example, devices can be bonded to the surfaces of catheter balloons, to add advanced functionality to this otherwise conventional implement.

1.4 Overview of Thesis

This thesis is organized into six major sections: basic strategy to generate flexible μ-ILEDs for the conventional large area lighting and displays in Chap. 2, design strategy to provide vertical light emitting diode configuration by using the protective anchors and backside metal deposition in Chap. 3, developing the stretchable μ-ILEDs array with serpentine interconnects in Chap. 4, developing the μ-ILEDs array with graphene interconnects for flexible/stretchable systems in Chap. 5, In-vivo demonstration using stretchable systems in Chap. 6, and introduction of wireless powering method for the implantable devices in Chap. 7.

1.5 References


CHAPTER 2
FLEXIBLE MICROSCALE INORGANIC LIGHT EMITTING DIODES FOR LARGE AREA LIGHTINGS AND DISPLAYS

This chapter presents epitaxial semiconductor multilayers that are designed for selective release of active layers from a source wafer to yield isolated arrays of ultrathin \( \mu \)-ILEDs. Transfer printing techniques for manipulating the resulting \( \mu \)-ILEDs in schemes enable formation of large scale arrays on foreign substrates in arbitrary spatial layouts, thereby offering unusual aspects. Significant components of this chapter were published as S.-I. Park, Y. Xiong, R.-H. Kim, P. Elvikis, M. Meitl, D.-H. Kim, J. Wu, J. Yoon, C.-J. Yu, Z. Liu, Y. Huang, K.-C. Hwang, P. Ferreira, X. Li, K. Choquette and J.A. Rogers, “Printed Assemblies of Ultrathin, Microscale Inorganic Light Emitting Diodes for Deformable and Semitransparent Displays”, *Science*, **2009**, 325. 977-981.

2.1 Introduction

Display devices represent ubiquitous, central components of nearly all consumer electronics technologies. Organic light emitting diodes (OLEDs) are rapidly emerging as an attractive alternative to backlit liquid crystals due to their comparatively high refresh rates, contrast ratios, power efficiencies and capacity for vibrant color rendering [1,2]. Inorganic light emitting diodes can also form displays, with properties such as brightness, lifetime and efficiency that can exceed those possible with OLEDs [3,4]. These displays exist, however, only in ultra-large area, low resolution formats (square meters; billboard displays), limited by processing and assembly procedures that do not scale effectively to small (\(< ~200 \times 200 \mu m\)), thin (\(< ~200 \mu m\)) light emitters or to dense, high pixel count arrays. An ability to replace
existing methods for fabricating ILEDs (i.e. wafer sawing, serial pick-and-place, wire bonding and packaging on a device-by-device basis) and for incorporating them into displays (i.e. robotic assembly into tiles followed by interconnection using large quantities of bulk wiring) with those that more closely resemble the planar, batch processing of OLEDs would greatly expand the application opportunities.

2.2 Experiment

2.2.1 Basic Epitaxial Design

This section describes the basic epitaxial design for flexible AlGaInP μ-ILEDs capable of releasing only active layers from the source wafer and their transfer printing to foreign substrates. Transfer printing technique enables the use of thin film processing, eliminating the requested back-end procedures in conventional ILEDs such as wafer sawing, serial pick-and-place, and wire bonding. The schematic, scanning electron microscopy, and the table of Fig. 2.1 describe epitaxial semiconductor multi-layers grown on a GaAs substrate, capable of the release of active layers (6 nm thick In$_{0.56}$Ga$_{0.44}$P wells, with 6 nm thick barriers of Al$_{0.25}$Ga$_{0.25}$In$_{0.5}$P on top and bottom), cladding films (200 nm thick layers of In$_{0.5}$Al$_{0.5}$P:Zn and In$_{0.5}$Al$_{0.5}$P:Si for the p and n sides, respectively), spreaders (800 nm thick layers of Al$_{0.45}$Ga$_{0.55}$As:C and Al$_{0.45}$Ga$_{0.55}$As:Si for the p and n sides, respectively) and contacts (5 nm thick layer of GaAs:C and 500 nm thick layer of GaAs:Si for the p and n sides, respectively), from a GaAs wafer by selective undercut etching of an AlAs sacrificial layer in a diluted hydrofluoric solution (49% HF : D.I. water = 1 : 100 volumetric). The AlAs can be removed by etching with hydrofluoric (HF) acid (AlAs + 3HF → AsH$_3$ + AlF$_3$↓), in procedures that do not alter the overlying layers or the underlying substrate.
2.2.2 Fabrication Procedures

Figure 2.2 provides key process steps sequentially, which begins with forming a pattern of vertical trenches through the epitaxial layers by inductively coupled plasma reactive ion etching (ICP-RIE; Unaxis SLR 770 System, 2 mTorr, Cl$_2$: 4 sccm, H$_2$: 2 sccm, Ar: 4 sccm, RF1: 100 W, RF2: 500 W) through a mask of SiO$_2$. Creating a pattern of photoresist posts (i.e. ‘breakaway’ anchors) located at two of the four corners of each defined pixel, followed by immersion in concentrated HF leads to the undercut release of an organized array of $\mu$-ILEDs. The anchors (Fig. 2.3a) hold the devices in their lithographically defined locations to prevent liftoff into the etching bath, even after complete undercut. Next, an automated printing tool brings a soft elastomeric stamp (Fig. 2.3b) with features of relief embossed onto its surface into aligned contact with a selected set of these $\mu$-ILEDs. Peeling the stamp back fractures the photoresist anchors and leaves the devices adhered via Van der Waals interactions to the raised regions of relief.

2.2.3 Measurement of Emission Spectra

Emission spectra were measured using a spectrometer (Ocean optics, HR4000; ~0.5 nm resolution) which enabled signal collected through an optical fiber directly mounted in an electrical probing station. The optical fiber collects emitted light and transports it to the spectrometer.

2.2.4 Fatigue Test
To evaluate the fatigue performance of flexible $\mu$-ILED displays, multiple cycling tests were performed under repetitive bending and releasing up to 100,000 times using automated bending tester. The testing was performed at a rate of roughly one cycle per second.

2.3 Results and Discussion

2.3.1 Heterogeneous Anchor

For transfer printing process, the anchor design is one of key factors to obtain high yield in a manner that maintains perfect registrations. The engineering design of the breakaway anchors is such that they are sufficiently robust to hold the $\mu$-ILEDs in their lithographically defined locations during the undercut etching and drying processes but sufficiently fragile to enable high yield liftoff during printing. This type of anchoring scheme (i.e. heterogeneous anchoring) is much more efficient in active materials utilization and versatile in design choices than corresponding methods demonstrated for transistors [5] and solar cells [6], where peripheral parts of the devices themselves serve as the anchors (i.e. homogeneous anchoring). Figure 2.4 provides microscope images describing the process flow from definition of pixels, to formation of breakaway anchors, to undercut release, and to transfer printing, respectively.

2.3.2 Characterizations of Transfer Printed $\mu$-ILEDs

To obtain low contact resistance, ohmic contacts to both n- and p-GaAs are indispensable. One strategy involves additional processing on the source wafer to yield released devices with integrated ohmic contacts, suitable for printing and interconnection even on low temperature substrates such as plastic or rubber. An alternative is to use low temperature approaches to establish ohmic contacts directly on such substrates. The second
strategy was pursued for this study (alternative approach will be described in Chap. 3), using processes that involve temperatures below 175 °C where the temperature range is compatible with various plastic substrates. Figure 2.5 and 2.6 provide two point transmission-line method (TLM; pattern is provided in Fig. 2.5a) analysis of the contact resistances associated with n-GaAs (Pd/Ge/Au = 5/35/70 nm) and p-GaAs ohmic contacts (Pt/Ti/Pt/Au = 10/40/40/70 nm), respectively. Here, the main purpose of TLM measurement is to obtain reasonably good ohmic contacts both for n- and p-GaAs by optimizing annealing temperature and time without causing any damages to plastic substrates. In case of n-GaAs region, the current-voltage (I-V) measurements reveal non-ohmic behavior as deposited state (Fig. 2.5b). However, contact resistance, decreases as the annealing temperature and time increase as shown in Fig. 2.5c-d, and good p-ohmic contact is made at the condition that is compatible with a plastic substrate. On the contrary, measurements of contact resistances of p-GaAs regions manifest ohmic behaviors without any annealing processes (Fig. 2.6). Unexpectedly, the post annealing process degrades ohmic behavior, probably due to very thin layer of p-GaAs (5 nm thick). Such degradation can be addressed by increasing the thickness. Figure 2.7a and 2.7b show the schematic illustration and optical microscope image of μ-ILEDs with ohmic contacts printed onto a thin layer of polyurethane on a glass substrate, respectively. Figure 2.7c-f provides electrical and optical characteristics of a set of such devices, recorded on the wafer before undercut etching and after printing. The processing in this case used a passivation scheme to eliminate moderate degradation in performance associated with the HF etching step on unprotected devices (more details in chapter 3). The current-voltage characteristics and optical output power of transfer printed devices are comparable to those on the wafer (25 devices were measured for the current-voltage characteristics). The
representative peak emission wavelength of the transfer printed μ-ILED was ~673nm with ~50nm of full width at half maximum (FWHM), comparable to the μ-ILED on a wafer, indicating no appreciable strains were induced during the undercut release process.

2.3.3. Bendable, Addressable μ-ILEDs Arrays

This section introduce two representative methods to construct μ-ILEDs in array geometries and yield lighting elements or addressable displays by establishing electrical connections to transfer printed μ-ILEDs. Here, the small thickness (~2.5 μm) of the devices enables the use of conventional thin film processing, thereby providing a route to displays and related devices that is simpler, more scalable and applicable to much smaller pixel dimensions than established wire bonding and packaging techniques. Process begins with formation of selectively opened epoxy layer for p-GaAs and n-GaAs contacts, defining connection paths from subsequent metal interconnect to active pixel area through an epoxy insulation layer. Figure 2.8a and 2.8b show the exploded schematic illustration and its image of the most basic interconnect scheme, respectively. A collection of devices with various shapes is transfer printed onto an array of metal mesh (width = 10 μm, spacing = 50 μm) that acts as a bottom electrode contact on a transparent substrate, and then established a top contact with an epoxy insulating layer which has contact opening on a p-GaAs region. Figure 2.8b shows an optical micrograph of various devices both with different sizes and shapes, as well as those with shapes that spell ‘LED’. The smallest dimension demonstrated here was 25×25 μm². The results indicate bright emission, even out to the edges of the devices, consistent with the relatively low surface recombination velocity in AlInGaP materials [7, 8].
For a passive addressable display system, two metal interconnects are requested. Fig. 9a provides the schematic illustration of metal interconnect scheme capable of the electrical access from top, which is composed of two spin cast epoxy layers and two (i.e., column and row) metal (Cr (30 nm) /Au (300 nm)) electrodes. Figure 9b shows photograph images of a display (16×16 µ-ILEDs array) that uses this design, formed on a sheet of plastic (PET, 50 µm thick). Coordinated control of the voltage applied to row and column electrodes independently enables the passive matrix addressing as shown in the figure. The passive matrix addressing was successfully demonstrated where letter “B” and “N” were displayed in a bent state; the addressable display system was the wrapped around a mannequin thumb finger and a cylindrical flask (the inset image).

2.3.4 Large Area Display

Relative larger system can be achieved from a densely packed source wafer by “step and repeat” printing technique, which has potential to reduce the cost for large area displays. Figure 2.10a shows a micrograph of a densely packed array of anchored, undercut µ-ILEDs on a source wafer. Figure 2.10b presents images of collections of µ-ILEDs printed onto a thin sheet of polyethylene terephthalate (PET, 50 µm thick), shown as in a flat or wrapped around a cylindrical glass support (1600 devices, in a square array with pitch of 1.4 mm; radius of cylinder ~25 mm). The overall fabrication yields, including delineation and undercut of the µ-ILEDs and subsequent printing of them onto the target substrates, were 100%. The devices were selected to have sizes (i.e. 250×250 µm²) large enough to be visible in the images. Figure 2.11 provides optical images of fully interconnected 3×9 µ-ILEDs array integrated on a PET substrate. One important outcome is the ability to form displays that can offer an effectively
high level of transparency, where only the $\mu$-ILEDs and the electrodes are opaque because the cumulative area of all of the $\mu$-ILEDs is much smaller than that of entire display region. Fig. 2.11a illustrates the operation of such a system positioned above a sheet of paper with printed logos; the focus of the image is on the paper, thereby illustrating a practical level of transparency for application in a heads-up display, for example. Figure 2.11b shows the same device, highlighting bidirectional emission characteristics. Uniform emissions and stable operations are apparent in the current-voltage characteristics with different bending radius up to 2.5 cm (Fig. 2.11c) and fatigue test (Fig. 2.11d) as well as lit up images.

2.4 Conclusion

The schemes described in this chapter for creating thin, small inorganic LEDs and for integrating those into display and lighting devices create design options that are unavailable with conventional procedures. The planar processing approaches for interconnect resemble those that are now used for organic devices and, for example, large area electronics for liquid crystal displays, thereby conferring onto inorganic LED technologies many of the associated practical advantages. In large area, high pixel count systems (e.g. one million pixels in a square meter), the ability to use LEDs with sizes much smaller than those of the individual pixels is critically important to achieve efficient utilization of the epitaxial semiconductor material, for reasonable cost. The minimum sizes of devices in this chapter are limited only by the resolution and registration associated with manual tools for photolithography.

2.5 References


2.6 Figures

![Figure 2.1](image)

**Figure 2.1** Schematic illustration (top left) and SEM image (top right) that describe the stack design of AlGaInP µ-ILED, respectively. The summary table of epitaxial layers are provided in the bottom frame.
Figure 2.2 Schematic illustrations of processing steps for retrieving μ-ILEDs from a GaAs source wafer. Here, the sacrificial layer is undercut etched in a diluted HF solution for the time according to dimensions of isolated μ-ILEDs.
Figure 2.3 (a) Schematic illustration of ‘breakaway’ photoresist (PR) anchors at the four corners of the device. (b) Schematic illustration describing selective lift-off process using the PDMS stamp which has embossed feature onto its surface with different pitch from the source wafer.
Figure 2.4 Microscope images representing key process steps for yielding a set of transfer printed μ-ILEDs on a glass substrate.
Figure 2.5 (a) Optical microscope image of transmission line model (TLM) patterns with gaps of 10, 20, 30, 40, 50, 60, and 70 μm. (b) I-V curves associated with n contacts as a function of annealing temperature. (c) Resistance as a function of gap length, for the n contact metallization, evaluated at different annealing temperatures. (d) Resistance as a function of gap length, for the n contact metallization, evaluated at different annealing time.
Figure 2.6 (a) I-V curves associated with p contacts as a function of annealing temperature. (b) Resistance as a function of gap length, for the p contact metallization, evaluated at different annealing temperatures.
Figure 2.7 (a) Schematic illustration of the representative μ-ILED with ohmic metal contacts that is transfer printed on a foreign substrate. (b) Microscope image of a set of μ-ILED with ohmic metal contacts corresponding to Fig. 2.7(a). Current-voltage characteristics of 25 representative devices before undercut etching on the GaAs wafer (c), and after transfer printing onto an epoxy coated glass substrate (d). (e) Current-emission characteristics of before undercut etching on the GaAs wafer, and after transfer printing onto a epoxy coated glass substrate. (f) Spectral characteristics of emission for a typical device on a wafer and after transfer printing cases.
Figure 2.8 (a) Exploded view schematic illustration of an array of μ-ILEDs contacted by a bottom metal mesh (n contacts) and a top metal film (p contacts). Devices are isolated by a layer of epoxy that has photopatterned opening to p-GaAs contact regions. (b) Optical micrographs of two sets of μ-LEDs with various shapes in their lights on-states (top frame: various shapes; bottom frame: characters ‘LED’).
Figure 2.9 (a) Exploded view schematic illustration of an array of µ-ILEDs for a passive matrix addressable display. Two photopatterned epoxy layers and metal interconnects are constructed using the conventional thin film processing. (b) Images of a flexible display that incorporates a 16x16 array of µ-ILEDs in the layout shown in (a), on a sheet of plastic (PET), wrapped around the thumb of a mannequin hand (main frame: radius ~8 mm) and a cylindrical glass tube (inset: radius ~12 mm).
Figure 2.10 (a) Collection of PR anchored, undercut released \( \mu \)-ILEDs on a source GaAs wafer. (b) Large scale collection of \( \mu \)-ILEDs (1600 devices, in a square array with pitch of 1.4 mm) printed onto a thin, flexible sheet of plastic, shown here in a flat geometry (main image) or wrapped onto a cylindrical glass substrate (inset image).
Figure 2.11 (a) Array of 3×9 μ-ILEDs on a sheet of plastic substrate in its on-state. Focus are made on to logo, thereby revealing the semi-transparent property of the large area display system. (b) Same array wrapped around a plastic cup, indicating high level of back side emission from the array. (c) Current-voltage characteristics of this array (Fig. 2.11a) as a function of bending radius. (d) Fatigue test at bending radius of 2.5 cm. Each measurement was done in a flat configuration of the system.
CHAPTER 3
INORGANIC LIGHT EMITTING DIODES WITH VERTICAL METAL ELECTRODE STRUCTURES

In this chapter, design strategy of anchor and device is introduced to have high performance \( \mu \)-ILEDs by protecting active layers during the undercut release process. Additionally, this strategy enables generating fully formed, vertical \( \mu \)-ILED system on a flexible substrate. Significant components of this chapter are submitted for review as R.-H. Kim, S. Kim, Y.M. Song, H. Jeong, T.-i. Kim, J. Lee, K. Choquette, and J.A. Rogers, “Flexible Vertical Light Emitting Diodes,” *Small.*

3.1 Introduction

Recent researches report that electronic devices based on inorganic semiconductors in their ultrathin geometries can offer high levels of mechanical flexibilities (e.g., bendability, stretchability) comparable to those possible with organic materials, being readily applicable to new emerging biomedical and related areas that cannot be addressed with conventional inorganic devices that are in a flat, rigid, and brittle platform [1-5]. Liquid or vapor phase epitaxy on unusual substrates or top-down approaches (i.e., photolithographic definition of active layers on a wafer and subsequent undercut release) can provide those structures. In case of top-down approaches, the selective etching property of a sacrificial layer over active layers and transfer printing techniques enable integration of thin layers of active components on foreign substrates. In particular, engineering designs of supporting structures (i.e., anchors), to hold the isolated, photopatterned active components at their lithographically defined locations
during selective etching process of a sacrificial layer, are critically important to build high performance devices and generate high-yield assembly into certain layouts. One strategy is to form photoresist (PR) posts around photopatterned pixels, being designed to (1) have strong adhesion to the underlying substrate, thereby maintaining spatial organization on a source wafer, but (2) be easily broken upon applied pressure during a lift-off / peeling-back process by a soft elastomeric stamp for high yield transfer printing process [6]. However, in case that the sacrificial layers do not have high degree of etching selectivity over the active multilayers such as epitaxial stacks for light emitting diodes or laser diodes, specially designed anchoring scheme are highly requested. In the following, engineering designs and procedures that are well suitable for this purpose while retaining other requirements for high yield transfer printing process are proposed. Additionally, the design strategy allows an alternative method for vertical light emitting diodes (VLED) structure on a plastic substrate without critical and costly wafer bonding process through modifications of proposed procedures. The results provide simple but interesting design strategies for systems of this type.

3.2 Experiment

Thin epitaxial layers, composed of p-GaAs:C / p-spreading layer (Al$_{0.45}$Ga$_{0.55}$As:C) / p-cladding layer (In$_{0.5}$Al$_{0.5}$P:Zn) / quantum well (Al$_{0.25}$Ga$_{0.25}$In$_{0.5}$P / In$_{0.56}$Ga$_{0.44}$P / Al$_{0.25}$Ga$_{0.25}$In$_{0.5}$P) / n-cladding (In$_{0.5}$Al$_{0.5}$P:Si) / n-spreading (Al$_{0.45}$Ga$_{0.55}$As:Si) / n-GaAs:Si, grown on a 500 nm thick layer of Al$_{0.96}$Ga$_{0.04}$As on a GaAs wafer serve as active materials. The epitaxial stack design provides the selective elimination of an Al$_{0.96}$Ga$_{0.04}$As sacrificial layer over a GaAs substrate in a hydrofluoric (HF) acid solution [8]. Figure 1 illustrates the designs and key process steps for fabricating µ-ILEDs, in procedures that reinforce the etching
selectivity of a sacrificial layer to active layers. Process begins with lateral delineation, composed of dual etchings (1\textsuperscript{st} dry etching by inductively coupled plasma reactive ion etching (ICP-RIE, Cl\textsubscript{2}/H\textsubscript{2}/Ar = 4/2/4 sccm, pressure = 2 mTorr, plasma power = 100 W, inductor power = 500 W), 2\textsuperscript{nd} wet etching with phosphoric acid based solution (H\textsubscript{3}PO\textsubscript{4} : H\textsubscript{2}O\textsubscript{2} : D.I. = 1 : 13 : 12)) through a photopatterned mask of SiO\textsubscript{2}, where the first and second etching exposes the surface of the n-GaAs layer and the GaAs substrate, respectively as shown in Fig. 1a. The schematic illustration and scanning electron microscopy (SEM) in Fig. 3.1a, collected after dual etching processes, describe the resulting isolated pixels on the wafer, with terraced stairs for pre-defined n-GaAs regions and exposed sidewalls of the sacrificial Al\textsubscript{0.96}Ga\textsubscript{0.04}As, where the isolated devices have lateral dimensions of 140×140 μm\textsuperscript{2} (dimension of p-GaAs = 80×80 μm\textsuperscript{2}, covered by remaining mask SiO\textsubscript{2}). Creating patterns of photoresist (Shipley, SPR 220-3.0) that cover all around the isolated devices to protect active layers (from remaining mask SiO\textsubscript{2} to n-spreading layers) while having the sidewalls of Al\textsubscript{0.96}Ga\textsubscript{0.04}As sacrificial layers uncovered for subsequent undercut etching (Fig. 3.1b; which we refer to as a protective anchor to distinguish it from previous reports), followed by immersion in a diluted HF solution leads to the undercut release of isolated devices as shown in the schematic illustration and SEM image of Fig. 1c. The inset SEM image in Fig 3.1c highlights released device from the GaAs wafer by removal of the sacrificial layer, while being remained at their original locations after the undercut process in a HF solution. Finally, Fig. 3.1d manifests selective transfer printing capabilities using the proposed anchor scheme by showing the fracture of PR anchor takes place at shallow features upon peeling the stamp back (Fig. 3.2). Overall, the key feature of the protective anchor scheme is such that it has strong adhesion to underlying substrate to hold μILEDs in their lithographically defined locations during the undercut
etching but sufficiently fragile to enable high yield liftoff during printing with capability of full protection against the specific etchant.

### 3.3 Results and Discussion

For undercut release and transfer printing of devices with high yield, it is important to determine optimum undercut etching time, which is highly dependent on Al mole fraction, thickness of the sacrificial layer ($\text{Al}_x\text{Ga}_{1-x}\text{As}$), and concentration of the etchant as well as lateral dimensions of isolated devices. Figure 3.3a presents the tilted view scanning electron microscope (SEM) image of the transfer printed $\mu$-ILED that is generated via normal anchor scheme without protection during undercut etching in a diluted HF solution ($\text{HF} : \text{deionized water (D.I.)} = 1 : 99$ volumetric) for 3 hours. It reveals that the active layers of interest in this study have laterally etched regions at the top and bottom of the quantum well layer, corresponding to p and n-cladding layers ($\text{In}_{0.5}\text{Al}_{0.5}\text{P}$), with relatively high Al content ($\geq 0.5$) among epitaxial stacks, respectively. The measured lateral etch distance of the cladding layer was $\sim 4.3 \, \mu\text{m}$ as shown in the bottom frame of Fig 3.3a. Figure 3.3b provides the quantitative results of lateral etch rates of the sacrificial and cladding layers as a function of etch time in the same HF solution. From the graph, the etch rate of the sacrificial and cladding layer was $0.84 \, \mu\text{m/min}$ and $0.023 \, \mu\text{m/min}$, respectively, and the calculated etch selectivity of the sacrificial to cladding layer was $\sim 35:1$. Such tiny amount of damaged cladding layers lead to undesirable device performance as shown in Fig. 3.3c, where we provide the current-voltage (I-V) measurements of the transfer printed $\mu$-ILED with different dimensions after formation of p (Pt: 10 nm / Ti: 40 nm / Pt: 40 nm / Au: 70 nm) and n-type ohmic (Pd: 5 nm / Ge: 35 nm / Au: 70 nm) contacts. The result reveals that damaged cladding layers lead to increase in turn-
on voltage of the device, compared to the device on a wafer, which can be explained by
decrease in cross-sectional area along the current path. Such explanation is supported by the
significant dependence of turn-on voltage on dimensions of the transfer printed device; the μ-
ILED with larger dimension exhibits lower turn-on voltage, otherwise almost identical as
shown in Fig. 3.3d.

On the contrary, the μ-ILEDs, transfer printed through the protective anchor scheme do
not show any performance degradations. Figure 3.3e presents I-V characteristics of a set of
such devices before and after undercut etching and transfer printing. As expected, I-V
characteristics of both sets of devices are almost identical, indicating effectiveness of the
protective anchor scheme, together with the undamaged regions of remaining mask SiO₂ after
undercut etching and transfer printing (Fig. 3.4). The associated optical output power is also
enhanced with protective anchor scheme, compared to normal anchor scheme as shown in Fig.
3.5; the optical output intensity of the μ-ILED that is fabricated without protective anchors
exhibits early intensity drop at 2.5 mA while the μ-ILED is operational in a much higher
forward injection current. The drooping optical output intensity at the driving current of 7.1
mA is associated with degradation by generated heat due to poor heat dissipation on a glass
substrate.

To build high performance electronic assemblies on flexible sheets of plastic or other
unusual substrates, deposition and other related processes are need to be kept below
temperatures that are compatible with those substrates. In case of μ-ILEDs, the fully formed
concept eliminates the constraints associated with the high temperature annealing process
required for forming ohmic contacts. By exploiting the anchor scheme proposed in this
chapter, one interesting outcome is its capability in generating the fully formed AlGaInP μ-
ILEDs with ohmic contacts on a GaAs wafer and then, transfer printing of them with undamaged ohmic contacts onto a plastic substrate. The left frame of microscope image in Fig. 3.6 corresponds to a set of fully processed, undercut etched \( \mu \)-ILEDs with patterns of protective anchors. The image of transfer printed \( \mu \)-ILEDs on a PDMS substrate after removal of protective anchors by acetone is provided in the right frame of Fig. 3.6.

The vertical LED configuration is more desirable because it removes several disadvantages to the lateral LED configuration, such as current crowding at high forward injection current, reduced reliability, and shorter lifetimes. However, the lateral LED configuration is more general especially when the epitaxial semiconductor materials are integrated on an insulating substrate without costly and environment sensitive metal bonding process. Here, the protective anchor scheme and terraced shape of device allow a simple method to generate vertical \( \mu \)-ILEDs on an insulating substrate via modifications of the fabrication procedures proposed in this study. Figure 3.7a-c provide schematic illustrations (left frame) and microscope images (right frame) describing the associated process flow. After lifting up the undercut released devices with a slab of PDMS stamp from a GaAs wafer (Fig. 3a), thinning process of n-GaAs by a wet etchant \((\text{H}_3\text{PO}_4 : \text{H}_2\text{O}_2 : \text{D.I.} = 1 : 13 : 12)\) can be performed as shown in the inset microscope image without affecting other regions of lifted up devices. Because all the active regions are encapsulated by PR except the bottom of n-GaAs, no additional photo-patterning process is needed. Then, forming n-type ohmic metal at the backside of n-GaAs via deposition using an e-beam evaporator as shown in 3.7b, where wrinkled PDMS surfaces are created due to mismatches in the thermal expansion coefficients of metal and PDMS, is followed by transfer printing. Schematic illustration and micrograph in Fig. 3.7c represent the surface of PDMS stamp after transfer printing. Interestingly, soft
contact of PDMS stamp to an adhesive and associated pressure, which is applied upon transfer printing, do not deliver metal layers that was deposited on a PDMS stamp to target substrates. This result, thereby facilitates subsequent metal interconnects, otherwise transferred metal can cause the particle induced bridges or disconnection of interconnects. Step height (sum of device and PR thickness) and shadowing effect associated with device design prohibits edge over metal deposition as shown in the SEM image of Fig. 3.7d. Finally, microscope image of transfer printed μ-ILEDs with backside n-type ohmic contacts on a glass substrate coated with the adhesive layer of epoxy (SU8_2) is provided in Fig. 3.7e. Inset micrograph highlights the backside of these device with the deposited metal layers integrated on a transparent substrate.

The schematic illustration in Fig. 3.8a represents the vertical LED configuration that can be achieved via the procedure described in Fig. 3.7. After transfer printing of μ-ILEDs with backside n-type ohmic contacts and removal of PR, overlying thin n-GaAs layer is wet etched through remaining mask SiO₂ until exposure of the bottom metal (Pd/Ge/Au, from top to bottom), where top Pd metal serve as an etching stop layer against phosphoric acid based etchants. The microscope image of a set of resulting devices after separate formation of p-type ohmic metal contacts on the p-GaAs is provided in Fig. 3.8b. Figure 3.8c presents the luminance-current-voltage (L-I-V) characteristics of this device in a vertical configuration with different n-GaAs thicknesses, which is done by thinning process as described in Fig. 3.7a. Here, the thickness of n-GaAs affects the transmission of light that are reflected by backside n-type ohmic metal. As expected, relative optical output power monotonically increases with thinner n-GaAs while showing invariant I-V characteristics. Further enhancement in optical output power is expected by employment of high reflective metal at the emission wavelength such as Al and Au, instead of Pd / Ge / Au presented here. The re-plotting of the results as a
function of the thickness of n-GaAs reveals an exponential increase with the decrease in the thickness. Figure 3.9 shows the calculated reflectance curves of VLEDs with five different n-GaAs layer thicknesses (from 50 to 450 nm with 100 nm step) in the wavelength range of 600-750 nm (It is noted that the reflectance is steadily increased as the wavelength increases due to the reduced material absorption.). Even though each reflectance spectrum has a certain wavy pattern, which is caused by the interference of multi-layer stacks, it supports expectation that the reflection from the bottom Au metal is rapidly increased as the thickness of n-GaAs layer decreases [7-10]. At a 670 nm, the tendency of reflected power versus the n-GaAs thickness is well agreement with the experimental results. The lower turn-on voltage with vertical LED configuration as shown in the graph is also noted, which is related to decrease in ohmic loss along the lateral direction through n-GaAs. The vertical µ-ILEDs can be constructed into system levels by using the conventional thin film processing as reported elsewhere. Here, spin casting of thin dielectric layer (epoxy; SU-8; 1.2 μm thickness) that has openings on p- and n-type ohmic contacts and establishing metal interconnects to transfer printed µ-ILEDs yields such a system in array geometries as shown in Fig. 3.10. The uniform emission characteristics are clear both from images obtained with and without external illuminations, indicating that all µ-ILEDs have similar contact resistances and uniform distribution of resistance.

3.4 Conclusion

The results presented in this chapter establish simple engineering schemes of anchors that can protect active layers during undercut etching process to generate the released device layout for transfer printing. A unique property of anchors scheme enables integration of the fully formed devices on a wafer and produce a smart way to vertical LED configuration. The
same procedures and strategies should also be applicable to other classes of devices that have complex active layers than those illustrated here.

3.5 References


3.6 Figures

Figure 3.1 Schematic illustrations and corresponding SEM images showing key process steps to achieve the transfer printed µ-ILEDs with undamaged active layers during the undercut release etching in a diluted HF solution.
Figure 3.2 (a) Optical micrographs of $9 \times 9$ µ-LEDs, picked up with a PDMS stamp (left) and after transfer printed on to an epoxy coated glass substrate (right). (b) SEM image showing the narrow feature of the protective anchors. (c) Microscope images describing the selective transfer printing process. From left to right frames, it shows formation of anchors, pickup (top) and transfer printing (bottom), and ‘after selective pick-up on a wafer.”
Figure 3.3 (a) Tilted view SEM image of the transfer printed $\mu$-ILED that is generated via normal anchor scheme without protection during undercut etching in a diluted HF solution. (b) Lateral etching rate of Al$_{0.96}$As$_{0.04}$ and Al$_{0.5}$In$_{0.5}$P layers. (c) Current-voltage characteristics with different dimensions of $\mu$-ILEDs. (d) Voltage at the current of 0.1 mA with actual dimensions of $\mu$-ILED in cases of ‘on wafer’ and ‘after transfer’. (e) Current-voltage of a set of $\mu$-ILED before (left frame) and after undercut etching and transfer printing (right frame). In case of transfer printing, protective anchors are exploited.
Figure 3.4 Microscope images of a set of μ-ILED before and after transfer printing. Before transfer printing (left frame), protective anchors were photopatterned and undercut etching was carried out. The image in the right frame shows μ-ILEDs after transfer printing and removal of protective anchors. Top remaining SiO$_2$ indicate μ-ILEDs are not damaged.
Figure 3.5 Relative optical output power as a function of driving current with three different cases (on wafer, transfer printed via normal anchor scheme, and transfer printed via protective anchor scheme. Here, photo-detector was placed right on top of µ-ILED.
Figure 3.6 Microscope images of a set of $\mu$-ILED before and after transfer printing. In the left image, both p- and n-ohmic metal contacts were formed before formation of protective anchors and undercut etching. The image in the right frame shows $\mu$-ILEDs after transfer printing and removal of protective anchors. Both metal contacts were not damaged during the undercut process.
Figure 3.7 (a)-(c) Schematic illustrations and microscope images of key process steps for generating vertical LED configuration by selective deposition of metal layers at the backside of the picked-up µ-ILEDs. (d) SEM image after deposition of metal layers. (e) Microscope images of µ-ILEDs after transfer printing. Inset image highlights the deposited metal at the backside of devices.
Figure 3.8 (a) Tilted (top frame) and vertical (bottom frame) views schematic illustrations of vertical LED configuration, respectively. (b) Microscope image of a set of μ-ILEDs in a vertical configuration, which is transfer printed on an epoxy coated glass substrate. (c) Luminance-current-voltage (L-I-V) measurements with different n-GaAs thicknesses. (d) Re-plotting of Fig. 3.8c as a function of n-GaAs thickness.
Figure 3.9 Simulation results that explain the results in Fig. 3.10. Reflectances from the metal layer at the backside of the device were calculated with different n-GaAs thicknesses (left frame). Right frame corresponds to re-plotting of the graph in the left frame as a function of n-GaAs thickness.
Figure 3.10 Optical images of a 5×5 μ-ILEDs array in vertical configurations. Bottom images were obtained without external illuminations.
CHAPTER 4

STRETCHABLE INORGANIC LIGHT EMITTING DIODES ARRAY


4.1 Introduction

All established forms of inorganic LEDs and PDs incorporate rigid, flat and brittle semiconductor wafers as supporting substrates, thereby restricting the ways that these devices can be used. Research in organic optoelectronic materials is motivated, in part, by the potential for alternative applications enabled by integration of thin film devices on flexible sheets of plastic [1-3]. Many impressive results have been achieved in recent years, several of which are moving toward commercialization [4, 5]. There is growing interest in the use of organic and inorganic micro/nanomaterials and devices in similarly unusual forms on plastic [6-9], paper [10-12], textile [13], rubber [14], and other flat or curved [15-17] substrates. This chapter extends basic concepts that yield flexible systems into new areas and implements the results in mechanically optimized layouts to achieve arrays of inorganic LEDs and PDs in systems that can accommodate extreme modes of mechanical deformation, for integration on substrates of diverse materials and formats. Specifically, this chapter describes three advances, in the following order: (1) experimental and theoretical aspects of mechanical designs that
enable freely deformable, interconnected collections of LEDs and PDs on soft, elastomeric membranes, bands and coatings, (2) strategies for achieving high effective fill factors in these systems, using laminated multilayer constructs, (3) device examples on diverse substrates and in varied geometrical forms.

4.2 Experiment

The devices and integration methods presented in chapter 2 are compatible with strategies to stretchable electronics, thereby providing a route to conformable displays and lighting systems of the type. The fabrication scheme to yield stretchable arrays uses a dual transfer process that involves first printing the semiconductor materials to a temporary substrate (glass plate coated with a trilayer of epoxy / polyimide (PI) / poly(methylmethacrylate) (PMMA)) for forming contacts, interconnections and structural bridges, and encapsulation layers. Dissolving the PMMA releases fully formed interconnected collections of devices. The second transfer printing step achieves integration on elastomeric sheets (e.g. poly(dimethylsiloxane), PDMS) or other substrates coated with thin layers of PDMS, with strong bonding only at the locations of the devices. For all examples described in the following, μ-ILEDs and the μ-IPDs have lateral dimensions of 100×100 μm² and thicknesses of 2.53 μm, corresponding to volumes that are orders of magnitude smaller than those of commercially available devices [18].

4.2.1 Fabricating Arrays of μ-ILEDs with Serpentine Interconnects

Figure 4.1 present the key process steps to fabricate arrays of μ-ILEDs and IPDs in mesh designs with serpentine interconnects on glass substrates. The released squares of
epitaxial material formed according to procedures described in the chapter 2 were transfer printed onto a glass substrate coated with layers of a photo-definable epoxy (SU8-2; MicroChem Corp.; 1.2 μm thick), polyimide (PI; Sigma-Aldrich; 1.2 μm thick), and poly(methylmethacrylate) (PMMA A2; Microchem.; 100 nm thick) from top to bottom. Next, another layer of epoxy (SU8-2, 2.0 μm) was spin-cast and then removed everywhere except from the sidewalls of the squares by reactive ion etching (RIE; PlasmaTherm 790 Series) to reduce the possibility of partial removal of the bottom n-GaAs layer during the 1st step of an etching process (1st step: \( \text{H}_3\text{PO}_4 : \text{H}_2\text{O}_2 : \text{DI} = 1 : 13 : 12 \) for 25 seconds / 2nd step: HCl : DI = 2 : 1 for 15 seconds / 3rd step: \( \text{H}_3\text{PO}_4 : \text{H}_2\text{O}_2 : \text{DI} = 1 : 13 : 12 \) for 24 seconds) that exposed the bottom n-GaAs layer for n-contacts. Next, another layer of epoxy (1.2 μm thick) spin-cast and photopatterned to expose only certain regions of the top p-GaAs and bottom n-GaAs, provided access for metal contacts (non-Ohmic contacts) and interconnect lines (Cr / Au, 30 nm / 300 nm) deposited by electron beam evaporation and patterned by photolithography and etching. These interconnect lines connected devices in a given row in series, and adjacent rows in parallel. A final layer of spin cast epoxy (2.5 μm) placed the devices and metal interconnects near the neutral mechanical plane (Fig. 4.2). Next, the underlying polymer layers (epoxy / PI / PMMA) were removed in regions not protected by a masking layer of SiO\(_2\) (150 nm thick) by RIE (oxygen plasma, 20 sccm, 150 mTorr, 150 W, 40 min). Wet etching the remaining SiO\(_2\) with buffered oxide etchant exposed the metal pads for electrical accesses; thereby completing the processing of arrays of \( \mu \)-ILEDs (and/or \( \mu \)-IPDs) with serpentine interconnects.

4.2.2 Transfer Printing of Stretchable Arrays

The schematic illustrations and optical images in Fig. 4.3 provide the second transfer
printing step. Dissolving the PMMA layer of the structure with acetone at 75 °C for 10 minutes released the interconnected array of devices from the glass substrate. Lifting the array onto a flat elastomeric stamp and then evaporating layers of Cr / SiO₂ (3 nm / 30 nm) selectively onto the backsides of the devices enabled strong adhesion to sheets or strips of PDMS or to other substrates coated with PDMS.

4.2.3 Stretching Tests and Electrical Characterization

Stretching tests were performed using custom assemblies of manually controlled mechanical stages, capable of applying strains along x, y, and diagonal directions. For fatigue testing, one cycle corresponds to deformation to a certain level and then return to the undeformed state. Each fatigue test was performed up to 1000 cycles to levels of strains similar to those shown in the various figures. Electrical measurements were conducted using a probe station (4155C; Agilent), by directly contacting metal pads while stretched, bent, or twisted.

4.3 Results and Discussion

4.3.1 Design Consideration for Stretchable Arrays

Figures 4.4 presents optical images, schematic illustrations of arrays of μ-ILEDs connected by serpentine shaped ribbons that serve as either structural bridges or electrical interconnects, transferred to a thin, pre-strained sheet of PDMS (~400 μm thick). The devices are connected in series, such that all of them turn on and off together; a single failed device leads to failure of the entire array. The interconnects consist of thin films of metal with photo-defined layers of epoxy on top and bottom to locate the metal at the neutral mechanical plane.
Detailed geometries appear in Fig. 4.4b. Releasing the pre-strain yields non-coplanar layouts in the serpentes via a controlled, non-linear buckling response, as shown in the left frame of Fig. 4.4a (~20% pre-strain). The right frame and inset of Fig. 4.4a present a schematic illustration and magnified optical image of a representative μ-ILED, respectively. These design choices are informed by careful studies of the mechanics through three dimensional finite element modeling (3D-FEM) of the complete systems; they represent highly optimized versions of those reported recently for silicon circuits [19] and μ-ILEDs [20]. The results enable stable and robust operation during large scale uniaxial, biaxial, shear and other mixed modes of deformation, as described in the following. Figure 4.5a and 4.6a show tilted view scanning electron microscope (SEM) images and corresponding optical microscope images of adjacent μ-ILEDs and non-coplanar serpentine interconnects formed with ~20% biaxial pre-strain before (left) and after (right) uniaxial stretching (~60%), respectively. The separations between adjacent pixels change by an amount expected from the pre-strain and the applied strain, where a combination of in- and out-of-plane conformational changes in the serpentes accommodate the resulting deformations in a way that avoids any significant strains at the positions of the μ-ILEDs. In particular, 3D-FEM modeling results (Fig. 4.5b) reveal peak strains in the metal interconnect and the μ-ILEDs that are >300 times smaller than the applied strain. Figure 4.6c shows similar results for ~59% stretching along the diagonal direction, corresponding to Fig. 4.6b.

Figure 4.7a presents two dimensional, in-plane stretching of a 6×6 array of μ-ILEDs along horizontal (left) and diagonal (right) directions. The uniform and constant operating characteristics of all devices are clearly apparent as well as in the current-voltage (I-V) characteristics (left frame of Fig. 4.7b). The applied strains, calculated from the separations of
inner edges of adjacent pixels before and after stretching, reach ~48% and ~46% along the horizontal and diagonal directions, respectively. The current-voltage characteristics are invariant even after 100,000 cycles of 75% stretching along the horizontal direction (right frame of Fig. 4.7b).

4.3.2 Various Deformation Modes with Stretchable Arrays

Uniaxial stretching and compressing are among the simplest modes of deformation. Others of interest include biaxial, shear and related. The results of Fig. 4.8 demonstrate the ability of the stretchable array designs to allow these sorts of motions, through large strains induced by pneumatic pressure, achieved by inflation of a thin (500 μm) membrane of PDMS that supports an array similar to that of Fig. 4.7a. Injecting air through a syringe in a specially designed cylinder that serves as a mount for the device deforms the initially flat array (top frame of Fig. 4.8a) into a balloon shape (bottom frame of Fig. 4.8a). Fig. 4.8b shows four pixels in the ‘flat’ (top) and ‘inflated’ states (bottom) during operation, with external illumination. The area expansion induced in this manner can reach ~85% without any device failures. The current-voltage characteristics also show no appreciable differences between the flat and inflated states (Fig. 4.8c). 3D-FEM is used to model the inflation induced deformation of a circular elastomeric membrane, with the same thickness (500 μm) and diameter (20 mm) as in experiment, but without a mounted μ-ILED array. As illustrated in Fig. 4.8d and 4.9, both the circumferential and meridional strains reach ~37.3% when inflated to a height of 8.3 mm, the same as in the bottom frame of Fig. 4.8a. Measured displacements of devices in the system of the bottom frame of Fig. 4.8b indicate strains of ~36%, which are comparable to values calculated by 3D-FEM. This observation suggests an important conclusion: with the
designs reported in this chapter, the arrays provide negligible mechanical loading of the soft, elastomeric membrane support, consistent with the very low effective modulus provided by the optimized, non-coplanar serpentines.

Corkscrew twisting (Fig. 4.10a) provides another well-defined mode of deformation that is of interest. Here, large shear strains occur in addition to stretching / compressing in the axial and width directions. The device test structure in this case consists of a 3×8 array of µ-ILEDs transferred to a band of PDMS without pre-strain (See Fig. 4.11 for details). Optical images of flat, 360°, and 720° twisting deformations with (left) and without (right) external illumination (Fig. 4.10a) reveal uniform and invariant emission. These strains lead to out-of-plane motions of the serpentines, as shown in Fig. 4.10b. The µ-ILEDs remain attached to the PDMS substrate due to their strong bonding [19]. Electrical measurements indicate similar I-V characteristics with different twisting angles (Fig. 4.10c). Figure 4.10d presents distributions of various strain components, evaluated at the surface of a band of PDMS with thickness 0.7 mm by 3D-FEM: axial stretching (left frame), width stretching (middle frame) and shear (right frame). The results demonstrate that the PDMS surface undergoes both extreme axial/width stretching and shear deformations, with shear dominating, and reaching values of ~40% for the 720° twist. The distributions of strain for the bare PDMS substrate can provide reasonably good estimates for the system. These controlled uniaxial (Fig. 4.7a), biaxial (Fig. 4.8a) and twisting (Fig. 4.10a) modes suggest an ability to accommodate arbitrary deformations. As two examples, Fig. 4.12a and b show cases of stretching onto the sharp tip of a pencil and wrapped onto a cotton swab. The array of 6×6 µ-ILEDs pulled onto the pencil (white arrows indicate stretching directions) experiences local, peak strains of up to ~100%, estimated from distances between adjacent devices in this region. Similar but milder and more
spatially distributed deformations occur on the cotton swab, with an 8×8 array. In both cases, observation and measurement indicate invariant characteristics, without failures, even in fatigue tests (Fig. 4.12c).

4.3.3 Stacked, Laminated Layouts for High Area Fill Factors

A key feature of the layouts that enable these responses to various modes of deformation is the relatively small area coverage of active devices, such that the serpentine structures can absorb most of the motions associated with applied strain. An associated disadvantage, for certain applications, is that only a small part of the overall system emits light. This limitation can be circumvented with layouts that consist of multilayer stacks of devices, in laminated configurations, with suitable spatial offsets between layers. The exploded view schematic illustration in Fig. 4.13a shows this concept with four layers. Integration is accomplished with thin coatings of PDMS (~300 μm) that serve simultaneously as elastomeric interlayer dielectrics, encapsulants and adhesives. Here, each layer consists of a substrate of PDMS (300 μm thick) and an array of μ-ILEDs. The total thickness of the four layer system, including interlayers of PDMS, is ~1.3 mm. Optical images of emission from a four layer system appear in Fig. 4.13b. Figure 4.13c shows a two layer case, where each layer lights up in a different pattern. The inset on the right illustrates the same system in a bent state (bending radius = 2 mm), where the maximum strain in top and bottom GaAs layers is only 0.006% and 0.007%, respectively as shown by 3D-FEM simulation (Fig. 4.14). The PDMS interlayers restrict the motion of the serpentine, but by an amount that reduces only slightly the overall deformability. The extent of free movement can be maximized by minimizing the modulus of the encapsulant. The PDMS mixed in a ratio to yield a Young’s modulus of ~0.1 MPa [21] was
used to retain nearly ~90% of the stretchability of the unencapsulated case [22].

4.3.4 Integration with Various Substrates

The favorable mechanical characteristics of stretchable systems enable integration onto a variety of substrates that are incompatible with conventional optoelectronics. As demonstration examples, the μ-ILED devices on swatches of fabrics, tree leaves, sheets of paper, and pieces of aluminum foil were built (Fig. 4.15). In all cases, transfer printing successfully delivers the devices to these substrates with thin (~50 μm) coatings of PDMS that serve as planarizing (Fig. 4.16) and strain isolating layers, and as adhesives [23]. Bending and folding tests for each case indicate robust operation under deformed states. The smallest bending radii explored experimentally were 4 mm, 2.5 mm, and 400 μm for the fabric, leaf, and paper, respectively. Theoretical modeling [23], using Young’s moduli and thicknesses of 1.2 MPa, 800 μm, 23.5 MPa, 500 μm, 600 MPa and 200 μm for the fabric, leaf, and paper [24-26], respectively, shows that the fabric, leaf and paper can be completely folded, in the sense that the strain in the GaAs remains much smaller than its failure strain (~1%) even when the bending radius equals the substrate thickness. Without the strain isolation provided by the PDMS, the fabric can still be folded, but the leaf and paper can only be bent to minimal radii of 1.3 mm and 3.5 mm, respectively. This result occurs because the Young’s modulus of PDMS (0.4 MPa) is much smaller than those of leaf and paper (i.e., strain isolation), while the Young’s moduli of PDMS and fabric are more similar. Random wrinkling, including multidirectional folding with inward and outward bending can be accommodated, as is apparent in the devices on paper and aluminum foil (~30 μm). In images of the latter case (Fig. 4.15d), the number density of wrinkles reaches ~200 per cm$^2$ with approximate radii of curvature as small
as 150 μm).

4.4 Conclusion

In summary, the advances in mechanics, high fill factor multilayer layouts and biocompatible designs provide important, unusual capabilities in inorganic optoelectronics, as demonstrated by successful integration onto various classes of substrates. Areas for additional work range from the development of related strategies for μ-ILEDs based on materials such as GaN and multispectral biomedical systems suitable for clinical use.

4.5 References


4.6 Figures

**Figure 4.1** Schematic illustration of fabrication processes for μ-ILEDs arrays on a carrier glass substrate after transfer printing.
Figure 4.2 (a) Schematic illustration of the cross sectional structure at an island, with an approximate thickness for each layer. The inset corresponds to an SEM image of a μ-ILEDs array after transfer printing to a thin PDMS substrate with prestrain of ~20 %. (b) Schematic illustration of the cross sectional structure at metal interconnection bridges, with approximate thicknesses of each layer.
Figure 4.3 (a) Schematic illustration (left frame) and corresponding microscope (top right frame) and SEM (bottom right frame) images of a 6×6 μ-ILEDs on a handle glass substrate coated with layers of polymers (epoxy / PI / PMMA). (b) Schematic illustration (left frame) and corresponding microscope (top right frame) and optical (bottom right frame) images of a 6×6 μ-ILEDs array which is picked up with a PDMS stamp for transfer printing. A shadow mask for selective deposition of Cr/SiO₂ (thickness: 3nm/30nm) covers the retrieved array on a soft elastomeric PDMS stamp. (c) Schematic illustration of transfer printing to a pre-strained thin (thickness: ~400 μm) PDMS substrate (left frame) and microscope (top right frame) and SEM (bottom right frame) images of the transferred μ-ILEDs array on a prestrained thin PDMS substrate. Prestrain value was ~20%.
Figure 4.4 (a) Optical image of a 6×6 array of μ-ILEDs (100 μm × 100 μm, and 2.5 μm thick, in an interconnected array with a pitch of ~830 μm) with non-coplanar serpentine bridges on a thin (~400 μm) PDMS substrate (left frame). Schematic illustration (right) and corresponding photograph (inset) of a representative device, with encapsulation. (b) Schematic illustration of top encapsulation layers indicating some of the key dimensions.
Figure 4.5 (a) Tilted view SEM images of adjacent μ-ILEDs (yellow dashed boxes) before (left, formed with ~20% pre-strain) and after (right) stretching along the horizontal direction (red arrows). (b) Strain distributions determined by 3D-FEM for the cases corresponding to frames in (a).
Figure 4.6 Optical microscope images of two adjacent pixels in μ-ILEDs array with serpentine bridges before (left frame) and after (right frame) stretching along the horizontal (a) and diagonal direction (b), respectively. The upper and lower images show optical micrographs in emission light off (upper) and on (lower) states. The distance between adjacent pixels appears in the lower images and used for calculation of applied strains. (c) FEM simulation under external stretching along the diagonal direction (left frame), and strain contours in the GaAs active island (top right frame) and the metal bridge (bottom right frame).
Figure 4.7 (a) Optical images of a stretchable 6×6 array of μ-ILEDs, showing uniform emission characteristics under different uniaxial applied strains (top left: 0%, bottom left: 48% along horizontal direction; top right: 0%, bottom right: 46 % along diagonal direction). (b) I-V characteristics of this array measured in the strained configurations shown in (a) (left) and voltage at 20 μA current for different cycles of stretching to 75 % along the horizontal direction (right).
Figure 4.8 (a) Tilted (left) view optical images of a stretchable array (6×6) of μ-ILEDs on a thin (~500 μm) PDMS membrane in a flat configuration (top) and in a hemispherical, balloon state (bottom) induced by pneumatic pressure. (b) The magnified view of (a) from the top. The yellow dashed boxes highlight the dimensional changes associated with the biaxial strain. (c) I-V characteristics of the array in its flat and inflated state. (d) Distribution of meridional and circumferential strains determined by 3D-FEM.
Figure 4.9 Spatial distribution of FEM results of the right frame of Fig. 4.8d and analytical solutions
Figure 4.10 (a) Optical images of an array of µ-ILEDs (3×8) on a band of PDMS twisted to different angles (0° (flat), 360°, and 720° from top to bottom), collected with (left) and without (right) external illumination. (b) SEM image of the array when twisted to 360°. The serpentine interconnects move out of the plane (red box) to accommodate the induced strains. (c) I-V characteristics of the array twisted by various amounts (0 (flat), 360 and 720°). (d) Distributions of axial (left), width (center) and shear (right) strain determined by 3D-FEM for twisting to 720°.
Figure 4.11 Schematic illustrations of a 3×8 µ-ILEDs array integrated on a thin PDMS substrate with detailed dimensions (upper frame: registrations of the µ-ILEDs on a PDMS donor substrate, lower frame: entire view of the printed 3×8 µ-ILEDs array). The inset on top represents an optical microscope image of this µ-ILEDs array on a handle glass substrate before transfer printing.
Figure 4.12 (a) Optical images of an array of μ-ILEDs (6×6), tightly stretched on the sharp tip of a pencil, collected with (left) and without (right) external illumination. The white arrows indicate the direction of stretching. (b) Optical images of a stretchable 8×8 array, wrapped and stretched downward on the head of a cotton swab. The inset image was obtained without external illumination. (c) I-V characteristics of the array in (a) before (initial), during (deformed) and after (released) deformation. The inset provides a graph of the voltage needed to generate a current of 20 μA, measured after different numbers of cycles of deformation.
Figure 4.13 (a) Schematic, exploded view illustration for a stacked device formed by multilayer lamination. (b) Optical images of a four layer stack of $4\times4$ arrays with layer-to-layer offsets designed to minimize overlap of interconnect lines with positions of the $\mu$-ILEDs. The images show emission with different numbers of layers in operation ($1^{st}$ layer on, $1^{st}$ and $2^{nd}$ layers on, $1^{st}$, $2^{nd}$ and $3^{rd}$ layers on, and $1^{st}$, $2^{nd}$, $3^{rd}$ and $4^{th}$ layers on). (c) Optical images of a two layer stack of $8\times8$ arrays, with different layers in operation. The inset shows the device in a bent state (bending radius ~2 mm) with both layers on.
Figure 4.14 The strain distribution of the two-layer system in the stacked array bent to a radius of curvature 2 mm, as shown in Fig. 4.13c. The black dashed rectangles demonstrate the positions of µ-ILEDs.
Figure 4.15 (a) Optical image of a 6×6 μ-ILEDs array with serpentine metal interconnects, integrated on fabrics, in its bent and on state (bending radius ~4.0 mm). The inset shows the device in its flat and off state. (b) Optical image of an 8×8 μ-ILEDs array with a human pattern, integrated on a fallen leaf, in its bent and on state. The inset image was collected with external illumination. (c) Optical image of an array of μ-ILEDs (8×8) on a piece of paper, in a folded state (bending radius ~400 μm) during operation. The inset shows the device in its flat state. (d) Optical image of a 6×6 array on a sheet of aluminum foil under crumpled state. The inset shows the device in its flat state.
Figure 4.16 SEM images of various substrate such as fabrics (a), fallen leaves (b), paper (c), and Al foils (d) before (left frame) and after (right frame) coating of thin layer of PDMS.
CHAPTER 5
STRETCHABLE, TRANSPARENT GRAPHENE INTERCONNECTS FOR
MICROSCALE INORGANIC LIGHT EMITTING DIODES


5.1 Introduction

The excellent mechanical, thermal and electronic properties of graphene have motivated both wide-ranging scientific and engineering studies [1]. Recent advances in synthesis and processing [2] have created interest in practical applications as robust, transparent conductors for touch screens, photovoltaic cells and light-emitting diodes (LEDs). In these systems, graphene could serve as an attractive substitute to more traditional materials such as TCOs (transparent conducting oxides), due to its favorable mechanical properties and its potential to reduce costs. Recently, such uses of graphene have been reported by many groups, including possibilities for use in organic and inorganic LEDs [3-6]. Previous reports are limited, however, to single pixel demonstrations, in modes that do not fully exploit the unique mechanics afforded by graphene compared to TCOs. Further process developments and alternative strategies are needed for interconnected arrays of LEDs, and for applications of graphene in unusual areas such as stretchable electronics and optoelectronics. In this chapter, the use of graphene as a stretchable, transparent electrode, and interconnect for μ-ILEDs in a
manner that exploits its extremely low flexural rigidity to enable conformal contacts to structures that present significant surface relief is explored. When configured into serpentine geometries, graphene provides robust interconnects for the stretchable $\mu$-ILEDs array, where reversible, linear elastic behavior is observed for strains exceeding 100%. Device demonstrations and detailed examination of the materials and mechanics aspects highlight some appealing features of graphene used in this manner.

5.2 Experiment

5.2.1 Preparation of CVD-Grown Graphene

Graphene was prepared by chemical vapor deposition (CVD). A 50 $\mu$m thick Cu foil (provided by Alfa Aesar) wrapped around a quartz rod was inserted into a quartz reaction tube (1 inch diameter) and then heated to 1000 °C at a ramp speed of 24 °C/min under flowing hydrogen gas, where the pressure of the tube is kept at 0.26 Torr. After flowing a reacting gas mixture (CH$_4$:H$_2$=850:50 sccm) for 30 min under 2.6 Torr, the sample was cooled to room temperature with a rate of 20 °C/min. The pressure was increased to ambient when the temperature reached 200 °C. Figure 5.1a shows the experimental sequence. The graphene grows on both the top and bottom surfaces of the copper foil. Typically, the graphene from one side is removed by oxygen plasma etching with the other protected with a PMMA layer. The foil was then placed in a 1 mole of aqueous solution of FeCl$_3$ to eliminate the copper. After ~10 hours, floating graphene with PMMA was transferred to deionized (D.I.) water to wash out the etchant and to prepare the film for lamination on the LED substrate (Fig. 5.1b).

5.2.2 Preparation of Isolated $\mu$-ILEDs and Integration with Graphene
Figure 5.2 schematically illustrates key process steps for fabricating μ-ILEDs (p-GaAs / p-AlGaAs / p-InAlP / quantum well (AlGaInP / InGaP / AlGaInP) / n-InAlP / n-AlGaAs / n-GaAs) with transparent graphene electrodes. The receiving substrate consists of a printed array of AlGaInP μ-ILEDs (100×100 µm$^2$; 2.53 µm thickness), formed and processed according to chapter 2 and 4. These devices support pre-defined ohmic metal n-contacts and etched regions for p-contacts. A spin-coated thin dielectric layer (epoxy; SU-8; 1.2 µm thickness), patterned to expose both contacts, encapsulates all other parts of the structure, as shown in the schematic illustration of Fig. 5.2 (boxed image). After lamination of graphene, washing away the PMMA with acetone and then gently drying lead to spontaneous mechanical sagging of the graphene, in a manner that establishes conformal coverage over the relief features associated with the μ-ILEDs and their dielectric overcoats. Photolithography and reactive ion etching pattern the graphene into interconnect structures, thereby completing the fabrication.

5.3 Results and Discussion

5.3.1 Characterization of Graphene

To characterize the typical CVD grown graphene employed in this study, an optical image of graphene, transferred to a 300-nm-thick layer of SiO$_2$ on a Si substrate was presented (Fig. 5.3a). This image displays uniform contrast, except for some isolated dark regions, indicated by blue triangles. Raman spectroscopy (633 nm excitation) over a representative area (dashed white box in Fig. 5.3a) yields a map of the ratio of peak intensities in the G and 2D bands, $I(G)/I(2D)$, as shown in Fig. 5.3b (pixel size ~3 µm; beam diameter ~1 µm). Most areas have ratios $I(G)/I(2D) < 0.5$, consistent with monolayer graphene [8]. The small regions
with dark contrast (blue triangles) correspond to ratios of ~1.5 which are a few graphitic islands. The SEM image in Fig. 5.3c also shows expected rippled structures (white) in the transferred graphene film, created due to mismatches in the thermal expansion coefficients of copper and graphene [9, 10].

5.3.2 Sagging Down Mechanism of Graphene

A key feature of the graphene film as implemented in this study is its ability to conform to significant surface topography. This behavior results from its exceptionally low flexural rigidity, $EI \sim 1.1 \times 10^{-19}$ J (per unit width) for monolayer graphene [11], which is 6 orders of magnitude smaller than that of PMMA (100-nm thick, elastic modulus 2.89 GPa) [12]. The resulting contact (i.e. intimate, conformal lamination) provides robust electrical interconnects between devices, even for cases where the associated relief is significant, as illustrated schematically in Fig. 5.4a. Step heights from the top of the epoxy layer to the surfaces of the p- and n-contact regions are ~1.2 and ~3 µm, respectively. Surface profilometry measurements (Sloan Dektak) and optical micrographs at different stages of the process flow appear in Fig. 5.4b and Fig. 5.5, respectively. These results show that, after removal of the PMMA, the graphene conforms nearly perfectly to the underlying relief structures. The mechanism relies on low flexural rigidity of graphene, which can lead to the bending energy that is much smaller than the adhesion energy associated with contact to the GaAs, even for substantial relief heights. Mechanics shows that sagging of graphene onto GaAs occurs when

$$\frac{9EIh^2}{\gamma L^3} < 0.01$$ (1)

where $EI$ is the flexural rigidity (per unit width), $h$ is the total height of the relief (sum of step
height of p (or n) contact region(s) and the thickness of epoxy layer), \( L \) is the step length, and is the work of adhesion between graphene and GaAs (per unit width). Schematic illustration is provided in Fig. 5.6a. For \( EI = 1.1 \times 10^{-19} \text{ J} \) (for graphene), \( h = 3 \) \( \mu \text{m} \) as in experiments, and \( \gamma \approx 0.15 \text{ J/m}^2 \) [13], a step length \( L \) as small as a few micrometers still ensures sagging. The percentage of contact coverage between graphene and GaAs is given analytically by

\[
1-2\left[18EIh^2/\left(\gamma L^4\right)\right]^{1/4},
\]

and is shown in Fig. 5.6b. For \( L = 20 \) \( \mu \text{m} \) as in experiments, 99% and 60% areas of overlying films of graphene and PMMA (100nm)/graphene, respectively, come into conformal contact. Here, the graphene (or PMMA) layer is modeled as beam to form conformal integration onto the p and n-contact regions. The sagging profile \( w \) is characterized by the sagging height \( h \) and un-contacted length \( a \) to be determined, as shown in Fig. 5.6a. The boundary conditions for the deflection and rotation are \( w=0 \) and \( w'=0 \) at \( x=0 \), and \( w=h \) and \( w'=0 \) at \( x=a \), which give the sagging profile

\[
w=3h(x/a)^2-2h(x/a)^3.
\]

The total energy \( U \) is the sum of potential energy and bending energy as

\[
U = -\gamma(L-2a)+12\left(EIh^2/a^4\right),
\]

where \( \gamma \) is the work of adhesion between graphene and GaAs, and \( EI \) is flexural rigidity of graphene. Energy minimization \( dU/da = 0 \) gives

\[
a=\left(18EIh^2/\gamma\right)^{1/4},
\]

and the total energy \( U_{\text{min}} = 48\left(EIh^2\right)^{1/4}(\gamma/18)^{3/4}-\gamma L \). Sagging requires that \( U_{\text{min}} \) be smaller than the energy of unsagged state (zero), which gives critical condition for sagging as

\[
EIh^2/\left(\gamma L^4\right) < 9/8192.
\]

It leads to Eq. (1) within one percent error. The contact coverage of graphene or bilayer of graphen / PMMA layer is defined by

\[
P = (L-2a)/L = 1-2\left[18EIh^2/\left(\gamma L^4\right)\right]^{1/4}.
\]
5.3.3 Electrical Characterization of Graphene

For use of graphene as electrodes and interconnects, the contact resistance, the sheet resistance and the optical transparency are all important; the last two aspects are the subject of many published studies [9, 13]. Low sheet resistance can be achieved either by growing multilayer graphene directly or by creating it through multiple stacking of single layers [8, 14]. The latter method is preferred here due to improved control and yield in transfer onto relief features. To evaluate properties of stacked films after transfer of different numbers of layers ($N_S$), Raman spectroscopy was performed for $N_S = 1, 2,$ and $4$ as shown in Fig. 5.7a. The results suggest that physical properties of monolayer graphene persist in such stacks, unlike the behavior of exfoliated multilayers, where the mobility decreases with increasing layer number [10].

To examine the electrical characteristics of such graphene films and to establish their suitability for use as interconnects, four-probe geometries with various widths ($W$) and lengths ($L$), defined by photolithography and etching were prepared. In this chapter, contacts consist of a bilayer of Ti (2 nm) / Au (40 nm), as shown in Fig. 5.7b. Current flows through the two outer electrodes ($I_a$), and the voltage drop is measured across the inner two electrodes ($V_r$) as indicated by labels. Figure 5.8 presents the resistance as a function of channel length for $N_S = 1, 2,$ and $4$ with $W = 50 ~\mu$m. For each case, the resistance linearly increases with channel length. The slopes of the linear region indicate that the resistance per unit length (for the given $W$) decreases monotonically from ~43.3 $\Omega/\mu$m for $N_S = 1$, to ~20.8 $\Omega/\mu$m for $N_S = 2$, and to ~11.2 $\Omega/\mu$m for $N_S = 4$, thereby illustrating the ability to scale the resistances into ranges needed for practical use. The corresponding sheet resistance, $R_S$, as a function of $N_S$ appears in
Fig. 5.8b. The results suggest that $R_S$ decreases by as much as a factor of five as $N_S$ increases from one to four, which is lower than expected based on simple considerations, but is consistent with previous reports [9, 14]. Possible explanations of this behavior could be due to upper layers of graphene bridging cracks in underlying layers, or due to an increase in the charge carrier concentration after multiple transfers caused by intercalated impurities or trapped oxygen and water molecules. Using the dependence of $R_S$ on $N_S$, it is possible to estimate the variation of optical transmittance, $T$, with $N_S$, by assuming the optical conductivity for Dirac fermions in graphene is a universal constant, $G_{OP} = e^2/4\hbar$ ($=6.08 \times 10^{-5} \Omega^{-1}$), where $e$ and $\hbar$ are the elementary charge and the Planck constant, respectively. In this case, $T$ is also universal, given by $T = (1+N_S Z_0 G_{OP}/2)^{-2} \approx (1-0.025636N_S)$, where $Z_0$ ($=377 \Omega$) is the vacuum impedance [15, 16]. The value of $T$ predicted in this manner appears in Fig. 5.8c as a dashed line. To relate an effective $N_S$ to $R_S$, we define, $N_{Seff} = R_S / R_{SN}$, where $R_{SN}$ is $R_S$ of $N$-stacked films. By assuming $N_S = N_{Seff}$, we obtain data indicated by triangles in Fig. 5.8c, consistent with theoretical prediction. Measurements of $T$ at a wavelength of 673 nm, coincident with the emission of our $\mu$-ILEDs, also follow expectation as shown in Fig. 5.8c (see Fig. 5.8d for transmittance in the entire visible range). A stacked graphene film with $N_S = 4$ exhibits transparency as high as $T \sim 90\%$ with $R_S \sim 480 \Omega/$square.

5.3.4 Electrical and Optical Characterization

Figure 5.9 provides electrical and optical properties of a single $\mu$-ILED with graphene top electrodes ($N_s = 3$). As illustrated in Fig. 5.9a, the $\mu$-ILED with a graphene p-contact, and without any ohmic contact metal, exhibits a turn-on voltage (at $I = 20 \mu$A) that is $\sim 0.3$ V higher and a slope ($-I/R$) that is substantially lower than an otherwise identical $\mu$-ILED with
ohmic metal p-contact. Measurement of contact resistance with the two-point transmission line method (TLM, optical microscope in the inset of Fig. 5.9b) reveals non-ohmic behavior of a graphene to p-GaAs contact as shown in Fig. 5.9b. In spite of these non-ideal features, the associated optical output power is enhanced with the graphene electrode, as shown in Fig. 5.9c, due to its high level of transparency. For comparison, photographs and optical microscope images of these two types of μ-ILEDs at different driven currents appear in Fig. 5.10a and 5.10b, respectively.

Beyond single device demonstrations, graphene used in this manner can interconnect many μ-ILEDs in a scalable fashion, as shown in Fig. 5.11. The upper and lower images in Fig. 5.11 correspond to a 4×6 array of μ-ILEDs on a glass substrate, driven at a current of 1 mA. The uniform emission characteristics indicate that all devices have similar intimate contacts with graphene and uniform distribution of resistance across the overall system of interconnects. The right frame of Fig. 5.11 provides a magnified view of the white boxed region in the top frame of Fig. 5.11, to illustrate the high level of transparency provided by the graphene (see also Fig. 5.12a). As expected, the current-voltage (I-V) characteristics of such array devices (Fig. 5.12b) show higher take-off voltages and lower slopes, compared to those of similar arrays with metal interconnects (Cr/Au, 30/500 nm), due to higher contact and sheet resistances for the graphene case. Graphene films with higher $N_S$, used in combination with ultrathin metal ohmic p-contacts can lead to improvements in these properties [17].

5.3.5 Stretchable Arrays with Graphene Interconnects

The favorable mechanics of graphene represent a key advantage over traditional TCOs. To illustrate the compatibility of graphene interconnects with advanced, stretchable forms [18-
of semiconductor devices, we built arrays of μ-ILEDs interconnected by graphene traces in optimized, non-coplanar serpentine shapes [21]. The shapes and layouts of the serpentine interconnects were designed to minimize material strains due to extensional deformations. Details appear in the schematic illustrations of Fig. 5.13. Adapted versions of processes and strategies for dual transfer printing can be applied in this case. The designs involve series connections of μ-ILEDs using graphene with photo-patterned layers of epoxy on top and bottom in a manner that places the graphene near the neutral mechanical plane. Figure 5.14a and 5.14b present optical images of a resulting device on a sheet of PDMS (~400 μm thick). The inset of Fig. 5.14a highlights the non-coplanar characteristics of serpentine bridges. The top and bottom frame of Fig. 5.15a show the device undeformed (~18% prestrain) and under uniaxial tensile stretching to a strain of ~85%, respectively. Uniform and constant emission characteristics are clearly observable both with (left frame) and without (right frame) external illumination. The maximum stretching before mechanical failure is ~106%; this limit is shown in the optical microscope images of Fig. 5.15b. No noticeable changes in the I-V characteristics are observed with various stretching conditions up to 100% (Fig. 5.15c), thereby indicating that strains in this range are effectively accommodated by in- and out-of-plane conformational changes in the graphene serpentes, encapsulated by top and bottom layers of epoxy in a manner that avoids any significant deformation of the brittle μ-ILEDs. Additionally, finite element modeling indicates peak strains in the graphene interconnect layer and in the GaAs of active islands were >330 times smaller than the applied strain as shown in Fig. 5.16 and 5.17. The maximum strains are only 0.049% in graphene and 0.028% in GaAs for applied biaxial prestrain of 18%. For applied external strains of 106% along the horizontal direction, the maximum material strains are 0.38% and 0.12% in graphene and GaAs,
respectively.

5.4 Conclusion

In conclusion, this chapter demonstrates an unusual type of μ-ILED module with graphene interconnects, formed via simple top-down lamination of graphene films onto the structured surfaces of active device arrays. This approach exploits capillarity and generalized adhesion forces to drive conformal contact between the graphene and the devices, in a manner that is compatible with process and design strategies for conventional thin film technologies and stretchable arrays. These attributes suggest the potential for applications in certain existing and emerging uses of LEDs in information display, biomedical devices and others.

5.5 References


5.6 Figures

**Figure 5.1** (a) Graphical illustration for epitaxial growth of graphene on a sheet of Cu foil. (b) Schematic illustrations of fabrication procedures for the downside contact of a graphene film, grown on a sheet of Cu foil.
Figure 5.2 Schematic illustration of layouts and fabrication procedures for μ-ILEDs with transparent graphene electrodes
Figure 5.3 (a) Optical image of a graphene film transferred to a SiO\textsubscript{2}/Si substrate. The boundary (dashed arrow) indicates the patterned edge of the graphene film. (b) Raman map of I(G)/I(2D) ratio from the region indicated by the dashed white box in the microscope image of frame (a). (c) Typical scanning electron microscopy (SEM) image of the transferred graphene film.
Figure 5.4 (a) Schematic illustration of \( \mu \)-ILEDs with thin layers of epoxy inter-dielectrics showing recessed features at the p and n contacts. (b) Surface profiles of the device regions at different stages of the fabrication: top -- contact regions opening through a thin layer of epoxy; middle -- laminated with a thin bilayer of PMMA / graphene; bottom -- after removing the PMMA. The illustration at the bottom shows the corresponding layout of the \( \mu \)-ILED device.
Figure 5.5 Optical images of \( \mu \)-ILEDs at different stages corresponding to the data of frame Fig. 5.4a. Insets provide magnified views of individual devices.
Figure 5.6 (a) Schematic illustration of the theoretical modeling used to study sagging mechanisms of graphene films into relief features. (b) Scaling of the contact coverage as a function of a dimensionless combination of flexural rigidity $EI$, total height of the underlying relief $h$, width of the p (or n) contact region(s) $L$, and work of adhesion $\gamma$. 
Figure 5.7 (a) Raman spectroscopy of films with different numbers of graphene layers $N_s$ (= 1, 2, and 4) after multiple layer transfers. (b) Optical image of the four-probe geometry on patterned graphene.
Figure 5.8 (a) Resistance of films with different numbers of transferred graphene layers ($N_S = 1, 2, \text{ and } 4$) as a function of four channel lengths. (b) Sheet resistance of films ($R_S$) as a function of $N_S$, averaged over each of the four data points from (a). (c) Predicted (dashed line), calculated (triangles), and measured (circles) transmittances of graphene films with different numbers of layers, at a wavelength of 670 nm. (d) Measured transmittance with different number of layers over the wavelength range (400 ~ 1000 nm).
Figure 5.9 (a) Current-voltage measurements from a single μ-ILED with ohmic metal contacts (p-contact - Pt/Ti/Pt/Au, 10/40/10/50 nm; n-contact - Pd/Ge/Au, 5/35/50 nm) and with graphene electrodes and ohmic contact only for the n-GaAs region, respectively. (b) Current-voltage characteristics evaluated by two-point transmission line method (TLM) to assess the quality of the graphene / p-GaAs contact. The inset provides an image of the test structure used for this measurement. Thin bi-layer contacts (Cr/Au, 1 nm/10 nm) were formed directly on the graphene. (c) Current-luminance characteristics of a single μ-ILED with metal and graphene electrodes.
Figure 5.10 (a) Optical images of μ-ILEDs at different drive currents, with metal (top frames) and graphene (bottom frames) electrodes. (b) Optical microscope images (black and white) showing emission areas corresponding to the results in frame (a).
**Figure 5.11** Photographs of an array of 4×6 μ-ILEDs with graphene interconnects, with (top) and without (bottom) external lighting. This device was formed on a glass substrate. The photograph in the right frame highlights the high level of transparency that is possible with graphene interconnects.
**Figure 5.12** (a) Optical images of a 4×6 array of μ-LEDs with graphene interconnects in its off state. (b) Current-voltage characteristics of an array of 4×6 μ-ILEDs with metal (Cr/Au, 30/500 nm) and graphene (3 layers) interconnects, respectively.
Figure 5.13 Schematic illustration of 4×6 array of μ-ILEDs with serpentine graphene interconnect bridges (top) and its magnified view which is providing design strategy in details (bottom).
Figure 5.14 (a) Optical image of a 4×6 array of μ-ILEDs with non-coplanar serpentine graphene interconnect bridges on a thin (~400 μm) slab of PDMS in its off state. The inset provides a magnified view. (b) Optical image of the same system without external illumination.
Figure 5.15 (a) Optical images of a stretchable 4×6 array of µ-ILEDs before (top frame) and after (bottom frame) stretching along the horizontal direction. The left and right frames were collected with and without external lighting, respectively. (b) Optical microscope images of four pixels in this array before (left frame) and after (right frame) stretching along the horizontal direction. The top and bottom frames were collected with and without external lighting. (c) Current-voltage characteristics of this array measured in various stretching conditions along the horizontal direction.
Figure 5.16 Strain distributions determined by 3D finite-element model (FEM) for the cases corresponding to frames in 5.15b.
Figure 5.17 Strain distributions of top and bottom epoxy layers, determined by 3D-FEM for the cases corresponding to frames in Fig. 5.15a.
CHAPTER 6

BIOMEDICAL AND ROBOTICS APPLICATIONS WITH STRETCHABLE ARRAYS


6.1 Introduction

The provided materials and design strategies (stretchable arrays) in chapter 4 allow operation even upon complete immersion in saline solutions, biofluids, solutions of relevance to clinical medicine and soapy water, thereby opening new and unconventional opportunities for seamless integration of optoelectronics with biomedical and robotic systems. Specifically, this chapter describes four advances, in the following order: (1) low modulus, biocompatible encapsulation materials that preserve key mechanical properties and, at the same time, enable robust operation when integrated on or implanted in living systems, (2) flexible optoelectronic components for biomedicine, with \textit{in vivo} demonstrations on animal models, (3) illuminated plasmonic crystal devices, as high performance refractive index monitors for intravenous delivery systems and (4) waterproof optical proximity sensors that mount on the curved fingertips of vinyl gloves, for possible use in robotics or advanced surgical devices.

6.2 Experiment
6.2.1 Fabrication of thin plasmonic crystals on plastic substrates

Techniques of soft lithography to form structures of surface relief on thin layers of a photocurable polyurethane (PU, NOA 73, Norland Products) cast onto sheets of poly(ethylene terephthalate) is used. Sputter deposition (5 mTorr Ar environment; AJA sputtering system) of uniform, thin (~50 nm) layers of gold completes the fabrication. The geometry of the relief and the thickness of the gold were selected to optimize the performance of the plasmonic crystals at the emission wavelength of the μ-ILEDs (i.e. 673 nm).

6.2.2 Spectroscopic measurement of the plasmonic crystals

Transmission spectra of fabricated plasmonic crystals were measured using a Varian 5G UV–Vis–NIR spectrophotometer operating in normal incidence transmission mode, without temperature control. A flow cell was mounted on top of the plasmonic crystal and aqueous solutions of glucose with different concentrations/refractive indexes were injected with a syringe pump (Harvard Apparatus) at a flow rate of 0.2 mL/min. Transmission spectra over a wavelength range of 355-1400 nm were collected during the process to monitor changes in multiple plasmonic responses. Such data were used in the process of optimizing the layouts of the crystals, and for interpreting measurements collected with the flexible, illuminated and tube-integrated sensors.

6.2.3 Fabrication of flexible, illuminated plasmonic crystal sensors

The procedure for integrating a plasmonic crystal with μ-ILED light sources on a tube (Tygon R-3603, inner and outer diameter: 0.318 mm and 0.476 mm, respectively), began with
formation of a contact window by cutting an opening in the tube, to enable direct contact of fluid in the tube with the plasmonic crystal. The embossed side of the crystal was placed face down against the window and then sealed with a transparent adhesive tape. Next, a thin layer of PDMS was coated on the tape and adjacent regions of the tubing as a bonding layer for a transfer printed, stretchable array of μ-ILEDs aligned to the plasmonic crystal. This step completes the integration process. Light from the device was collected with a separate, commercial Si photodetector (ThorLabs, Model DET110) placed on the opposite side of the tubing. Output from the detector was sampled digitally at a rate of 10 kHz. Averaging times of 6 seconds were used for each recorded data point.

6.2.4 Animal experiment

All procedures were performed under approved animal protocols. A female Balb/c mouse was anesthetized with an intraperitoneal injection of a mix of ketamine/xylazine. The depth of anesthesia was monitored by palpebral and withdrawal reflexes to confirm that the animal had reached “stage 3” of anesthesia. Once the animal was lightly anesthetized, the back was shaved and cleaned at the incision site with 70 % ethanol, followed by a betadine surgical scrub. Previous implants were removed from the mouse and the animal was euthanized according to approved protocols. To validate the performance of sutures in real conditions, the incision opened during surgery was closed with a customized 16-gauge needle and three passes with the light emitting suture were performed to seal the wound. The suture was then tested by verifying the proper operation of the μ-ILEDs. For the implants, the incision was performed on the dorsal side of the mouse and the suturing was carried out across the dermal layers (outer layers and subcutaneous tissues) above the muscle tissue.
6.3 Results and Discussion

6.3.1 Stretchable Array Integrated on Unconventional Substrates

To deliver fully functional array on to various substrates including non-flat curvilinear surface is one of the key capabilities for biomedical applications. For example, thin threads and fibers represent such substrates of potential biomedical interest, due to their potential for use as sutures and implants, as described next. Figure 6.1a and 6.1b present images of an array of \( \mu \)-ILEDs (1×8) with serpentine metal bridges and a single \( \mu \)-ILED device with long (1.25 cm × 185 μm) metal interconnects, both on flexible, thin (~8 μm) ribbons mounted onto cylindrical supports. The left and right frames of Fig. 6.1c provide additional images with different thicknesses of conventional threads. Figure 6.1d shows related systems, consisting of \( \mu \)-ILED arrays on pieces of thread, and wrapped around a rod (left frame) and tied in a knot (right frame), respectively. As clearly illustrated in Fig. 6.1d, the optimized mechanical designs enable these systems to be twisted, bent and tied into knots without affecting the operation, even when encapsulated with PDMS. Here, threads of nylon (Fig. 6.1d) and cotton (Fig. 6.1c), with diameters down to ~0.3 mm (right frame of Fig. 6.1c), respectively were explored. Integration on these and other small substrates is challenging with the usual techniques for transfer printing. Instead, rolling the target substrates over the glass carrier substrate in a manner that avoids the use of a separate transfer stamp and the associated difficulties in alignment and contact can be exploited as shown in the schematic illustration and optical image of Fig. 6.2a.

As another example, the arrays of \( \mu \)-ILEDs mounted on the surface of an otherwise conventional catheter balloon (Fig. 6.2b) could enable highly localized photodynamic drug
delivery to treat selectively a variety of intraluminal tumors and cardiovascular disorders, including atherosclerotic plaque lesions [1-4]. Phototheraphy (e.g., stabilization of plaque) and spectroscopic characterization of arterial tissue [5-7] represent other possibilities. Thin threads and fibers represent other substrates of potential biomedical interest, due to their potential for use as sutures and implants. Uniform emission characteristics of this array both under deflated and inflated states are clear in Fig. 6.2b.

6.3.2 Photonic Suture Thread and Implanted Array

Figure 6.3 demonstrates the use of a device like those in Fig. 6.1d as a light emitting suture in an animal model, manipulated with a conventional suture needle starting from the
initial incision (upper left) to the completion of three stitches (lower left). The 1×4 array of μ-ILEDs in this case operates without any failures, due partly to favorable mechanics but also to
a fully encapsulating layer of PDMS as a soft, elastomeric and biocompatible barrier to the
surrounding tissue and associated biofluids. This layer prevents device degradation and
electrical shorting through the surrounding biofluid or to the tissue; its low modulus avoids
any significant alteration in the overall mechanics. The frames in Fig. 6.3 show a few of the μ-ILEDs in the array deployed subcutaneously, and others on the outer epidermis layer of skin 
(The white and blue arrows in the images correspond to pixels located on the subdermal and
epidermal, respectively. The yellow dotted arrows highlight the stitch directions.). These types
of light emitting, ‘photonic’, or ‘light-emitting’, sutures could be used for accelerated healing
[8-12] and for transducers of vital signs or physiological parameters such as blood
oxygenation and perfusion.

Alternatively, for longer term implantable applications, subdermal μ-ILEDs can
overcome scattering limitations and bring in-vivo illumination to deep layers of tissue. This approach could yield capabilities complementary to those of fiber-optic probe-based medical spectroscopic methods, by enabling real-time evaluation of deep-tissue pathology while allowing precise delivery of radiation in programmable arrays. Such devices can be formed in geometries of strips or threads, or of sheets. As an example of the latter, Fig. 6.4a shows a schematic exploded view for a 5×5 array of μ-ILEDs on a thin sheet of polyethylene terephthalate (PET; Grafix DURA-RAR, 50 μm thickness) film coated with an adhesive layer (epoxy) and encapsulated on top and bottom with PDMS. Thin (~500 μm) ceramic insulated gold wires that connect to metal pads at the periphery of the array provide access to external power supplies (Fig. 6.5). Figure 6.4b presents a picture of an animal model with the device implanted subdermally in direct contact with the underlying musculature. Figure 6.4c shows the same device before implantation. For continuous operation of implanted μ-ILEDs, short pulsed mode operation could minimize the possibility of adverse thermal effects and also, at the same time, allow the use of phase-sensitive detection techniques for increasingly sophisticated diagnostics, imaging and physiological monitoring.

6.3.3 Plasmonic Sensors

Use of μ-ILED technologies often requires integrated photonic structures for transmission/collection of light and/or for optical sensing of surface binding events or changes in local index of refraction. In this context, plasmonic crystals represent a useful class of component, particularly for latter purposes. Figure 6.6 summarizes an illuminated sensor device that combines thin, molded plasmonic crystals with arrays of μ-ILEDs, in a tape-like format that can be integrated directly on flexible tubing suitable for use in intravenous (IV)
delivery systems, for monitoring purposes. Figure 6.6a provides an exploded view schematic illustration of the system. The plasmonic structure, similar to those described recently [13], consists of a uniform layer of Au (50 nm) sputter deposited onto a thin polymer film embossed with a square array of cylindrical holes (i.e. depressions) using the techniques of soft lithography, as illustrated in Fig. 6.6b and 6.6c. The relief geometry (depth ~200 nm; hole diameter ~260 nm; pitch ~520 nm; see Fig. 6.5c, and inset of Fig. 6.5d) and thickness of the Au were optimized to yield measurable changes in transmission associated with surface binding events or variations in the surrounding index of refraction at the emission wavelength of the \(\mu\)-ILEDs [14]. Figure 6.6d provides transmittance data measured using a spectrometer over a relevant range of wavelengths, for different surrounding fluids. The completed microsensor devices appear in Fig. 6.7a and 6.7b. As different fluids (water and glucose) flow through the tubing, the amount of light that passes from the \(\mu\)-ILEDs and through the integrated plasmonic crystal changes, to provide highly sensitive, quantitative measurements of the index of refraction. The data of Fig. 6.7c show the response of a representative tube-integrated device, with comparison to calculations (Fig. 6.7d) based on data from corresponding plasmonic structures on rigid substrates, immersed in bulk fluids and probed with a conventional, bench-scale spectrometer (Fig. 6.8). This kind of system can be used for continuous monitoring of the dosage of nutrients, such as glucose illustrated in Fig. 6.7c-d, or of polyethylene glycol (PEG) as illustrated in 6.8c-d, or other biomaterials of relevance for clinical medicine.

6.3.4 Short Range Proximity Sensors

Integration of \(\mu\)-IPDs with such sensors can yield complete, functional systems. To
demonstrate this type of capability and also another application example, a flexible, short range proximity sensor that could be mounted on machine parts, or robotic manipulators, or for use in instrumented surgical gloves was built. This device exploits co-integration of μ-ILEDs and μ-IPDs in a stretchable format that provides both a source of light and an ability to measure backscatter from a proximal object. The intensity of this backscatter can be correlated to the distance to the object. The μ-IPDs use reversed biased GaAs diodes, as functional, although inefficient, detectors of light emitted from the μ-ILEDs. A schematic diagram of the integrated system appears in Fig. 6.9a. Figure 6.9b, 6.9c show this type of system, with 4×6 arrays of μ-ILEDs and μ-IPDs, integrated onto the fingertip region of a vinyl glove. As expected, the photocurrent measured at the μ-IPDs increases monotonically with decreasing distance to the object, as shown in the inset of Fig. 6.9c for different reverse bias voltages (-10, -5, and 0 V). Figure 6.10a provides I-V characteristics of μ-IPDs. Stacked geometries, such as those presented in Fig. 4.13, can also be used, as shown in Fig. 6.10b-e with higher sensitivity due to shorter backscatter path of light. Similar to other devices described in this chapter, encapsulation with PDMS renders the systems waterproof. The left and right frames of Fig. 6.11 show images of 4×6 array of μ-ILEDs on a vinyl glove, before and after immersion in soapy water. The uniform light emission characteristics of all devices in the array are clearly apparent. I-V characteristics are invariant even after operation in saline solution (~9%) for 3 hours (Fig. 6.11b) in this solution, proving the sustainability of this device inside the body or during use in a surgical procedure.

6.4 Conclusion
This chapter describes systems that consist of arrays of interconnected, ultrathin inorganic LEDs and PDs configured in mechanically optimized layouts on unusual substrates. Light emitting sutures, implantable sheets and illuminated plasmonic crystals that are compatible with complete immersion in biofluids and solutions of relevance to clinical medicine illustrate the suitability of these technologies for use in biomedicine. Waterproof optical proximity sensor tapes capable of conformal integration on curved surfaces of gloves and thin, refractive index monitors wrapped on tubing suitable for use in intravenous delivery systems demonstrate possibilities in robotics and clinical medicine. These and related systems may create important, unconventional opportunities for optoelectronic devices.

6.5 References


6.6 Figures

![Figure 6.1](image)

**Figure 6.1** (a) Optical images of a thin (~8 μm), narrow (820 μm) strip of μ-ILEDs (1×8) with serpentine interconnects on a rigid plastic tube (diameter ~3.0 mm). (b) Optical image of single μ-ILED with long straight interconnects, wrapped around a glass cylinder. (c) Optical image of single μ-ILED with long straight interconnects, integrated on a flexible thread with diameter of diameter ~0.7 mm (left frame), and diameter ~0.3 mm (right frame), respectively. (d) Image of a 1×8 array with serpentine metal bridges on a ~700 μm diameter fiber, wrapped around a glass tube (diameter ~1.4 mm, left frame) and, in a knotted state (right frame), respectively, resting on coins (pennies) to set the scale.
Figure 6.2 (a) Optical image of a $4 \times 6$ $\mu$-ILEDs array with serpentine bridge interconnects integrated on a glass tube using a rolling method for printing (left frame). Schematic illustration describing ‘rolling method’ (right frame). (b) Optical Images of a $6 \times 6$ array on a catheter balloon in its inflated (left frame) and deflated states (right frame).
Figure 6.3 Light emitting suture consisting of a 1×4 array of μ-ILEDs on a thread (diameter ~700 μm), demonstrated in an animal model with a conventional suture needle. The images correspond to one stitch in its off state, after one stitch, two stitches, and three stitches in the on state, in the clockwise direction from the top left frame, respectively. The yellow arrows indicate the suturing directions.
Figure 6.4 Schematic exploded view illustration of an array of $\mu$-ILEDs (5×5) on a thin PET film (50 μm thick) coated with an adhesive. Layers of PDMS on the top and bottom provide a soft, elastomeric encapsulation that offers biocompatibility and an excellent barrier to biofluids and surrounding tissue. (b) Optical image of an animal model with this array implanted under the skin, and on top of the muscle tissue. (c) Device before implantation.
Figure 6.5 Schematic illustration of the encapsulation of an implantable array of μ-ILEDs as described in Fig. 6.4.
Figure 6.6 (a) Schematic exploded view of the sensor/tube system. (b) Thin, molded plasmonic crystal on a plastic substrate wrapped around a cylindrical support, showing colors due to diffraction. (c) Atomic force microscope image of the surface of such a crystal. (d) Normal incidence transmission spectra collected with a commercial spectrometer over a range of wavelengths relevant for illumination with red µ-LEDs.
Figure 6.7 (a) Optical image of a sensor integrated on an flexible plastic tube, next to the tip of a pen. The inset shows the backside of the plasmonic crystal before integration of the μ-ILEDs. (b) Images of the tube-integrated sensor viewed from the μ-ILED side of the device, with different fluids in the tube. (c) Measurement results from a representative sensor, operated while integrated with a tube, as a sequence of aqueous solutions of glucose pass through. (d) The bottom frame shows the percentage increase in light transmitted from the μ-ILED, through the plasmonic crystal and measured on the opposite side of the tube with a silicon photodiode, as a function of glucose concentration. The calculations are based on the response of a separate, conventional plasmonic crystal evaluated using bulk solutions and a commercial spectrometer.
Figure 6.8 (a) Light intensity spectrum of single $\mu$-ILED, measured with conventional spectrometer (Ocean Optics, USA). (b) Transmitted light intensity spectrum through plasmonic nanohole array at the relevant wavelength range, calculated by multiplying single LED intensity in (a) and % transmittance by plasmonic crystal. (c) Measurement results from a representative sensor (top), operated while integrated with a tube, as a sequence of aqueous solutions of PEG (polyethylene glycol) pass through. (d) The percentage increase in light transmitted from the $\mu$-ILED, through the plasmonic crystal and measured on the opposite side of the tube with a silicon photodiode, as a function of PEG concentration.
Figure 6.9 Schematic illustration of co-integrated 2×6 arrays of μ-ILEDs and μ-IPDs to yield a thin, stretchable optical proximity sensor. (b) Optical image of the sensor, mounted on the fingertip region of a vinyl glove. (c) Optical images of an array of μ-ILEDs (4×6) with serpentine metal bridges, transfer-printed on the fingertip region of a vinyl glove. The inset shows a plot of photocurrent as a function of distance between the sensor and an object (white filter paper) for different reverse bias and different voltages.
Figure 6.10 (a) Plot of I-V characteristics of photodiodes at different distances between an optical proximity sensor and an approaching object as explained in Fig. 6.9. (b) Plot of I-V characteristics of 2\textsuperscript{nd} layer (an array of photodiode) as a function of the current level of 1\textsuperscript{st} layer (an array of \(\mu\)-ILEDs) under negative bias in the stacked device. (c) Plot of photocurrent of an array of 6\times6 \(\mu\)-PDs that is stacked on the layer of a 6\times6 \(\mu\)-ILEDs array as a function of operation current of \(\mu\)-ILEDs in the stacked device. (d) Plot of current-voltage characteristics of an array of 6\times6 photodiodes as a function of distance between the device and the approaching object in the stacked device. Voltage range of an array of 6\times6 \(\mu\)-PDs was from 0 V to -10 V during the 6\times6 \(\mu\)-ILEDs array was in emission light up state (operation current of \(\mu\)-ILEDs array: 3 mA). (e) Re-plotting of Fig. 6.10d as a function of distance between approaching object and \(\mu\)-PDs.
Figure 6.11 (a) Left and right frames correspond to images before and after immersion into soapy water, respectively. (b) IV characteristics of the same μ-ILEDs array as shown in (a) after operation in saline solution (~ 9%) for different immersion time.
CHAPTER 7
MATERIALS AND DESIGNS FOR WIRELESSLY POWERED IMPLANTABLE LIGHT EMITTING SYSTEMS

In this chapter, InGaN $\mu$-ILEDs are introduced to show the versatilities of the design strategies to yield flexible systems. In particular, the system is built to be operated via a wireless operation using inductive coupling. Significant components of this chapter are in press as Rak-Hwan Kim, Hu Tao, Tae-il Kim, Yihui Zhang, Stanley Kim, Bruce Panilaitis, Miaomiao Yang, Dae-Hyeong Kim, Yei Hwan Jung, Bong Hoon Kim, Yuhang Li, Yonggang Huang, Fiorenzo G. Omenetto, and John A. Rogers, “Materials and Designs for Wirelessly Powered Implantable Light Emitting Systems,” *Small*.

7.1 Introduction

Recent developments in flexible/stretchable electronics [1-3] and optoelectronics [4-6] demonstrate that high performance semiconductor device functionality can be achieved in forms that enable intimate, conformal contacts to static or time-dynamic curvilinear surfaces [7, 8], with promising applications in advanced biomedical devices and other areas that cannot be addressed with conventional technologies. For many clinical uses of such devices, the ability to provide continuous or periodic powering in a wireless mode is highly desirable [9-11]. In this chapter, a route to flexible and stretchable systems of micro-scale inorganic light emitting diodes ($\mu$-ILEDs) with wireless powering schemes is presented, for implantable devices that could be used to accelerate wound healing [12-14], activate photosensitive drugs [15-17], or to perform imaging and spectroscopic characterization of internal tissues [18, 19].
This chapter emphasize in the following aspects of materials, mechanics and thermal physics that enable systems of this type.

7.2 Experiment

7.2.1 Fabrication of InGaN μ-ILEDs in Releasable Geometries

The active material stacks were grown on double polished sapphire substrates (2 inch diameter, Cermet Inc.). As shown in Fig. 7.1, the composition included undoped GaN (3.8 μm), a buffer layer, n-type doped GaN (2 μm), multiple quantum wells (~0.14 μm), and p-type doped GaN (0.2 μm). Figure 7.2 illustrates the first part involving preparation of μ-ILEDs in formats that are compatible with techniques for integration by transfer printing from the sapphire substrate. After rinsing with diluted HCl (HCl : D.I. = 1 : 3) for 5 min to remove the native oxide of GaN and metal ions, bilayers of Ni (15 nm) / Au (15 nm) for current spreading were formed on p-type GaN by sputter deposition and subsequent photolithography. Annealing in oxygen and nitrogen atmosphere at a temperature of 500 °C for 5 minutes helped to reduce the contact resistances. Next, n-GaN recess regions were formed by chlorine based inductively coupled plasma reactive ion etching (ICP-RIE) through a masking layer of photoresist (AZ nLOF 2070, MicroChem.). Formation of rectangular metal contact pads (Cr (15 nm) / Au (300 nm) on the n and p-type GaN (25×25 μm²) using electron beam evaporation (Temescal, FC-1800) and photolithography completed the fabrication of arrays of fully formed devices on sapphire (Fig. 7.2a). The inset optical micrograph provides the fully formed InGaN μ-ILED (100 μm × 100 μm) with n-type and p-type ohmic contacts on sapphire. After passivation with SiNₓ (Fig. 7.2b), bonding this substrate to a silicon wafer (Fig. 7.2c) using an indium (In) and palladium (Pd) chemical alloy prepares the stack for backside
exposure with a KrF laser (Intensity = 0.9 J/cm², JPSA Inc.). This process enabled transfer of the devices to the silicon, bonded with an In-Pd alloy that forms between some fraction of the In and most of the Pd. Selectively etching of unalloyed In with HCl also removed residual Ga from the laser transfer, to leave isolated structures of In-Pd that hold the devices on the underlying wafer (Fig. 7.2e). All of the µ-ILEDs were transferred to a slab of PDMS with embossed features (3 μm in diameter, 1.2 μm in height, and 5 μm in space) on its surface (Fig. 7.2f); these structures provide sufficient adhesion for this transfer, but at a sufficiently weak level to allow efficient retrieval with a stamp (relief features with heights and lateral dimensions of 100 μm) designed for transfer printing. Removing the Pd (for unalloyed Pd) and Cr (adhesion layer) with commercial etchants (Transene) eliminated all of remaining the metal (besides that use for the contacts). The schematic in Fig. 7.2g illustrates transfer print-ready devices.

### 7.2.2 Preparation of Wireless Systems

Figure 7.3 provides key process steps. Selective transfer printing delivers µ-ILEDs in desired layouts to a temporary carrier substrate (glass) coated with a bilayer of epoxy (SU8_2; Microchem.; 1 μm) / poly(methylmethacrylate) (PMMA A2; Microchem.; 100 nm thick). Next, the processing uses adapted versions of procedures described in chapter 4 for dual transfer printing process, to yield patterned interlayer dielectric polymers (epoxy; 6.8 μm), interconnects and inductive coils (Cr (30 nm) / Au (1000 nm) and top electrodes (Cr (30 nm) / Au (500 nm)), with a final encapsulating passivation layer of epoxy (1.5 μm). The rectangular spiral inductor coil and the straight interconnect lines terminate at the p and n-type ohmic contacts, respectively, with a thin (~1 μm) layer of epoxy to separate these lines at their
crossing points. A schematic illustration of the resulting system is provided in Fig. 7.3a. Detailed geometries and dimensions of the metal interconnects appear in the optical micrograph (top frame) and the schematic illustration (bottom frame) of Fig. 7.3b. The final part of the process involves releasing the device and integrated inductor coil from the carrier substrate, to yield a complete, flexible or stretchable system upon mounting on a suitable substrate. The layouts exploit segmented mesh-type designs connected mechanically by polymer (i.e. epoxy / PMMA) bridges (Fig. 7.4) and released by dissolving the PMMA layer and transferring to a PDMS slab. Depositing a thin layer of Ti / SiO$_2$ (3 nm / 30 nm), as shown in the schematic illustration and the optical image of Fig. 7.3c, prepares the surface for bonding to a substrate of interest. The optical image of Fig. 7.3d shows a representative flexible wireless \( \mu \)-ILED system on a thin (50 \( \mu \)m) sheet of PET (polyethylene terephthalate) in its bent state (bending radius = 0.5 cm). A cross sectional view appears in Fig. 7.5.

7.2.3 Thermal Analysis: FEA

Three-dimensional FEA for the wireless \( \mu \)-ILED system gives the surface temperature and the \( \mu \)-ILED temperature, and validates the analytical model. 8-node linear heat transfer elements were used, and the refined meshes were adopted to ensure the accuracy. A volume heat source was applied within the \( \mu \)-ILED. The boundary conditions include the thermal convection at the top surface of epoxy (SU8), and a constant temperature at the bottom surface of Petri-Dish. Only 1/4 of the wireless \( \mu \)-LED system was studied due to symmetry.

7.2.4 Animal Model Evaluations

All procedures were carried out under approved animal protocols. A female Balb/c
mouse was anaesthetized with an intraperitoneal injection of a mix of ketamine–xylazine. The depth of anesthesia was monitored by palpebral and withdrawal reflexes to confirm that the animal had reached ‘stage 3’ of anesthesia. Once the animal was lightly anaesthetized, the back was shaved and cleaned at the incision site with 70% ethanol, followed by a betadine surgical scrub. Once stage 3 was confirmed, a small longitudinal incision was made through the skin and the sterile implants (ethylene oxide sterilized) were inserted. The incision was closed with a Dexon 5-0 suture. The animal was monitored until ambulatory and given a dose of analgesia (Buprenorphine subcutaneously) as soon as surgery was completed. The skin tissue for histology study was harvested after 3 weeks of implantation and washed in PBS, and fixed in 10% neutral buffered formalin before histological analyses. Samples were dehydrated through a series of graded alcohols, embedded in paraffin and sectioned at 8μm thickness. For histological evaluation, sections were deparaffinized, rehydrated through a series of graded alcohols, and stained with hematoxylin and eosin (H&E).

7.3. Results and Discussion

7.3.1 Inductive Coils Design and Characterizations

The critical design parameters for the wireless coils include trace width, spacing, thickness and numbers of turns. Choices of these parameters can be informed by electrical characterization of individual μ-ILEDs and integrated systems. As illustrated in Fig. 7.6a, current-voltage measurements of a μ-ILED with a rectangular spiral coil show the same turn-on voltage (at I = 20 µA) as an otherwise identical μ-ILED without the coil, but with a slightly higher resistance (i.e. lower slope; increase of ~0.9 V to maintain a current of 1 mA) due to the additional line resistance of the coil. Increasing the thickness of the metal (here ~1 μm)
minimizes this resistance. Because the systems reported here do not include rectifiers, the transmitted alternating current (AC) power from the primary coil appears directly at the $\mu$-ILED, through the receiving coil. As a result, the AC response of the $\mu$-ILED at in the radio frequency (RF) range is important to consider. Figure 7.6b summarizes the peak voltages ($V_{\text{peak}}$) required to achieve fixed brightness from a $\mu$-ILED, as a function of operating frequencies. The data show a monotonic increase in the peak voltage with operating frequency (sine wave, Fig. 7.6c), to an extent that leads to reverse-bias breakdown in attempts to operate the device at frequencies above ~60 MHz, qualitatively consistent with behaviors in conventional LEDs [20, 21].

7.3.2 Integration into Flexible System

Based on considerations discussed in section 7.3.1, inductor coils with resonance frequencies below 50 MHz are requested. The left frame of Fig. 7.7a shows an example during operation via inductive coupling at 40.9 MHz (consistent with separate measurements of an isolated primary coil (1 turn number, diameter = 5 cm, 12 AWG) with an external supply (input power = 22.3 dBm, detailed setup appears in Fig. 7.8a). Flat configurations such as this one offer ideal operating characteristics, but the designs also function in deformed or bent states. The right frame of Fig 7.7a shows an optical image of a system powered via inductive coupling (operating frequency = 48.5 MHz, input power = 23.4 dBm), while sharply bent ($r = 0.75$ cm). The observed increase in required input power is consistent with a corresponding change in the scattering parameter, $S11$, induced by concave bending (inset schematic illustration), as evaluated on an isolated coil using a network analyzer (HP 8573D, Fig. 7.8b) and a surface mount assembly (BNC, Fig. 7.8c). Figure 7.7b shows the resonant
characteristics of the device of Fig. 7.7a; the right frame reveals a systematic increase and decrease in resonance frequency and peak amplitude, respectively, with decreasing bending radius. A bending radius of 1 cm induces a ~21% increase in resonance frequency and ~90% decrease in the peak amplitude, implying significant reduction in the power transfer efficiency and, as a result, the operating range of the system, even if the primary coil is adjusted to match the shifted resonance frequency of the receiver. These observations can be explained by bending induced decreases in the inductance, which are linearly proportional to the area (or projected area) of a coil enclosed by a current loop, according to electromagnetism theory [22]. The damped resonance characteristics with bending are due, at least in part, to increases in the effective distance between the primary and receiver coils. Such disadvantages can be relaxed by reducing the overall dimensions of the system (also advantageous in implantable devices), to decrease the sensitivity to the curvature, in terms of the projected area, and the effective separation distances, as shown in Fig. 7.9. In good agreement with such expectations, the sample with smaller dimensions (1 cm$^2$) shows no noticeable dependence of resonance frequency on bending (Fig. 7.7c). The peak amplitude shows trends similar to those of the larger devices, but with less significant decreases (~65% decrease at a bending radius of 1 cm).

7.3.3 Integration into Multi-Pixels, Stretchable, Stacked System

Simple changes in the metal interconnect schemes (i.e., inductor coils) or introduction of stacked geometries represent other possibilities of interest. For example, Fig. 7.10a presents optical images of a system with four $\mu$-ILEDs, in flat (inset image of Fig. 7.10a) and bent (Fig. 7.10a, $r = 3$ cm) states, driven with a single spiral inductor coil (number of turns = 16, size = 4
cm$^2$) at a frequency of 27.5 MHz. The slight non-uniformity in brightness is due to an uneven distribution of current that occurs in this parallel interconnection scheme due to slight variations in device performance (the $\mu$-ILED indicated by the red arrow has relatively low output). Uniform emission characteristics can, nevertheless, be achieved in many cases, as shown in the inset image of Fig. 7.18b. The measured scattering parameter, S11 reveals RF characteristics similar to those of the system with a single $\mu$-ILED (Fig. 7.7b) in various bending deformations (concave and convex) as shown in Fig. 7.10b.

Replacing the straight inductor coils with those that have serpentine shapes (Fig. 7.10c) yields systems that can be stretched, i.e. capable not only of bending but of accommodating large strain (>1%) deformations with linear elastic mechanics. Such serpentine coils require additional space for the traces. In particular, the line spacings increase from 100 to 300 $\mu$m, as indicated by a red arrow in Fig. 7.10c. To compensate the increase in resonance frequency caused by the increase in spacings, additional turns in the serpentine coils (from 16 to 30) and reduced the line widths (from 100 to 75 $\mu$m) are incorporated; the result removed any significant change in frequency. The completed stretchable device, supported by a thin (~300 $\mu$m) sheet of PDMS, appears in Fig. 7.10d in flat (left frame) and stretched (right frame) configurations, respectively (enlarged images appear in Fig. 7.11a). The measured scattering parameter (S11 for both cases in Fig. 7.10e) indicates that the peak amplitude in the stretched state slightly decreases, with no noticeable change in resonance frequency. An optical image of a device stretched by ~8% along the diagonal direction, and powered with a primary coil at a frequency of 32.4 MHz, is provided in Fig. 7.10f (~7% compressed state appears in Fig. 7.11b). Fracture occurred beyond ~8%, primarily at crossed edges, as indicated in Fig. 7.11c. This behavior is consistent with finite element analysis (FEA), which shows stress
concentrations at the crossed edges (Fig. 7.12). FEA also suggests that enhanced stretchability can be obtained by adopting larger metal thicknesses (Fig. 7.13a) or narrower trace widths, using substrates with lower elastic modulus (Fig. 7.13b), and/or increasing the radius of curvature of serpentine coils.

As another possibility, multilayer stacked geometries can offer the ability to operate different μ-ILEDs at different driving frequencies. Separately fabricated systems that have different resonance frequencies can be co-integrated on a single substrate, using an interlayer dielectric and adhesive of PDMS (~50 μm thick). Figure 7.14a and 7.14b show a schematic illustration and an optical image, respectively. A sheet of PET serves as the support for a μ-ILED with a first coil (size = 1 cm², metal width = 25 μm, and turn numbers = 60), with a system with the dimensions of the one in Fig. 7.10a integrated on top. The resonance frequency in this stacked geometry is provided in Fig. 7.14c, showing two weak but noticeable resonances that match the resonances of individual devices before co-integration with slight offsets due to the mutual coupling between the coils (Fig. 7.14d shows the resonance frequency before co-integration).

7.3.4 Thermal Analysis and In-vivo Demonstrations

Solid state lighting devices have various possible applications in bio-medicine, ranging from phototherapy (e.g., accelerating wound healing and mitigating infection), to photodynamic drug delivery, to spectroscopic characterization of arterial blood and cognition, to optogenetics. Together with recent developments in flexible electronics/optoelectronics, the wireless operation capability introduced in this chapter enables such devices to be exploited in forms designed for these and other purposes. The small sizes of μ-ILEDs are important
because they facilitate passive thermal spreading, and enable integration using planar processing, in water-proof forms. Figure 7.15a and 7.15b show optical images and corresponding thermal images of a wireless μ-ILED and integrated coil, operated via inductive coupling at a resonance frequency of ~30 MHz with different input powers, respectively. The system uses a thin (50 μm) sheet of PET as a substrate, mounted on a plastic plate (~1.2 mm thick polystyrene, thermal conductivity: 0.156 W·m⁻¹·K⁻¹) for the measurements. The results show that heat is mostly generated (ambient temperature = 21.9 °C) and localized at the μ-ILED. As the input power increases (from left to right images), the peak temperature of the μ-ILED increases linearly with negligible changes in the temperatures of the interconnect regions (i.e., inductor coils) as shown in Fig. 7.15c. Analytical models and FEA of heat conduction reveal the mechanisms for heat dissipation and provide guidelines to minimize adverse thermal effects. Analytical solutions for surface temperatures agree well with experiments and FEA (Fig. 7.15d and Fig. 7.16). These models show that the inductor coil plays a critical role in the thermal transport, without which the μ-ILED temperature would increase significantly. The waterproof characteristics of the wireless μ-ILED system are demonstrated by results in Fig. 7.17a and Fig. 7.17b, which show operation underwater and completely immersed in phosphate-buffered saline (PBS) solution, respectively. After two weeks immersion of the system in PBS solution, no noticeable changes were observed in RF characteristics, as shown in Fig. 7.17c. The damped resonance properties in water or PBS solution are provided in Fig. 17d.

*In vivo* experiments demonstrate potential applications in implantable devices. Figure 7.18a presents pictures of an animal model with a wireless μ-ILED system laminated
conformally on a sub-dermal region and powered via inductive coupling with a primary coil at a frequency of 27.6 MHz with (left frame) and without (right frame) the skin covering in place, respectively. To facilitate handling and eventual contact, this device used a silk film as a bio-resorbable, water soluble substrate. Mounting the system on the sub-dermal surface and then dissolving the silk platform with saline solution, left only the coil and μ-ILED behind, and wrapped effectively on the tissue by interface water capillary interactions. A more conventional substrate, such as a sheet of PET, can also be used, as shown in the left frame of Fig. 7.18b, although with somewhat less favorable mechanics. To assess the bio-compatibility of the system, histological slices of tissues surrounding the implanted device (encapsulated by a thin layer of PDMS) was examined, showing absence of any severe inflammatory reaction in the neighboring tissues (right frame of Fig. 7.18b).

7.4 Methods

7.4.1 Mechanical Analyses of Stretchable System: FEA

The wireless μ-ILED system subject to diagonal stretching was studied via three-dimensional FEA, which models the detailed geometry of the system and gives accurately the strain distributions in the serpentine inductor coil. The structural layout of the wireless μ-ILED system is shown in Fig. 7.5 except that the PET substrate is replaced by PDMS (thickness 300 μm). The elastic modulus ($E$) and Poisson’s ratio ($ν$) are $E_{PDMS}=1.8$ MPa and $ν_{PDMS}=0.48$ for PDMS; $E_{IC}=79$ GPa and $ν_{IC}=0.44$ for inductor coil$^{[1]}$; and $E_{SU-8}=4.02$ GPa and $ν_{SU-8}=0.22$ for SU-8. 8-node 3D solid elements and 4-node shell elements were used for the PDMS and serpentine coil, respectively. Refined meshes (e.g., > 3 million elements) were adopted to ensure the accuracy.
For 8% stretching along the diagonal direction of the serpentine coil as in experiments (Fig. S9a), FEA gives lateral dimensions of the serpentine coil of 2.75 cm (compressed from the initial length of 2.86 cm), which is identical to that measured in experiments (Fig. 7.11a). The maximum principal strain is reached at the crossed edges of the outer serpentine coils (Figs. 7.12b and 12c). The region of strain concentration, highlighted by the red color in Fig. 7.12b, gives a principal strain that exceeds the fracture limit of Au (~2%). This result is consistent with the location of fracture observed in experiments.

7.4.2 Thermal Analysis: Analytical Modeling

A Cartesian coordinate system is set such that the origin is located at the center of the bottom surface of Petri-Dish. A schematic illustration of the device geometry and boundary conditions appears in Fig. 7.19. The thermal conductivity of epoxy (0.2 W·m⁻¹K⁻¹) is close to that of PET (0.24 W·m⁻¹K⁻¹) such that the two layers can be modeled as a single PET layer for simplicity. The steady-state heat conduction equation is \[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} = 0 \] for the PET substrate and the Petri dish, where \( T \) is the temperature. The \( \mu \)-ILED (length ~100 μm) is much shorter than the inductor coil (length ~30 mm), and serves as the heat source with the heat generation \( Q \). The \( \mu \)-ILED and inductor coils have similar thermal conductivities, and are modeled as a single structure with thermal conductivity \( k_{IC} \) and thickness \( H_{IC} \). The heat conduction equation is \[ k_{IC} \frac{d^2 T}{dx^2} - \frac{q_z}{H_{IC}} = 0 \], where \( q_z \) is the heat flux from the inductor coil into the PET substrate, and is to be determined by the continuity condition across the coil/PET interface. Other continuity conditions include \([T]=0\) across the coil/PET interface, and \([T]=0\)
and \([q_z]=0\) across the PET/Petri dish interface, where \([\ ]=0\) stands for the jump across the interface. The free, top surface of the PET has natural convection, but FEA shows that this effect is negligibly small, and is equivalent to the adiabatic condition. A constant temperature \(T_x\) is imposed at the bottom (Petri-Dish) surface. The temperatures of the wireless \(\mu\)-ILED system and PET surface are obtained as

\[
T_{\mu-ILED} = T_\infty + \frac{4Q}{\pi k_{PET}W_{IC}} \int_0^\infty \frac{\sin \frac{\omega}{2} B_0(\omega)}{1 + \frac{k_{IC}H_{IC}}{k_{PET}W_{IC}} B_0(\omega)\omega^2} d\omega, \tag{1}
\]

\[
T_{surface}(x,y) = T_\infty + \frac{4Q}{\pi^2 k_{PET}W_{IC}} \int_0^\infty \frac{\cos \frac{\omega x}{W_{IC}}}{1 + \frac{k_{IC}H_{IC}}{k_{PET}W_{IC}} B_0(\omega)\omega^2} \int_0^\infty \frac{\sin \frac{\xi}{2} \cos \frac{\xi y}{W_{IC}} B_1\left(\sqrt{\xi^2 + \omega^2}\right)}{\xi^2 \omega^2 + \xi^2 + \omega^2} d\xi, \tag{2}
\]

where the subscripts ‘IC’, ‘PET’ and ‘PD’ denote the inductor coil, PET substrate and Petri dish, respectively; \(W_{IC}\) is the width of the inductor coil; \(B_0(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\sin \frac{\xi}{2} B_1\left(\sqrt{\xi^2 + \omega^2}\right)}{\xi^2 + \omega^2} d\xi\)

\[
B_1(\eta) = \frac{k_{PD}}{k_{PET}} \tanh \frac{H_{PET}\eta}{W_{IC}} + \tanh \frac{H_{PD}\eta}{W_{IC}},
\]

and \(B_0(\omega) = \frac{k_{PD}}{k_{PET}} \tanh \frac{H_{PET}\eta}{W_{IC}} + \tanh \frac{H_{PD}\eta}{W_{IC}}\). The experiments give \(W_{IC}=100\mu m\), \(H_{IC}=1\mu m\), \(k_{IC}=318\ \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\) for inductor coil; \(H_{PET}=50\mu m\) and \(k_{PET}=0.24\ \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\) for PET substrate; \(H_{PD}=1200\mu m\) and \(k_{PD}=0.156\ \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\) for Petri-Dish. Only a small percentage of total input power in the primary coil converts into heat in the \(\mu\)-ILED in the experiment, which is determined as 9% by comparing the \(\mu\)-ILED temperature increase \(T_{\mu-ILED} - T_\infty\) in Eq. (1) to the experimentally measured value for a single input power 20 mW. For input powers
ranging from 10 mW to 29 mW (and the same 9% conversion to heat), the μ-ILED temperature in Eq. (1) and surface temperature in Eq. (2) agree well with experiments. Equation (1) also shows that the μ-ILED temperature increase $T_{\mu\text{-ILED}} - T_\infty$ depends on the thermal conductivity and thickness of inductor coil via their product $k_{IC}H_{IC}$; doubling $H_{IC}$ (or equivalently, doubling $k_{IC}$) reduces $T_{\mu\text{-ILED}} - T_\infty$ by ~30%.

7.5 Conclusion

The results presented in this chapter establish the foundations for a wireless μ-ILED technology suitable for bio-integration. RF characteristics of integrated systems show finite, but manageable, dependence on bending and stretchable deformations, and acceptable thermal behaviors, all suggesting a potential for use in implants. The same procedures and strategies should also be applicable to other classes of devices that are more complex than those illustrated in this chapter.

7.6 References


Figure 7.1 Schematic illustration of epitaxial layers grown on a sapphire substrate. Multiple quantum well structure is employed.
Figure 7.2 Schematic illustration of fabrication procedures for generating free-standing, fully-formed (i.e., with ohmic contacts), InGaN µ-ILEDs integrated on a structured PDMS.
Figure 7.3 (a) Illustration of a wireless μ-ILED system on a temporary glass substrate coated with a bi-layer of epoxy / PMMA. After selective transfer printing of μ-ILEDs, formation of two photopatterned layers of epoxy and two metallization processes define interconnects and wireless coils. (b) Optical micrograph (top frame) showing the interconnect scheme, consisting of a planar spiral coil (connected to p-type ohmic contact) and a bridging metal electrode (connected to n-type ohmic contact). Detailed dimensions of the planar spiral coil appear in the bottom frame. (c) Illustration (left frame) and corresponding optical image (right frame) of a wireless μ-ILED system, retrieved with an elastomeric stamp after removal of the PMMA. Deposition of Ti / SiO\textsubscript{2} covers the backside of the device, as preparation for bonding on a target substrate. (d) Schematic illustration of the process for transferring onto a flexible sheet (left frame) and optical image of a wireless μ-ILED system on a PET substrate (right frame) in its bent state (bending radius = 0.75 cm).
Figure 7.4 Optical image of the wireless μ-ILED system with spiral inductor coils on a temporary glass substrate, and supported by polymer bridges (epoxy)
Figure 7.5 Schematic illustration of the wireless μ-ILED system presenting a cross-sectional view of a completely integrated system on a PET substrate.
Figure 7.6 (a) The current-voltage (I-V) characteristics of an individual μ-ILED with and without integrated spiral inductor coils. (b) Peak voltages needed to produce currents of 0.1 mA as a function of operating frequency when operated in an alternating current mode. (c) Representative sine wave for measurements that appear in Fig. 7.6b.
Figure 7.7 (a) Optical images of a wireless μ-ILED system on a PET substrate powered via inductive coupling at an appropriate resonance frequency in its flat (left frame) and bent (right frame) state, respectively. (b) Measured scattering parameter, S11 as a function of bending radius in a concave shape (left frame). The graph on the right show an increase in resonance frequency and decrease in peak amplitude with decreasing bending radius. (c) Measured scattering parameter of inductor coils with reduced dimensions, as a function of bending radius in a concave shape (left frame). The graph on the right shows a negligible change in resonance frequency and decrease in peak amplitude with decreasing bending radius.
Figure 7.8 (a) Detailed setup for powering via inductive coupling. (b) Optical image of the network analyzer for measuring the scattering parameter. (c) Optical image of surface mounting assembly (SMA).
Figure 7.9 (a) Calculated $A/A_0$ (projected area in a bent state / projected area in a flat state) for two systems (small ($A = 1 \text{ cm}^2$) and large ($A = 4 \text{ cm}^2$)) as a function of bending radius. (b) Calculated effective distance of two systems as a function of bending radius.
Figure 7.10 (a) Optical image of a wireless system that includes four μ-ILEDs connected in parallel, powered via inductive coupling. (b) Measured scattering parameter, S11 in flat (solid line) and bent (dashed line) states (concave: blue, convex: red). (c) Optical micrograph showing the interconnect scheme for a stretchable design. Both spiral and cross-over metal lines adopt serpentine shapes, separated by a thin layer of epoxy at their crossing points. (d) Optical images of a wireless μ-ILED device in a stretchable format integrated on a thin slab of PDMS in its initial unstretched (left frame) and stretched (right frame; ~8 % along the direction indicated by red arrows in the figure) states, respectively. (e) Measured scattering parameter, S11 in unstretched (color in black) and stretched (color in red) states. (f) Optical image of a wireless μ-ILED system when stretched along the diagonal direction (~8 %, indicated by arrows). Image was collected while powering the device via inductive coupling.
Figure 7.11 (a) Optical images of the wireless μ-ILED system with serpentine coils in its unstretched (left frame) and stretched (right frame) state, respectively. Dimensions are displayed in figures. (b) Optical image of the same system in a compressed state, wirelessly powered via inductive coupling to a primary coil. (c) Optical micrograph showing the major failure points upon stretching beyond ~8 % along the diagonal direction.
Figure 7.12 (a) FEA of the wireless $\mu$-ILED system with serpentine coils in its unstretched state (left frame) and stretched state (right frame). (b) Experimental image (left frame) and distribution of maximum principal strain obtained by FEA (right frame) around the crossed edges of serpentine coil. The red color highlights the region of maximum strain exceeding the fracture limit (~2%) of gold. (c) The maximum principle strain distribution at the top region of the serpentine coil.
**Figure 7.13** The distribution of maximum principal strain for (a) the PDMS modulus of 1.8 MPa and 0.45 MPa; (b) the coil thickness of 1.0 μm and 4.0 μm.
Figure 7.14 (a) Schematic illustration of the stacked layout. (b) Optical image of a stacked wireless μ-ILED device formed by multilayer lamination. The red and blue arrows correspond to μ-ILEDs integrated with the smaller and larger coils, respectively. A wireless μ-ILED system with reduced overall size (~1 cm × 1 cm) printed on top of one with larger size (~2 cm × 2 cm). (c) Measured scattering parameter, S11 of the integrated, stacked system. (d) The measured scattering parameter of inner and outer coils before their integration.
Figure 7.15 (a) Optical images of a wireless μ-ILED system on a PET substrate at increasing input power (10.73, 15.72, 20.08, and 28.55 mW from left to right frames). (b) Thermal images of a wireless μ-ILED system on a PET substrate at increasing input power (10.73, 15.72, 20.08, and 28.55 mW from left to right frames). (c) Graphical representation of the increase in the peak temperature of the μ-ILED and interconnects (i.e., spiral coils). The surrounding temperature was 21.9°C. (d) Temperature increases predicted by analytical models and 3D FEA simulations.
Figure 7.16 FEA simulations (top frame) and analytical modeling (bottom frame) corresponding to Fig. 7.15b.
Figure 7.17 (a) Optical image of a wireless μ-ILED system on PET, completely immersed in water. The image was collected during inductive operation. (b) Optical image of a wireless μ-ILED system on PET, completely immersed in a PBS solution. The image was collected during inductive operation. (c) Measured scattering parameter, S11 before and after immersing the system in a PBS solution for two weeks. (d) Measured scattering parameter, S11 of the wireless μ-ILED with a rectangular coil which is underwater and completely immersed in PBS solution, respectively.
Figure 7.18 (a) Wireless μ-ILED system, laminated on the sub-dermal region of a mouse model (left frame). The device was driven by inductive coupling. The inset image provides the initial form of the device, integrated on a silk substrate. The optical image in the right frame corresponds to the state after covering the device with the dermis. The image is collected during operation, via inductive coupling through the skin. The exposure time of camera was set to 10 seconds for ease of viewing of blue light emission from the μ-ILED. (b) Image of an animal model with a wireless μ-ILED device implanted under the skin, and on top of the muscle tissue. The inset shows the device before implantation where four μ-ILEDs are integrated on a PET substrate (left frame). Histological section of tissue at the implant site, excised after 3 weeks (right frame; 1, corneum; 2, epidermis; 3, dermis, 4, muscular layer).
Figure 7.19 Schematic illustration of the device geometry and boundary conditions in the analytical model of heat conduction.
8.1 Summary

First, a simple method for creating ultrathin, microscale, inorganic light emitting diodes (μ-ILEDs) and for assembling and interconnecting them into unusual display and lighting systems was developed. The μ-ILEDs use specialized epitaxial semiconductor layers that allow delineation and release of large collections of ultrathin devices. Printing based assembly methods can integrate these devices on substrates of glass, plastic or rubber, in arbitrary spatial layouts and over areas that can be much larger than those of the growth wafer. The thin geometries of these μ-ILEDs enable them to be interconnected using conventional planar processing techniques.

Second, systems that consist of arrays of interconnected, μ-ILEDs and PDs configured in mechanically optimized layouts on unusual substrates were developed based on stretchable interconnects concept. Light emitting sutures, implantable sheets and illuminated plasmonic crystals that are compatible with complete immersion in biofluids and solutions of relevance to clinical medicine illustrated the suitability of these technologies for use in biomedicine. Waterproof optical proximity sensor tapes capable of conformal integration on curved surfaces of gloves and thin, refractive index monitors wrapped on tubing suitable for use in intravenous delivery systems demonstrated possibilities in robotics and clinical medicine.

Third, the fabrication and design principles for using transparent graphene interconnects in stretchable arrays of μ-ILEDs on rubber substrates were proposed. Demonstration of several appealing properties of graphene for this purpose, including its ability to
spontaneously conform to significant surface topography, in a manner that yields effective contacts even to deep, recessed device regions could provide reliable, cost effective interconnect schemes. Mechanics modeling revealed the fundamental aspects of this process, as well as the use of the same layers of graphene for interconnects designed to accommodate strains of 100% or more, in a completely reversible fashion. These attributes were compatible with conventional thin film processing and can yield high performance devices in transparent layouts.

Lastly, a route to flexible and stretchable systems of \( \mu \)-ILEDs with wireless powering schemes, for implantable devices that could be used to accelerate wound healing, activate photosensitive drugs, or to perform imaging and spectroscopic characterization of internal tissues was demonstrated.

### 8.2 Outlook

Successful integrations of \( \mu \)-ILEDs and \( \mu \)-IPDs on various flexible substrate, which enable intimate, conformal contacts to static or time-dynamic curvilinear surfaces, offer promising applications in advanced biomedical devices and other areas that cannot be addressed with conventional technologies. Moreover, improvement in performance and heterogeneous integration of diverse devices on the same flexible platform can offer various opportunities for future use of these kinds of systems. For example, difficulties in achieving \( \mu \)-ILEDs with higher brightness, better longevity, and reliability when the devices are integrated on a plastic substrate, arise from lack in heat dissipation methods. As introduced in Chap. 3, vertical LED configurations could be implemented on a flexible substrate without wafer bonding procedures. A modified version of those procedures can offer a solution to relieve the
associated problems to provide a heat dissipation method. The collection of picked up \( \mu \)-ILEDs on an elastomeric stamp (PDMS), which have the deposited Au at the backsides can be directly bonded to thin coatings of metal films at relatively low temperature \(<100^\circ\text{C}\), otherwise metal-metal bonding usually takes place at eutectic temperature of two metals that are in intimate contacts each other, under high applied pressures, and on extremely clean surfaces. For example, the temperature of 300 \(^\circ\text{C}\) in case of gold-gold bonding are requested, which can severely degrade polymers such as plastic target substrates, elastomer, and PR. This low pressure elastomer supported cold welding can be used for other relevant areas of interest that request vertical configurations with efficient release of generated heat.

As an example of heterogeneous integration, a spectrometry system is a good candidate which is a simple, yet versatile technique. It can be integrated with photonic or plasmonic structures for chemical or biological sensing, thereby providing various functions such as oximetry, event-related optical signal (EROS), and non-invasive monitoring of biological signals. By exploiting manufacturing / design approaches reported in this thesis, integration of various active components such as light emitting, photonic, and light detecting devices into a large area, flexible substrates enables such a system.