

GRAPHENE-BASED DEVICES FABRICATED BY LOW-COST METHODS ON NOVEL SURFACES

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A THESIS SUBMITTED TO
THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF APPLIED SCIENCE

GRADUATE PROGRAMME IN ELECTRICAL ENGINEERING
AND COMPUTER SCIENCE
YORK UNIVERSITY
TORONTO, ONTARIO

MAY 2021

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ABSTRACT

Graphene is a promising material due to its superior strength, high electrical conductivity, and high thermal conductivity. The large surface area, flexibility, and piezo-resistivity of graphene make it ideal for sensing applications. The focus of this project is graphene-based devices fabricated through different low-cost and rapid manufacturing methods for specific applications. In the first part of the project, the graphene properties fabricated by laser-induced graphene on polyetherimide are studied. The main innovation in this part is using a 3D printed substrate instead of conventional commercial substrates. Also, a set of material characterizations is conducted on 3D printed and commercial samples. In the second part, an inkjet printer is used to print graphene oxide on various substrates. Different reduction methods are studied to restore the conductivity of reduced graphene oxide. Finally, a silicon-based junction field-effect transistor (JFET) with a printed reduced graphene oxide top gate is designed and fabricated to detect pH.

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my gratitude to those who offered me support. First and foremost, I am grateful to my supervisor Dr. Gerd Grau. He supported me since the day I started my master's degree. I have learned how to become a researcher because of his guidance and perseverance. I have been so lucky to have him as my mentor and supervisor. I also would like to thank Dr. Simone Pisana who agreed to join my supervisory committee and offered me his help whenever I faced a challenge. I want to thank Dr. Reza Rizvi for kindly agreeing to participate in my oral examination. I also thank Dr. Derek Wilson for providing access to his lab.

I would like to acknowledge CMC Microsystems for the provision of products and services that facilitated this research, including the design kit for JFET layout, design rule checks (DRC), cloud infrastructure, and fabrication services using the open-gate silicon JFET (OG-JFET) platform. I am very grateful to Andrew Fung and Priyadarshini Mangannavar who helped me with different aspects of my project. I also would like to thank the 3IT institute at the University of Sherbrooke.

I want to thank Veronica Di Cecco at Royal Ontario Museum and Magdalena Jaklewicz at the Advanced Light and Electron Microscopy Facility at York University for providing fast characterization services whenever I was in a rush. I

also like to thank Ayatullah Elsayed for performing the thermal analysis test. I acknowledge the Ontario Center for the Characterization of Advanced Materials (OCCAM). I also thank Xin (Shane) Guo for providing me access to Profilometry equipment. I acknowledge the support of the Natural Sciences and Engineering Research Council of Canada (NSERC) and Mitacs accelerate program.

I like to thank all my labmates, especially Milad and Mohamad who made the lab work more enjoyable. I am most grateful to Paria for all the insights, supports, and friendship she offered me during this time.

I would like to thank my family and friends for supporting me through thick and thin. Finally, yet importantly, I want to thank my husband, Morteza. He always believed in me and encouraged me to follow my dreams. He always offered his support when I faced a challenge in my work. None of this would have been possible if it was not for him.

TABLE OF CONTENTS

ABSTRACT	ii
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	v
LIST OF TABLES	ix
LIST OF FIGURES	x
CHAPTER 1. INTRODUCTION	1
1.1 Graphene	1
1.2 Graphene Applications	3
1.2.1 Field Effect transistors (FET).....	3
1.3 Graphene Fabrication	5
1.4 Ink-jet Printing	8
1.5 Laser-induced Graphene	11
1.6 Thesis Organization.....	12
CHAPTER 2. LITERATURE REVIEW	14
2.1 Integration of Electronics with 3D Printing	14
2.2 Laser-Induced Graphene	15
2.3 Ink-jet Printing of Graphene and Graphene Oxide on Novel Surfaces..	18

2.4	Graphene-based Ion-Sensitive Field Effect Transistors	23
CHAPTER 3. LASER-INDUCED GRAPHENE.....		26
3.1	Introduction	26
3.2	Experimental	28
3.3	Effect of Different Parameters on Sheet Resistance	30
3.4	Material Characterization	35
3.4.1	Resistivity and Thickness	35
3.4.2	Raman Spectroscopy	39
3.4.3	Scanning Electron Microscopy	41
3.4.4	Thermal Analysis	47
3.4.5	X-Ray Photoelectron Spectroscopy.....	50
3.5	Strain Gauge Design.....	51
3.6	Conclusion.....	54
CHAPTER 4. INK-JET PRINTING GRAPHENE ON NOVEL SURFACES ..		55
4.1	Introduction	55
4.2	Experimental	57
4.2.1	Ink Preparation and Printing.....	57
4.2.2	Graphene Oxide Reduction	58

4.3	Printing on 3D printed PLA	60
4.4	Printing on Silicon and Silicon Nitride Wafer	67
4.5	Graphene Oxide Reduction	72
4.6	Conclusion.....	84
 CHAPTER 5. GRAPHENE BASED ION-SENSITIVE FIELD EFFECT		
TRANSISTORS.....		85
5.1	Introduction	85
5.2	Experimental	87
5.2.1	Silicon chip Design and Fabrication	87
5.2.2	Printing and Characterization on the Chip	90
5.3	Printing on JFET	91
5.4	JFET I-V Characteristics	94
5.4.1	Annealing Effect.....	95
5.4.2	Channel Length Effect.....	97
5.4.3	Reduced Graphene Oxide Top-gate	98
5.5	pH Detection	100
5.6	Conclusion.....	107
 CHAPTER 6. CONCLUSION AND FUTURE WORK.....		108

6.1	Conclusions	108
6.2	Future work	110
	References.....	112

LIST OF TABLES

Table 3-1. The properties of designed strain gauges with raster and vector mode.	53
Table 4-1. The used ink-jet printing parameters for jetting GO ink.	63
Table 4-2. Sheet resistance of photothermally reduced GO ink on Si and SiN substrate.	74
Table 4-3. The applied conditions and measured resistance of reduced GO ink via thermal route.	76

LIST OF FIGURES

Figure 1-1. Demonstration of fullerene, carbon nanotube, and graphite as the derivation of graphene.	2
Figure 1-2. An illustration of DOD ink-jet printing procedure with a piezoelectric actuator.....	10
Figure 2-1. a) Schematic of LIG process on PI. b) SEM image of LIG patterned into an owl shape. The scale bar is 1 mm. c) SEM image of the LIG film circled in (b). The scale bar is 10 μm . d) Cross-sectional of the LIG film on the PI substrate. The scale bar is 20 μm . The inset shows the porous morphology of LIG. e) Raman spectrum of a LIG film and the starting PI film. f) XRD of powdered LIG scraped from the PI film. Reproduced with permission [21]. Copyright 2014, Nature Publishing Group, Macmillan Publishers Limited.....	16
Figure 2-2. Inkjet-printed graphene patterns on a) normal paper, b) PET, c) PI, and d,e) glass slides at 30 and 40 printing passes, respectively. f,g) Profilometry scan of printed electrodes in panels d and e, respectively. Reproduced with permission [44]. Copyright © 2014, American Chemical Society.	20
Figure 2-3. The schematic diagram of 3D printing the ceramic substrate with an ink-jet printer and ink-jet printing of GO lines on the 3D printed ceramic substrate. Reproduced with permission [46]. © 2020 Elsevier Ltd and Techna Group S.r.l. All rights reserved.	22

Figure 3-1. Schematic illustration of 3D printing the substrate and the laser process.	
The conductive patterns for different applications can directly integrate into the smart objects.	27
Figure 3-2. Schematic illustration of a) laser process and b) one, two, and three pulses wide lines on PEI substrate.	29
Figure 3-3. a) Effect of scanning speed on sheet resistance and b) energy per unit area for different scanning speeds. With increasing laser power, the sheet resistance decreases for lower speeds, except for 1.2 cm/s. In this case, the polymer burns instead of engraving.	31
Figure 3-4. a) Pattern effect on sheet resistance, and b) calculated energy per unit area for different patterns. Sheet resistance decreases with increasing pattern width. It also decreases with increasing power until the material is ablated, and conductivity is lost (no data points on the graph for large powers).	33
Figure 3-5. The effect of polymer on sheet resistance. The lowest sheet resistance is obtained at 40% laser power for the rectangle pattern on the 3D printed substrate.	35
Figure 3-6. Cross-sectional optical micrographs of three pulse wide lines on 3D printed and commercial substrates for a,b) 10%, c,d) 20%, e,f) 30%, g,h) 40% laser power, respectively. Line width and depth increase with increasing laser power. The increase in the line width is clearer in 3D printed sample compared to commercial samples.	37

Figure 3-7. Resistivity and thickness as a function of laser power for three pulse wide lines in 3D printed and commercial samples. The increase in thickness and decrease in resistivity with increasing power combine to achieve a low sheet resistance.....	38
Figure 3-8. Raman spectra for rectangle patterns with different laser powers on a) 3D printed PEI and b) commercial PEI. Clear multi-layer graphene peaks can be observed at 40% power for the 3D printed PEI.	40
Figure 3-9. Raman spectrum for rectangle pattern with 40% laser power on 3D printed sample. The spectrum is obtained from a different position.	41
Figure 3-10. SEM images of the graphene surface in rectangle pattern samples at a) 10%, b) 20%, c) 30%, d) 40% laser power on 3D printed PEI substrate. The size of graphenic branches increases with increasing power. Surface defects are shown for e) 10%, f) 20%, g) 30%, and h) 40% laser power. Defect size initially increases from 10% to 20% power and then decreases up to 40%.....	45
Figure 3-11. SEM images of the graphene surface in rectangle pattern samples at a) 10%, b) 20%, c) 30%, d) 40% laser power on commercial PEI substrate. The size of graphenic branches increases with increasing power.	45
Figure 3-12. Low-magnification SEM images of the graphene surface in rectangle pattern samples at a) 10%, c) 20%, e) 30%, g) 40% laser power on 3D printed PEI substrate. SEM images of the graphene surface in rectangle pattern samples at b)	

10%, d) 20%, f) 30%, h) 40% laser power on commercial PEI substrate. At 30% and 40% power, commercial samples show different morphology.....	46
Figure 3-13. DSC thermograms and of 3D printed and commercial PEI. The sharp endothermic peak at the glass transition is due to the physical aging of 3D printed PEI.....	48
Figure 3-14. TG and DTG analysis of 3D printed and commercial PEI. The weight loss in 3D printed PEI is 3.5% more than the commercial sample.....	49
Figure 3-15. a) XPS analysis and b) atomic percentages of carbon and oxygen as a function of laser power for rectangle-patterned LIG on 3D printed PEI. c) XPS analysis and d) atomic percentages of carbon and oxygen as a function of laser power for LIG samples on commercial PEI.	51
Figure 3-16. The schematic illustration of a) Raster mode and b) Vector mode. The red arrow shows the direction of the laser.	53
Figure 4-1. The schematic illustration of reduction setup for Si and SiN wafers with hydrazine hydrate. The large petri dish was sealed and placed under the fume hood for 30 minutes.	60
Figure 4-2. a) A digital image of 3D printed PLA substrate with epoxy on top. b) The optical micrograph of PLA substrate with epoxy layer. The dashed line shows the boundary between the epoxy and PLA. c) Profilometry scan across the 3D printed substrate and epoxy layer, and d) the GO ink's contact angle on printed epoxy layer.....	62

Figure 4-3. The stream of ejected GO ink and spherical droplet formation without any satellite effect.	64
Figure 4-4. Optical micrographs of printed lines on epoxy on PLA with different drop spacing. The drop spacing is a) 100 μm , b) 90 μm , c) 80 μm , d) 70 μm , e) 60 μm , and f) 50 μm . A uniform line is achieved with 50 μm drop spacing. The lines are dried at 70°C for 30 minutes before observation under the microscope.....	66
Figure 4-5. Profilometry scan across printed lines with drop spacing of 50 μm . Graph a) is the thickness of initial bulging and, graph b) is the thickness of the uniform line.....	67
Figure 4-6. The contact angle of GO ink on Si substrate a) before and b) after the cleaning procedure. The contact angle of GO ink on SiN substrate c) before and d) after the cleaning. Rinsing the substrate with DI water improves the contact angle slightly only in the case of silicon.....	68
Figure 4-7. Optical micrographs of printed lines with different drop spacing on SiN substrate. The drop spacing is a) 70 μm , b) 80 μm , c) 90 μm , d) 100 μm , and e) 110 μm . A consistent line is achieved with 100 μm drop spacing. The lines are dried at 70°C for 30 minutes before observation under the microscope.....	70
Figure 4-8. The optical micrograph of printed square patterns on Si substrate. Due to the low contact angle of the GO ink on Si, it spreads on the surface in the form of a circular pattern.	71

Figure 4-9. Profilometry scan across printed patterns on a) SiN substrate and b) Si substrate. The patterns are dried at 70°C for 30 minutes.....	71
Figure 4-10. The sheet resistance of reduced lines on epoxy/PLA as a function of pulse number. The applied voltage is 3000 V, and the off-time is 10 ms for all samples.....	73
Figure 4-11. The sheet resistance of reduced patterns as a function of pulse number on Si and SiN substrates. The applied voltage is 3000 V, the on-time is 5 ms, and the off-time is 10 ms for all samples.....	75
Figure 4-12. The sheet resistance of thermally reduced GO ink printed on Si and SiN substrates. The details of each case can be found in Table 4-3. Case 0 is before reducing the samples.....	77
Figure 4-13. The sheet resistance of printed patterns on Si and SiN substrates, before and after reducing with hydrazine hydrate.	78
Figure 4-14. Profilometry scan across multiple (5x) printed patterns on a) SiN substrate and b) Si substrate. The patterns are printed 5 times and dried at 70°C for 30 minutes after each printing. By increasing the number of printing passes, the thickness increases significantly.....	79
Figure 4-15. The sheet resistance of reduced GO printed for 1 and 5 times printing on a) Si and b) SiN substrate with different methods. The xenon reduction parameters: applied voltage=3000 V, on-time=5 ms, off-time=10 ms, and the number of pulses=250. The thermal reduction parameters: temperature=300°C,	

time=90 min, and vacuum atmosphere. The numbers in the tables are the calculated sheet resistance in Ω/sq	80
Figure 4-16. The conductivity of printed GO pattern on PLA and SiN substrates reduced with different methods. The xenon reduction parameters for PLA: applied voltage=3000 V, on-time=2 ms, off-time=10 ms, and the number of pulses=3. The xenon reduction parameters for SiN: applied voltage=3000 V, on-time=5 ms, off-time=10 ms, and the number of pulses=250. The thermal reduction parameters: temperature=300°C, time=90 min, and vacuum atmosphere. The printed column represents the conductivity of GO before any reduction treatment.	82
Figure 4-17. Raman spectra for printed GO pattern on PLA and reduced GO patterns on PLA and SiN substrates.....	83
Figure 5-1. The final design of the JFET chip. The channel widths are 1 and 2 mm. The channel lengths are etched onto the substrate as labels next to devices. The green parts on the design layout are top side metal contact, the red mark in the middle is the silicon alignment marker, and the dark blue layer is the passivation opening to the channels.....	88
Figure 5-2. Schematic illustration of the fabricated chip with the printed reduced graphene oxide as top-gate. The minimum required dimensions are shown in the figure. © 2018 CMC Microsystems. All rights reserved.....	89
Figure 5-3. The fabricated chips by CMC at 3IT.Nano (Université de Sherbrooke). The designed chips on the wafer are diced into individual dies.	89

Figure 5-4. Optical micrograph of printed GO lines on the open channel of the JFET before any surface treatments. Instead of continuous lines, individual droplets are formed.	92
Figure 5-5. a) The printed GO line on the JFET channel after plasma treatment, and b) the GO lines after drying at 70°C for 15 minutes. The red circles show the boundaries of printed lines.	93
Figure 5-6. The optical micrograph of multiple (10x) printed GO lines a) after drying process and b) after reducing with HH vapor.	94
Figure 5-7. a) Output characteristics and b) transfer curves of an unannealed JFET. c) Output characteristics and d) transfer curves of annealed JFET. The chips were annealed at 300°C for 30 minutes under the vacuum atmosphere. The channel length is 100 μm , and the width is 1 mm for all samples.	96
Figure 5-8. Output characteristics of JFETs with a) 50 μm and b) 200 μm channel length. Transfer curves of JFETs with c) 50 μm and d) 200 μm channel length. The channel width is 1 mm for all of the devices. The chips were annealed at 300°C for 30 minutes under a vacuum atmosphere.	98
Figure 5-9. Output characteristics of JFETs with back-gate bias a) without rGo top gate and b) with rGo top gate. Transfer curves of JFET c) without rGo top gate and d) with rGo top gate. The channel length is 120 μm , and the width is 1 mm for all of the devices.	99

Figure 5-10. Effect of different pH on I_d - V_d characteristics of JFETs a) without and b) with printed rGO top-gate. The channel length is 150 μm , and the channel width is 1 mm for all devices.	102
Figure 5-11. a) Output conductance and b) conductance change as a function of pH for JFET without top-gate c) Output conductance, and d) conductance change as a function of pH for JFET with rGO top-gate. The JFET with rGO top-gate shows the same trend for different gate voltages.	103
Figure 5-12. Drain saturation current for different channel lengths with rGO gate as a function of the solutions' pH.	104
Figure 5-13. a) Extracted transconductance and b) transconductance change as a function of pH for different channel lengths in JFET with rGO top-gate. The channel width is 1 mm for all devices.	105
Figure 5-14. The change in transconductance after 10 times testing for JFET with rGO top gate. The channel length of the device is 200 μm , and the channel width is 1 mm.	106

CHAPTER 1. INTRODUCTION

1.1 Graphene

Graphene is made up of a monolayer of carbon atoms bound within a hexagonal structure. Graphene can be used in different carbonic materials as the main building block. Figure 1-1 illustrates graphene and its derivatives. It was first discovered in 2004 by A. K. Geim and K. S. Novoselov when working on naturally occurring 2D materials [1]. Since then, graphene has attracted considerable interest due to its remarkable properties.

The honeycomb structure of graphene is due to sharing sp^2 electrons between carbon atoms. Each unit cell contains two carbon atoms, and the lattice constant for graphene crystal is 2.46 Å. The interatomic length of the covalent bonds between the carbon atoms is 1.42 Å. In multi-layer graphene, layers are interconnected with a weak van der Waals force [2]. Graphene is a semi-metal with zero bandgap. It exhibits the highest carrier mobility at room temperature due to the overlap between its conduction band and valence band at two points (K and K') in the Brillouin zone [3].

The mechanical properties of graphene are exceptional. The high strength, stiffness, and toughness of graphene make it ideal for various applications. The sp^2 bonds in the hexagonal lattice of graphene withstand deformations. The defect-free layer of graphene is known as the strongest discovered material with an intrinsic strength of

130 GPa. It is also stretchable up to 20% of its initial length [4]. Graphene is considered as an excellent heat conductor with thermal conductivity of ~ 4000 W/m.K. The specific heat of pristine graphene sheets at room temperature is 0.7 J/g.K, which is approximately 30% higher than that of the diamond. The specific heat can be manipulated by making interfaces between graphene and another material [5].

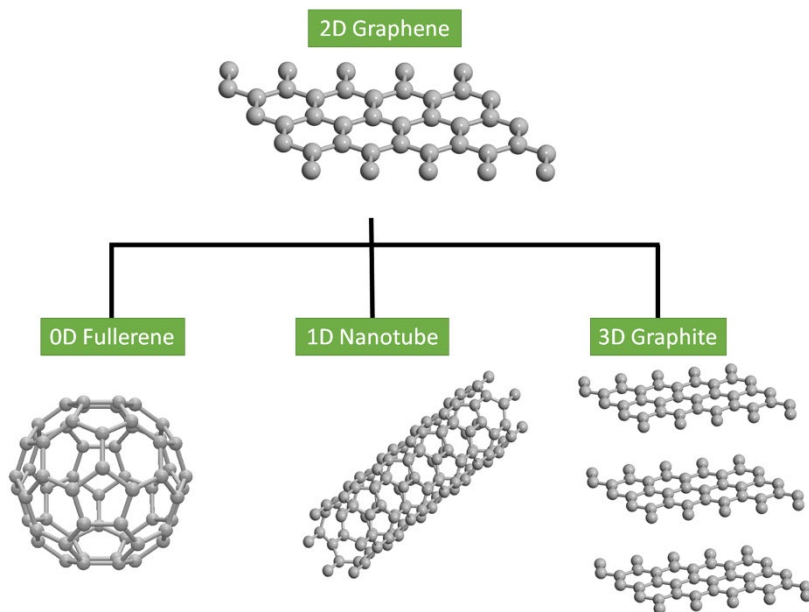


Figure 1-1. Demonstration of fullerene, carbon nanotube, and graphite as the derivation of graphene.

Graphene can be in the forms of single layer, bilayer, and multilayer. Based on the fabrication methods, different kinds of graphene can be achieved. The number of layers can change the properties of graphene. One of the main differences between

single-layer and multilayer graphene (MLG) is the band gap. The single-layer graphene has zero bandgap, while the electronic structure and the MLG bandgap can be tuned. Therefore, MLG can be used in a wide range of applications like optoelectronics [6]. Also, the thermal conductivity is different for MLG. In MLG structure, when the number of layers increases, each layer is confined by neighboring layers. This confinement and interaction with other layers reduces phonon transport. Hence, the thermal conductivity of multilayer graphene will be reduced compared to single-layer graphene [7].

1.2 Graphene Applications

The large surface area of graphene and its ability to transfer electrons or holes along its surface makes it ideal for electrode fabrication in energy storage devices, such as batteries, capacitors, and solar cells. Electrical conductivity combined with flexibility and high restorability enables applying graphene in electronic nano-devices, sensors, and wearable devices [8]. Besides, the ability to functionalize the surface of graphene expands its applications into biomedical engineering [9].

1.2.1 Field Effect transistors (FET)

Transistors are semiconductor devices that act as amplifiers or switches in circuits. Generally, there are source, drain, and gate as the terminals in transistors. By

applying current or voltage to one pair of terminals, the current through another pair can be manipulated. Transistors are usually embedded in integrated circuits, but some of them can be utilized individually. A field-effect transistor (FET), for instance, is one of the devices that can be modified and used to detect chemical and biological species. FET is a type of transistor device in which the conductivity can be controlled by applying an electric field [10].

The current path between source and drain electrodes is known as the channel, which can be made of N-type or P-type semiconductors. The flowing current in the channel is controlled by the gate voltage. Low noise, high off-state resistance, and an extensive safe operating range are advantages of FETs. Among all the materials for FET fabrication, graphene is a promising candidate due to its high carrier mobility. Several physical and chemical stimuli can be detected with graphene field-effect transistors (GFETs) [11].

One type of FET is the ion-sensitive field-effect transistor (ISFET) that can measure ion concentration in solutions. The typical use of ISFET is to measure H^+ or OH^- in solutions. Therefore, they are used as pH sensors [12]. In comparison to GFETs, in ISFETs, the top gate is replaced by a reference electrode, and the electrolyte is in contact with the sensing layer. An ion-sensitive material or membrane is used to adsorb H^+ or OH^- ions reversibly. This binding creates an electrical potential proportional to the logarithm of ion concentration, hence controls the surface

potential and current of ISFET. Graphene is one of the most promising candidates for pH sensors. In most works, graphene is used as the FET channel, and the ISFETs with graphene channels show very high sensitivity in the Dirac point voltage in the range of 6 mV/pH to 99 mV/pH [13].

1.3 Graphene Fabrication

Generally, there are two different approaches to fabricate graphene: bottom-up and top-down. In the top-down methods, single graphene sheets are the results of graphite layer separation. The van der Waals forces that hold the layers need to be overcome to separate the graphite layers and fabricate graphene. Although these bonding forces are weak, the separation process can be challenging. Exfoliating the sheets without damaging them, re-agglomeration of sheets after separation, numerous steps, and low yield are some of these challenges [14]. Unlike the top-down methods, in the bottom-up approaches, carbon molecules obtained from alternative sources are the building block. These methods are usually chemical-based, and the nanoscale structure can be controlled. A high temperature is needed to have a high level of graphitization and good material quality. The bottom-up methods are usually suitable for graphene nanoribbons and graphene flakes but not for graphene sheets with a large surface area [15].

There are various techniques to synthesize graphene, but the turning point in graphene history is mechanical exfoliation. In this top-down method, the scotch tape is used to peel off graphite or graphite oxide layers and produce graphene sheets. However, the uneven thickness of the obtained films and the high cost due to low yield in this process makes it impractical for mass production [16]. Although the mechanical exfoliation can synthesize single-layer and multilayer graphene, the obtained single-layer usually has a tiny surface area [17].

The most popular approach for synthesizing high-quality graphene with a large surface area is chemical vapor deposition (CVD). This bottom-up technique is based on carbon solubility in transition metals such as Ni, Pd, Ru, and Cu. The substrate is exposed to hydrocarbon gases at high temperatures and saturates with carbon. After cooling the substrate, the solubility of carbon decreases, and a thin film of graphene forms on the surface. Different parameters like temperature, gas flow, and pressure can control the growth process. Also, doping of graphene is possible with this method [18]. Both single-layer and multilayer graphene can be synthesized through the CVD method. Although CVD techniques are scalable, they are not cost-effective, and the by-products of the process are usually toxic. However, the main challenge in this technique is to transfer the synthesized graphene to another substrate.

Deposition methods are the best solution for transferring graphene to different substrates. Most of the deposition methods do not synthesize graphene on the substrate but pattern and improve it for a specific application. Graphite oxide or graphene oxide can be deposited on a substrate with these methods and reduced into graphene through different treatments afterward. Spin coating, supersonic spray, and dip coating are some of the straightforward and inexpensive options in this category [16]. Also, another promising technique to deposit graphene is printed electronics. Various patterns can be deposited on large-scale flexible substrates for different applications [19]. Although the initial efforts in printed electronics were toward displays and lighting, now it is promising for different industries such as automotive and transportation, consumer electronics, healthcare, packaging, aerospace, construction, and architecture [20]. Ink-jet printing, screen printing, gravure printing, and extrusion printing are examples of printed electronics techniques [19]. The thickness of graphene can be controlled easily with process parameters in these methods. The details of this process can be found in section 1.4.

Radiation-based techniques with different light sources such as UV, xenon flash, or laser are another example in the top-down category. The interaction of light with the graphite oxide leads to high-quality graphene in a short time. These methods are challenging for industrialization due to radiation concerns. Also, the cost efficiency is lower than batch chemical processes that produce graphene [16]. Recent studies introduced a new radiation-based technique on high-temperature

polymers that leads to graphene fabrication [21]. There is no need to transfer the fabricated graphene to another substrate. This technique can be extensively used to fabricate multilayer graphene. The details of this process can be found in section 1.5.

1.4 Ink-jet Printing

Printed electronics is a printing technology to fabricate various electronic devices, like electronic circuits, displays, sensors. In contrast to silicon technology, printed electronics is based on organic or printable inorganic conducting, semiconducting, and insulating materials. It is a low-cost method due to inexpensive equipment and materials. Also, the ability of on-demand printing makes the process rapid. This method is scalable and suitable for different sizes of devices. The whole process is digital and mostly ecofriendly, and the toxic waste is low. Finally, the fabricated devices with this method can be thin and lightweight [22]. The field of printed electronics is pervasive, including a large number of different materials and printing technologies. Printing can be done on various substrates such as glass, flexible polymers, and sometimes on metals. Several methods are the subcategory of printed electronics, such as screen printing, gravure printing, and ink-jet printing [23].

Ink-jet printing is one of the printed electronics methods that can directly pattern different functional materials on a substrate. This technique is based on the

jettability of fluids through a nozzle. By applying precise digital control of the jetting, the drops land on the substrate at the desired position and form different patterns and structures [24].

The ink-jet printing process falls into two different categories; continuous printing and drop-on-demand (DOD) printing. In continuous ink-jet, a constant flow of droplets is generated and continuously ejected toward the substrate. The ejected droplets will be positioned into different patterns with an applied electric field. The remaining droplets can be collected by a gutter and restored to the reservoir. In drop-on-demand ink-jet, jetting is on-demand, and droplets are formed when required. Two different actuation mechanisms are used to form droplets in DOD printers. In thermal DOD, the ink chamber is heated and vaporized. The evaporation causes a bubble to form, and droplets are generated. In piezoelectric DOD printers, a voltage pulse is applied to a piezoelectric transducer (PZT). Propagation of an acoustic wave in the ink channel due to PZT actuation leads to droplet ejection. The piezo DOD type is more common than thermal DOD for industrial and research use. The velocity and the volume of an ejected droplet from a piezo DOD print head can be controlled by varying the actuating voltage. Also, the waveform used for the droplet formation can affect the droplet's volume and velocity [25]. Figure 1-2 demonstrates an illustration of the DOD ink-jet printer.

The ink properties such as viscosity and surface tension can play a crucial role in the quality of printed patterns. In addition to ink properties, some of the process parameters such as nozzle size and voltage are also vital in ink-jet printing. The nozzle size affects the droplet size and final resolution of the printed feature. The size of droplets and velocity are also a function of applied voltage. As voltage increases, velocity and volume increase. However, droplet size is mainly determined by the nozzle diameter. It is recommended to use a smaller nozzle size to have smaller printed features [26].

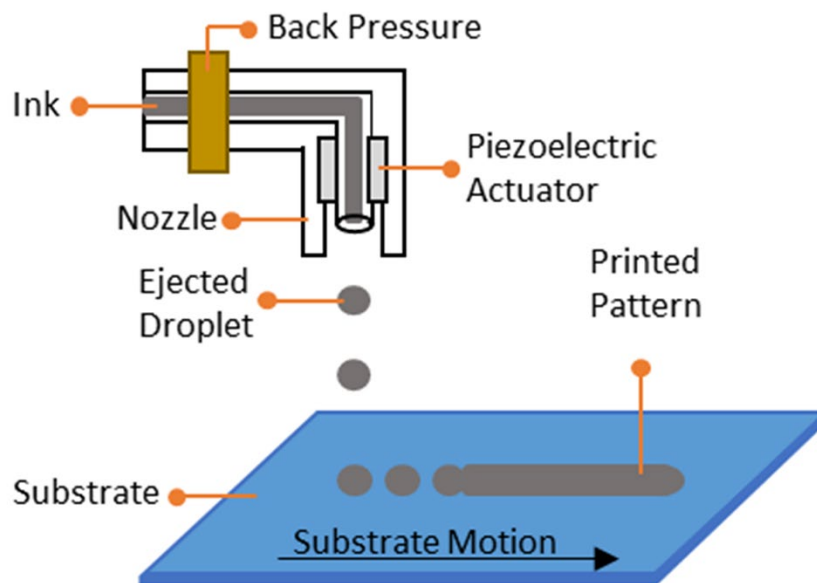


Figure 1-2. An illustration of DOD ink-jet printing procedure with a piezoelectric actuator.

1.5 Laser-induced Graphene

Laser-induced graphene (LIG) is one of the new techniques to fabricate graphene patterns on polymeric substrates. It is a one-step laser-based process that transforms a polymer to laser-induced graphene as a conductor. LIG can be generated on polyimide (PI), polyetherimide (PEI), Polyetheretherketone (PEEK), and other high-temperature polymers by applying a CO₂ laser. The laser beam scans the surface of polymers, and interaction between the laser and polymers leads to this transformation [21]. The whole process is straightforward and low-cost and allows customizing different patterns rapidly. Also, having graphene as a conductive material exploits all its exceptional properties. Moreover, the C-C bonds in the polymers absorb the CO₂ laser band centered at 10.6 μm easily, resulting in a high degree of graphitization. The ambient condition and lack of any chemical solvent make this process appealing to industries [27].

Different polymers have been studied to see their interaction with the laser beam, but only a few converted into LIG. The transformation in these polymers can be related to the aromatic segment of their molecule chains. Not only can polymers be converted through LIG, but also cloth, paper, and other lignin-containing carbon materials can take advantage of this technique [28]. Laser parameters play a significant role in the properties of obtained LIG. By optimizing the laser power and scanning rate, the conductivity and morphology of the graphene can be easily

adjusted for different applications. Also, defocusing the laser by altering the z-axis distance can change the quality of LIG. The LIG can be fabricated directly for various applications like microfluidics devices, sensors, micro-supercapacitors, and electrocatalysts [29].

1.6 Thesis Organization

In this thesis, a study of graphene-based sensing devices fabricated by low-cost methods is presented. Conductors are fabricated with the one-step LIG technique on 3D printed substrates. Ink-jet printing is used to print graphene oxide ink on a 3D printed substrate. The printed patterns are converted to reduced graphene oxide (rGO) through various approaches. Finally, by combining two complimentary microfabrication techniques, a novel type of graphene sensor for detecting pH is fabricated.

In chapter 2, a complete literature review on multiple topics is presented. This review includes laser-induced graphene (LIG), ink-jet printing of graphene oxide inks, and ion-sensitive field effect transistors based on graphene. The gaps and challenges in each topic are investigated.

In chapter 3, the conversion of 3D printed and commercial polyetherimide (PEI) to LIG is demonstrated. Different properties of the fabricated materials are

characterized. Different pattern designs are fabricated. A version of this chapter has been submitted as a journal paper: Tavakkoli Gilavan, M., Rahman, M. S., Khan, A. M., Nambi, S., Grau, G. "One-step fabrication of low resistance conductors on 3D printed structures by laser-induced graphene (LIG)".

In chapter 4, the ink-jet printing of graphene oxide ink on novel surfaces is demonstrated. The utilized substrates include polylactic acid (PLA), silicon, and silicon nitride wafers. Different methods of reduction are investigated to achieve the highest conductivity for graphene oxide.

In chapter 5, the design of a silicon chip containing junction field-effect transistors (JFET) with open gates is demonstrated. The JFET is used as the sensor platform, and graphene oxide ink is ink-jet printed onto the open gate of the transistor. The reduced graphene oxide acts as a sensor transducer to detect different pH.

In chapter 6, the main results of this study are summarized, and suggestions for future work are presented.

CHAPTER 2. LITERATURE REVIEW

2.1 Integration of Electronics with 3D Printing

Recently, the integration of electronics into 3D printed structures has been studied extensively. One method to fabricate a conductive 3D printed structure is to use carbon-based filaments. Multiple different carbon-based filaments have been explored for this application [30], [31]. The combination of carbon nanotubes and thermoplastic polyurethane (CNT/TPU) is one of the most well-studied conductive 3D printing filaments. In one report, CNT/TPU filament was used to fabricate multiaxial force sensors, and the average conductivity of the filament was 7 S/m [32]. In another study, an extruded filament of CNT/TPU nanocomposite was created for fused deposition modeling (FDM) 3D printing. By loading 5 wt.% of CNT, the achieved conductivity was less than 10 S/m [33]. By using polybutylene terephthalate (PBT) with CNT, the obtained conductivity of the filament was around 20 S/m [31]. Also, graphene can be one of the promising candidates to fabricate 3D printed conductors. In one study, graphene/PBT filament was used to fabricate nanocomposites. The results showed a conductivity of 3 S/m for this filament[31]. In another report, the electrical conductivity of acrylonitrile-butadiene-styrene (ABS) and graphene blend was investigated. By using different methods for blending, the best result for electrical conductivity was 7.29 S/m [34]. Further studies showed highly conductive graphene/poly-lactic acid (PLA) filament

for flexible circuit fabrication with a conductivity of 476 S/m [35]. Although this filament is highly conductive, the fabrication of graphene and the filament itself is a complex process that leads to high cost [36].

2.2 Laser-Induced Graphene

Laser-induced graphene is another choice to fabricate conductors for electronics. Although LIG is relatively new, there are several studies based on this technique. One of the first works in this area was the preparation of porous graphene from a commercial PI sheet (Figure 2-1). The CO₂ laser radiation made the LIG structure suitable for energy storage devices with outstanding electrochemical performance. Based on the theoretical modeling in this work, the enhanced capacitance is due to the defect-rich boundaries in LIG. The lowest sheet resistance was 15 Ω /sq, achieved at 5.4 W laser power [21]. In another work, the fabrication of flexible and stackable supercapacitors was studied in detail. The PI sheets were first scanned with a CO₂ laser and converted to LIG, and then single or stacked supercapacitors were assembled. Poly(vinyl alcohol) (PVA) solution in H₂SO₄ was used as the solid-state polymeric electrolyte for supercapacitors. The large areal capacitance for the fabricated device (larger than 9 mF/cm²), along with the flexibility of PI, made it ideal for the next generation portable microelectronics [37].

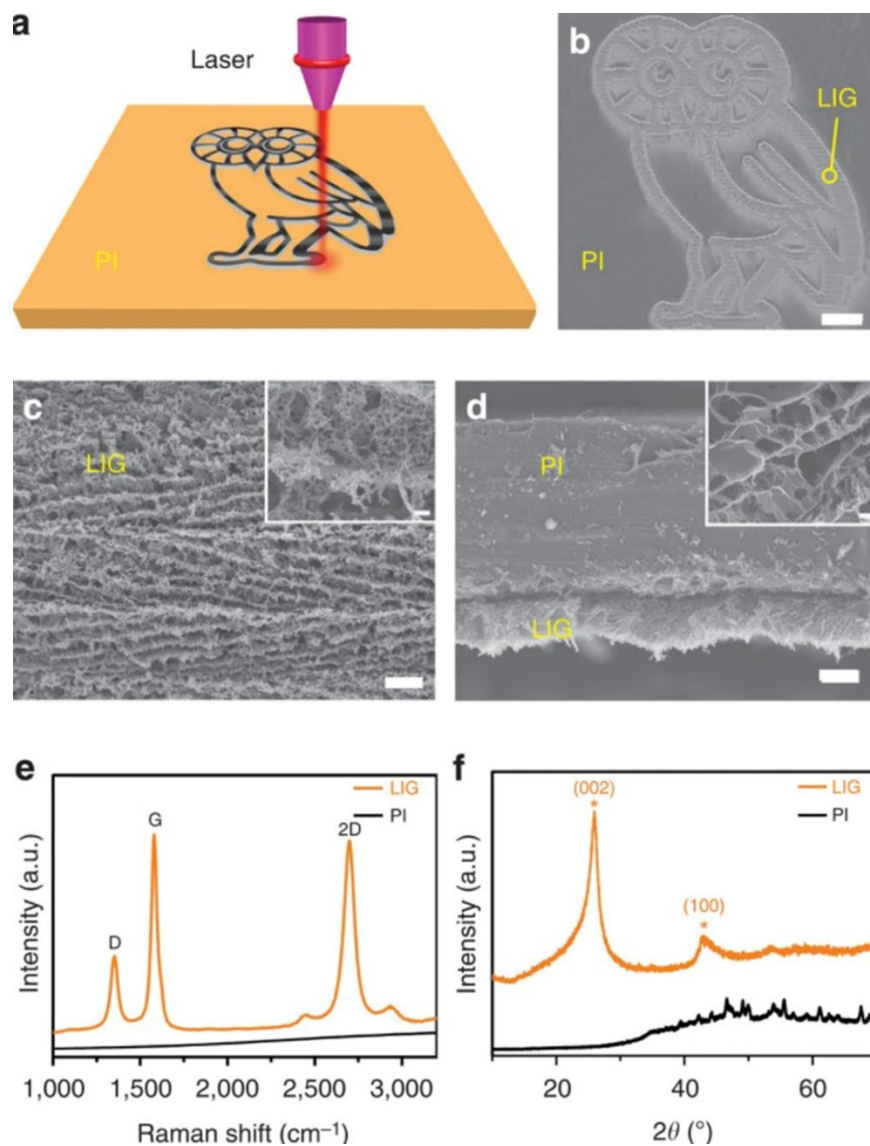


Figure 2-1. a) Schematic of LIG process on PI. b) SEM image of LIG patterned into an owl shape. The scale bar is 1 mm. c) SEM image of the LIG film circled in (b). The scale bar is 10 μm . d) Cross-sectional of the LIG film on the PI substrate. The scale bar is 20 μm . The inset shows the porous morphology of LIG. e) Raman spectrum of a LIG film and the starting PI film. f) XRD of powdered LIG scraped from the PI film. Reproduced with permission [21]. Copyright 2014, Nature Publishing Group, Macmillan Publishers Limited.

The scope of LIG research is not limited to PI as the precursor. Natural resources like wood are another option. The lignocellulosic structure in wood with high lignin content can turn into high-quality graphene with the LIG technique. The conductive patterns on the wood showed sheet resistance of around 10 Ω/sq . The low achieved sheet resistance on the wood was used as electrodes for water splitting to evolve hydrogen and oxygen [38]. In another study, ULTEM PEI was treated with the CO_2 laser beam, but the performance was poor compared to PI. The laser defocus level was varied from 0 at the focal plane to 2 mm to improve the results. The lowest sheet resistance was 15 Ω/sq , and it was achieved at 0.75 mm defocus level [28]. All of the studies mentioned above used flat substrates to prepare the LIG. There are only a few studies that integrated additive manufacturing with LIG. A copolymer blend of PEI and polycarbonate (PC) (Ultem 9085) was used as the 3D printed substrate in one of the studies. The conductive layer was fabricated by CO_2 laser direct scanning in ambient air. The lowest obtained sheet resistance was 15.9 Ω/sq [39]. In the most recent work, 3D printed PEEK was used as the precursor. The optimum laser power was 7.5 W at a scan rate of 100 mm/s, and multiple lasing was used to improve LIG quality. The sheet resistance was not reported in this study. However, the sheet resistance of engraved patterns can be calculated based on the represented information, and it was around 5.4 Ω/sq . The fabricated LIG presented high sensitivity to bending and stretching [27].

2.3 Ink-jet Printing of Graphene and Graphene Oxide on Novel Surfaces

Graphene and graphene oxide (GO) inks have been used widely for ink-jet printing. Electronic grade papers are one of the substrate options for ink-jet printing. Different graphene inks have been formulated for paper substrates. In one work, two types of graphene inks have been demonstrated, and their printing behaviors on the paper substrates have been studied. The ink-jet printed graphene on paper was simple and cost-effective and suitable for conductive films' mass production [40]. In another study, 2D graphene strain gauges were ink-jet printed on PEL P60 paper, and the obtained gauge factor was close to 150. Fabrication of graphene strain sensors on paper obtained sensitive, low-cost, flexible devices, and ink-jet printing allowed large-area fabrication [41].

The most conventional substrates for ink-jet printing graphene and GO inks are flexible plastics. Poly(ethylene terephthalate) (PET) is one of the common substrates for ink-jet printing graphene inks. In one study, ink-jet printed graphene thin film was fabricated for thermoelectric applications. The ink was made from exfoliated graphite, and it was dispersed in isopropyl alcohol (IPA) with polyvinylpyrrolidone (PVP). The fabricated graphene film showed a high thermoelectric power factor at room temperature. The fabricated graphene film on the transparent and flexible PET substrate can be used as a wearable device to harvest energy from body heat [42]. In one study, the graphene transparent

conductive films (TCFs) on PET substrate were compared with indium tin oxide (ITO) based TCFs. The ink was made of commercial graphene powder dispersed in ethylene glycol and ethyl cellulose as a polymeric stabilizer. Although the achieved sheet resistance for graphene TCFs was higher than ITO-based TCFs, the flexibility and stability of printed graphene allow its application in flexible optoelectronic devices [43].

In another study, pristine graphene has been used to fabricate flexible electrodes on PET, polyimide (PI), regular printing paper, and glass slides (Figure 2-2). The ink was made of graphene flakes, and conductive patterns were printed using a piezoelectric Dimatix material printer. The change in electrical resistivity of printed electrodes after 1000 bending cycles was insignificant, and the prepared graphene ink showed great potential for fabricating flexible electronic devices [44]. Different graphene-based ink has been developed to print on flexible boards like polyimide (PI) films. The ink was made from graphite nanosheets and sodium n-dodecyl sulphate (SDS), and the pH was adjusted by ammonia to improve the ink's stability. Using PI substrates allowed the high-temperature heat treatment to improve printed graphene patterns' conductivity [45].

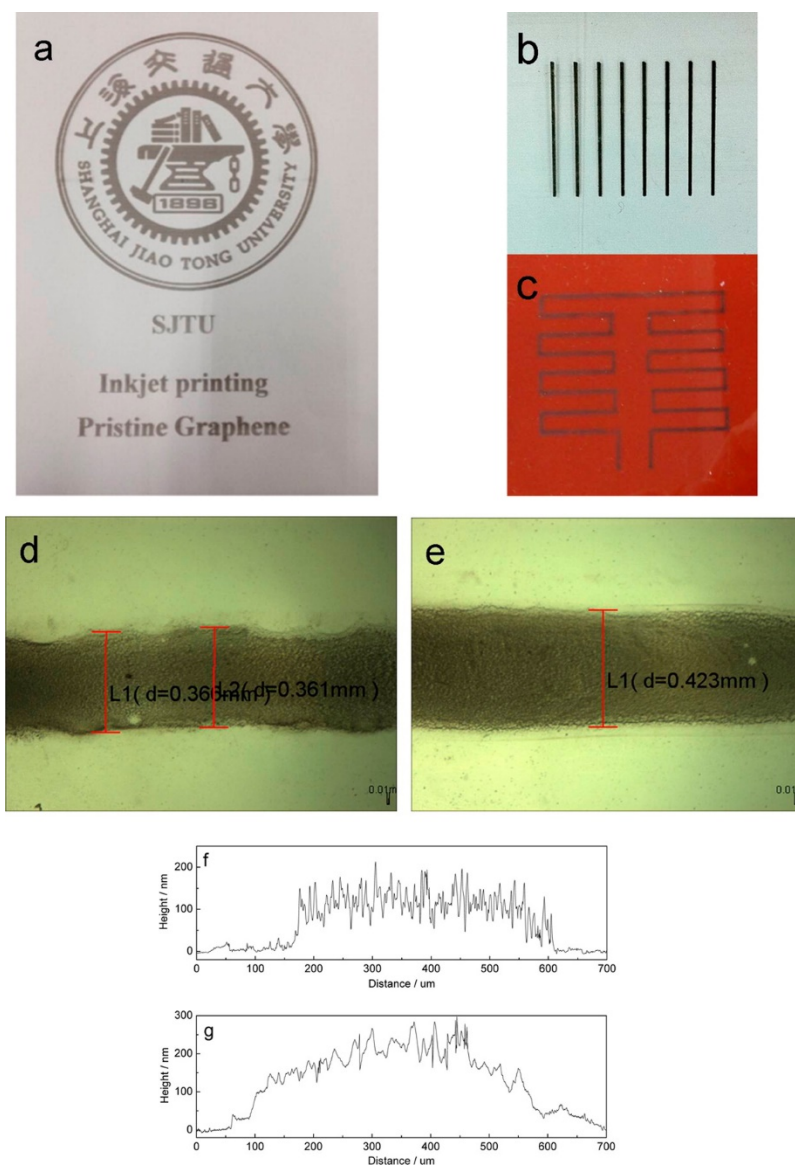


Figure 2-2. Inkjet-printed graphene patterns on a) normal paper, b) PET, c) PI, and d,e) glass slides at 30 and 40 printing passes, respectively. f,g) Profilometry scan of printed electrodes in panels d and e, respectively. Reproduced with permission [44]. Copyright © 2014, American Chemical Society.

Although there are numerous studies on ink-jet printing graphene on polymeric substrates, printing on 3D printed substrates has not been studied extensively. The only used 3D printed substrate for printing graphene ink is ceramic-based. However, the 3D substrate is not fabricated with the most commonly used fused filament fabrication (FFF) method. Figure 2-3 demonstrates the fabrication process of the ceramic substrate and GO patterns. A thermal-bubble inkjet was used to print the 3D alumina substrates and GO patterns. The combination of alumina and graphene gave good thermal conductivity, chemical stability, high strength, and electrical conductivity. The fabricated device can be used for pressure sensors [46].

The integration of 3D printed polymeric substrates and ink-jet printed graphene-based patterns can open up many applications to flexible wearable devices. Various geometries and structures can be used as 3D printed substrates, and conductive patterns can be applied with ink-jet printing onto them.

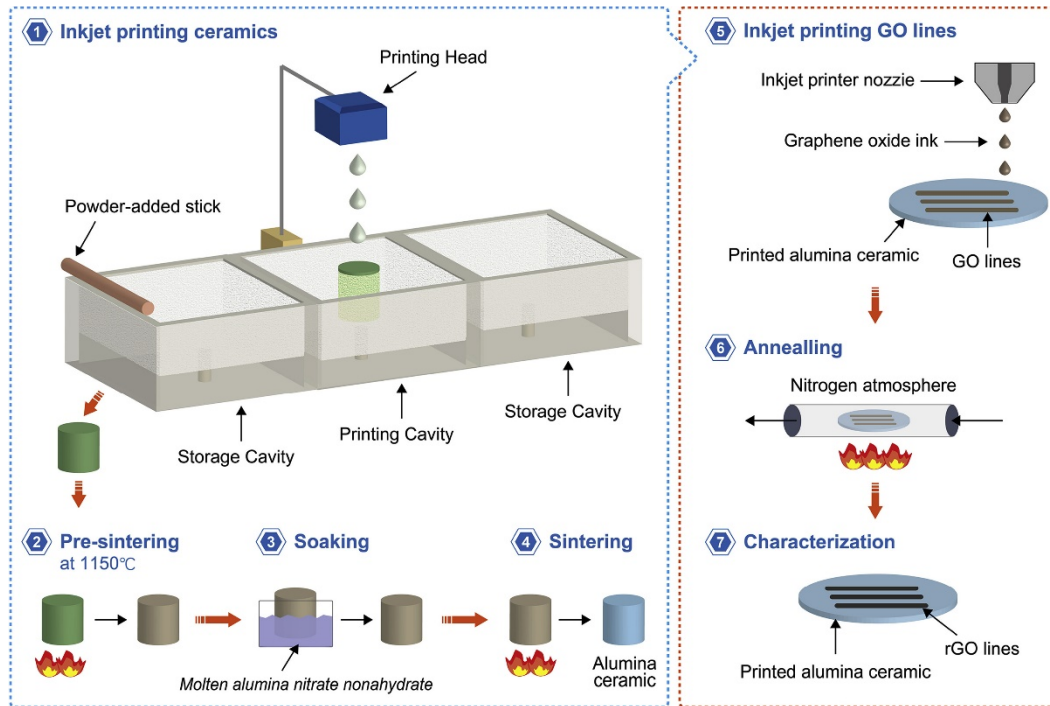


Figure 2-3. The schematic diagram of 3D printing the ceramic substrate with an ink-jet printer and ink-jet printing of GO lines on the 3D printed ceramic substrate. Reproduced with permission [46]. © 2020 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Printing on Si wafers is not as conventional as printing on plastic substrates. Few studies have been reported on printing graphene or GO inks on Si/SiO₂ wafers to fabricate different devices. In one work, the graphene powder was fabricated with liquid-phase exfoliation, and the ink was formulated for ink-jet printing. The surface-treated silicon was used as the substrate, and graphene ink was printed on it as a transistor channel. The combination of Si wafer and graphene as the channel showed high mobility [47]. In some cases, the printed graphene on silicon was used

as microsupercapacitors. About 100 devices were printed and connected on the Si wafer to form a power bank. The fabricated supercapacitors showed high areal capacitance and were reliable for up to eight months [48].

In one study, the graphene ink was made by exfoliated graphite in ethanol, and ethyl cellulose was used as the polymeric stabilizer. Properties of the ink were optimized for printing, and a silicon substrate (Si/SiO₂) with thermally grown oxide was used to study the wetting behavior. After measuring the thickness and resistance of printed patterns on Si/SiO₂, the formulated ink was printed on PI substrate to test as a flexible conductor [49]. In most works, printing on Si/SiO₂ substrate is to probe the electrical properties or characterize the printed graphene. Optimizing the printing process on Si wafers needs more investigation.

2.4 Graphene-based Ion-Sensitive Field Effect Transistors

Graphene-based FETs have been used to detect various ions, like Cu²⁺ [50], K⁺ [51], NO₃⁻ [52], and Hg²⁺ [53]. Also, pH detection with graphene-based transistors is widespread. In one study, mechanically-exfoliated graphene was used in high-quality solution-gate FETs for pH detection. Graphene was used as the channel on a doped silicon substrate. The Au/Ti source and drain were fabricated by conventional e-beam lithography, metal deposition, and a lift-off method. The results showed changes in conductance by varying the pH value. By increasing the

pH, the Dirac points of the graphene device shifted to the positive side, and the pH value could be detected by the device [54]. In another study, solution-gate rGO FET was fabricated with rGO film as the active channel for pH sensing. Due to the presence of functional groups on the rGO channel, the sensing mechanism of H^+ ions could be explained by the site-binding theory [55]. The effect of defects and grain boundaries of graphene on its sensing ability was studied in another work. Lithography was utilized to fabricate transistors with single-crystal and polycrystal graphene channels on a Si/SiO₂ substrate. The results showed that grain boundary density and functional groups on the silicon surface can change the pH sensitivity of the device [56]. In another study, the graphene-based pH sensor was fabricated on a Si/SiO₂ wafer and flexible PI. The fabricated device was used to measure the pH of seawater. The real-time pH detection results were stable, and the sensitivity was high [57].

Although there are numerous studies on graphene-based FET, few utilized ink-jet printing to fabricate the graphene layer. The printed graphene was used as the transistor channel in one work, and surface-treated silicon was used as the FET substrate. The combination of Si wafer and graphene as the channel showed high mobility [47]. In another study, graphene was printed on Si/SiO₂ wafer as the bottom-gate, source, and drain of FET. Hexagonal boron nitride was used as the dielectric, and molybdenum disulfide (MoS₂) combined with fluorine polymer as the semiconductor. The fabricated FET showed good performance and potential for

biosensing [58]. However, none of these devices are used for pH detection. Also, in all FET devices, graphene is used as the channel material and not the gate. The integration of silicon FET with ink-jet printed graphene as the top-gate for the pH sensing application needs to be studied.

CHAPTER 3. LASER-INDUCED GRAPHENE

3.1 Introduction

3D printing is a promising technology for additive manufacturing. Complex designs can be turned into solid parts layer by layer and can easily be customized [59]. 3D printing has been employed in various industries such as aerospace, construction [60], or medical devices [61]. The integration of electronics into 3D printed structures would enable smart objects to be printed with additional functionality such as sensing, actuation, or energy storage [62]. Multiple carbon-based filaments have been explored for this application, and graphene is a promising candidate for fabricating 3D printed conductors. Graphene is exceptional due to its superior strength [63], high electrical conductivity [64], and high thermal conductivity [65]. Besides, the large surface area and piezo-resistivity of graphene make it ideal for sensing applications [31].

Recently, a simple one-step laser-based process has been developed to fabricate conductors that transform a polymer substrate into laser-induced Graphene (LIG) [21]. LIG can be generated on polyimide (PI), polyetherimide (PEI), polyether ether ketone (PEEK), and other high-temperature polymers by applying a CO₂ laser [28]. The graphene is easily patterned by scanning the laser beam. The conductivity and morphology of graphene can be easily tuned for various applications by optimizing the laser conditions.

This study demonstrates laser-induced graphene on 3D printed PEI with 50 times lower sheet resistance compared to literature. Unlike literature, low resistance is obtained from a single lasing without needing to defocus the laser beam on the polymer. These results open up many applications to fabricate smart objects. Products can be 3D printed with conductive LIG directly integrated into or onto the structure. PEI is particularly promising because it is an engineering plastic with superior mechanical properties. Additionally, 3D printed substrates have different densities, porosity, and crystallinity compared to commercial sheets, which can affect the LIG process and the conductivity and morphology of the generated graphene. Figure 3-1 illustrates the integration of LIG into 3D printing.

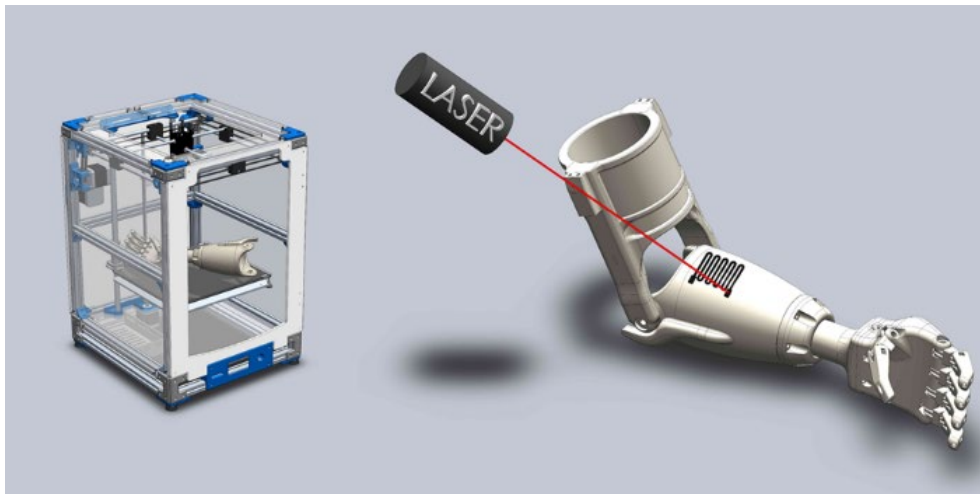


Figure 3-1. Schematic illustration of 3D printing the substrate and the laser process. The conductive patterns for different applications can directly integrate into the smart objects.

3.2 Experimental

The 3D printed substrates were designed using CAD software (Solidworks). Polyetherimide (ULTEM 1010) was used as the starting filament and 3D printed by fused deposition modeling (FDM) using a Stratasys Fortus 450mc printer. A CO₂ laser cutter (VersaLASER System (VLS2.30)) with a 10.6 μm wavelength was used for engraving the 3D printed substrates. The maximum laser power was 30 W, and the average power was varied by pulse width modulation. The spacing between pulses was 1000 dots per inch, and the laser spot size was 76 μm . The optimum laser scan rate was 2.54 cm/s in all the experiments. The effect of pattern size was studied with lines that were one, two, or three pulses wide as well as rectangles that were 100 pulses wide. Figure 3-2 shows the illustration of the laser process. For further study of the laser interaction with the polymer, two different laser modes were used for engraving strain gauges.

The 3D printed substrate was compared to a commercial PEI sheet (ULT-0090-E) with the same thickness as the 3D printed substrate. The laser process was the same as for the 3D printed substrates using the rectangle pattern.

The sheet resistance was measured using a four-point configuration for rectangle patterns using a four-point probe resistivity measurement system (Signatone Pro4) and for line patterns using a probe station with a semiconductor parameter analyzer (Keithley 4200A). Raman spectra were obtained with a Horiba Scientific (Model:

LabRAM ARAMIS) Raman Microscope using 532 nm laser excitation with a laser power of 50 mW. To prepare samples for thickness measurement, they were coated with epoxy resin and then cured in room temperature for 24 hours. The thickness of graphene layers was measured by optical microscopy. A field emission scanning electron microscope (FE-SEM) (Thermofisher Quanta 3D) was used to observe the morphology of engraved patterns. X-ray photoelectron spectroscopy (XPS) was performed using a K-alpha X-ray photoelectron spectrometer system. All of the survey spectra were recorded in 1 eV step size with a pass energy of 200 eV. Elemental spectra were recorded in 0.1 eV step sizes with a pass energy of 25 eV. Thermogravimetric analysis (TGA) (TGA55, TA Instruments) was carried out between 100 and 800°C at 10°C/min under air. A differential scanning calorimeter (DSC) (DSC250, TA Instruments) was used for the DSC analyses between 100 and 400°C at 10°C/min under air.

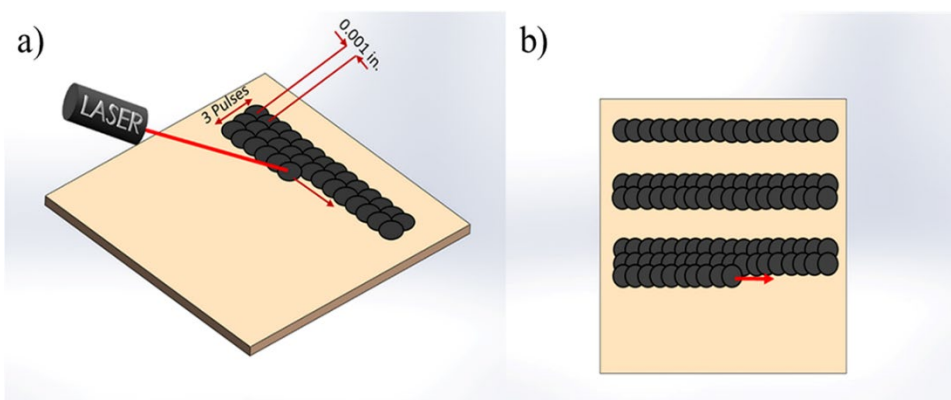


Figure 3-2. Schematic illustration of a) laser process and b) one, two, and three pulses wide lines on PEI substrate.

3.3 Effect of Different Parameters on Sheet Resistance

Three different parameters and their effect on sheet resistance are studied in this work: 1) laser scanning rate, 2) different patterns, and 3) polymer effect. To see the effect of scanning rate on sheet resistance of laser-induced graphene, different speeds are applied. A specific range for power is chosen, and the speed is varied from 1.2 to 5 cm/s. Figure 3-3 (a) shows sheet resistance for rectangles engraved with different power and speed. Most of the samples follow the same trend, and increasing the laser power and decreasing the scanning speed leads to lower sheet resistance. By using 1.2 cm/s as the scanning speed, the polymer mostly burns instead of engraving. Based on the results, the optimum speed for engraving graphene is 2.5 cm/s. For a better comparison between different parameters, energy per unit area (E_A) for rectangle patterns is calculated here, based on the following equation [66]:

$$E_A = \frac{xP}{v} N \quad (\text{Eq. 3-1})$$

In this equation, x is percentage power, v is scanning speed, P is maximum laser power, and N is DPI in SI units. Figure 3-3 (b) shows the calculated energy per unit area for different scanning speeds. With increasing the energy per unit area, the transformation to graphene is better, and the sheet resistance is decreasing. When scanning speed is 2.5 cm/s, 827.4 J/cm² gives the lowest sheet resistance, which is 1.17 Ω/sq .

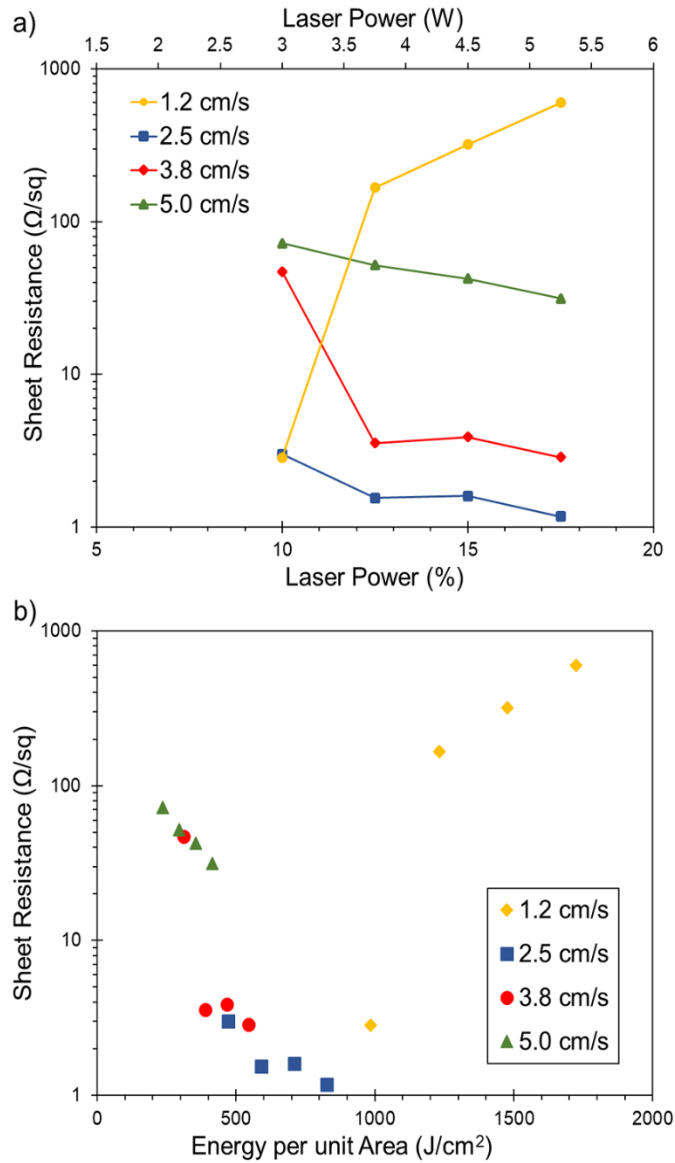


Figure 3-3. a) Effect of scanning speed on sheet resistance and b) energy per unit area for different scanning speeds. With increasing laser power, the sheet resistance decreases for lower speeds, except for 1.2 cm/s. In this case, the polymer burns instead of engraving.

To study the pattern effect, lines with different width (1, 2, 3 pulses) and rectangle patterns are engraved on the 3D printed substrate. Figure 3-4 (a) shows sheet

resistance for different patterns engraved with different power. By increasing laser power, the sheet resistance for all the patterns initially decreases. In the case of one pulse wide line, by increasing power to 90%, the lowest obtained sheet resistance is 6.39 Ω/sq . The lowest sheet resistance for two pulse wide lines is 2.56 Ω/sq . When the laser power is increased to more than 70%, the materials start to degrade and ablate. Three pulses wide lines exhibit a sheet resistance of 1.92 Ω/sq at 40% power, which is three times better than the lowest sheet resistance for one pulse wide line. When the laser power is increased to more than 40%, the materials start to degrade and ablate. Sheet resistance and the optimum power both decrease as the width of lines increases. The limiting case with a large width is a rectangle. As multiple lines are engraved, the thermal field of each line affects the adjacent lines, which improves the transformation to graphene. Therefore, the lowest obtained sheet resistance is 0.3 Ω/sq in a rectangle pattern.

Figure 3-4 (b) shows the energy per unit area for different patterns. The energy per unit area for lines (E_{AL}) is calculated with Eq. 3-2 [67]:

$$E_{AL} = \frac{xPn}{v} / (w + \frac{n-1}{N}) \quad (\text{Eq. 3-2})$$

Where x is laser percentage, P is maximum laser power, v is scanning speed, N is DPI in SI units, n is the number of passes, and w is the width of the laser beam. To obtain 0.3 Ω/sq in a rectangle pattern, 1850 J/cm^2 is needed.

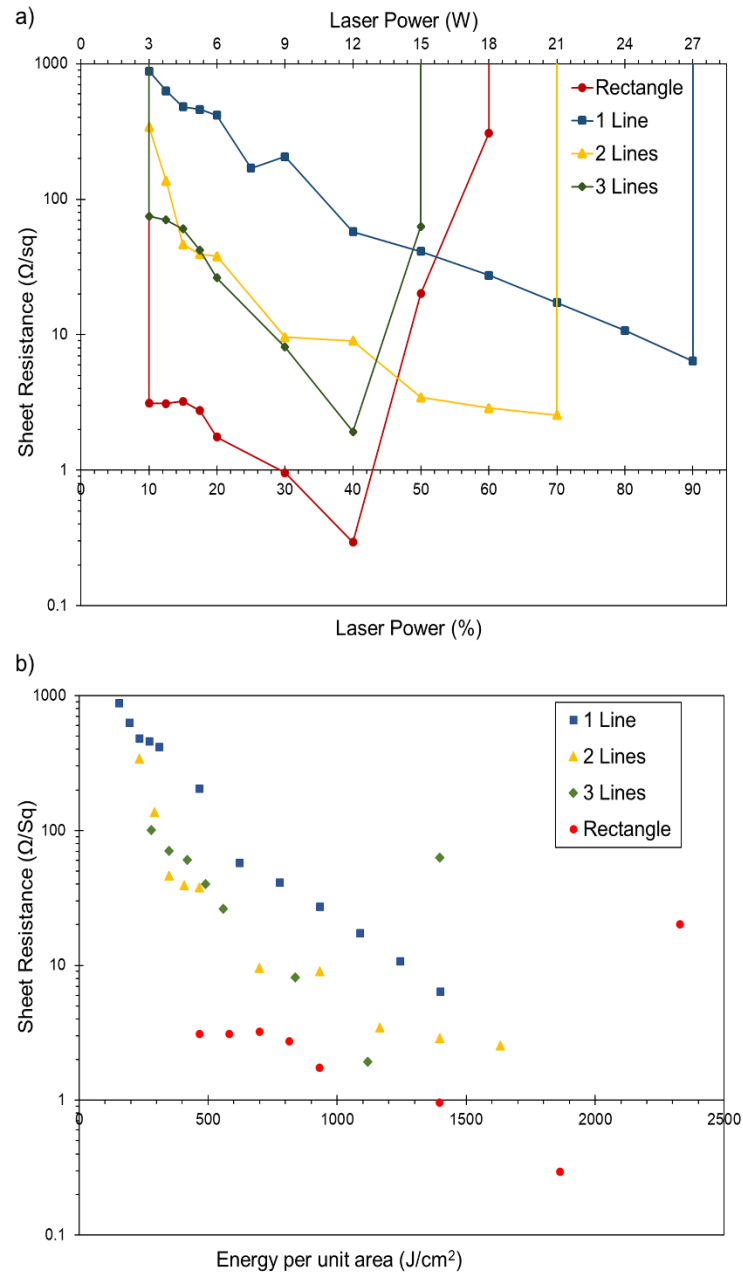


Figure 3-4. a) Pattern effect on sheet resistance, and b) calculated energy per unit area for different patterns. Sheet resistance decreases with increasing pattern width. It also decreases with increasing power until the material is ablated, and conductivity is lost (no data points on the graph for large powers).

The LIG patterns on the 3D printed substrate are compared to the patterns on a commercial PEI sheet with the same thickness as the 3D printed sample to see the polymer effect. As shown in Figure 3-5, the sheet resistance decreases for both polymers with increasing laser power up to 40%. By increasing the laser power to more than 40%, the polymers start to degrade. Although the decreasing trend in sheet resistance is similar for both polymers, the 3D printed substrate shows lower sheet resistance for the same laser power. The optimum power is 40% for both 3D printed and commercial substrates. With the optimum power, the sheet resistance for the engraved pattern on the 3D printed substrate is 0.3 Ω/sq and for the commercial sample is 1.79 Ω/sq . The sheet resistance for the 3D printed substrate is 6 times lower than the commercial sample, which demonstrates the advantage of using 3D printed PEI.

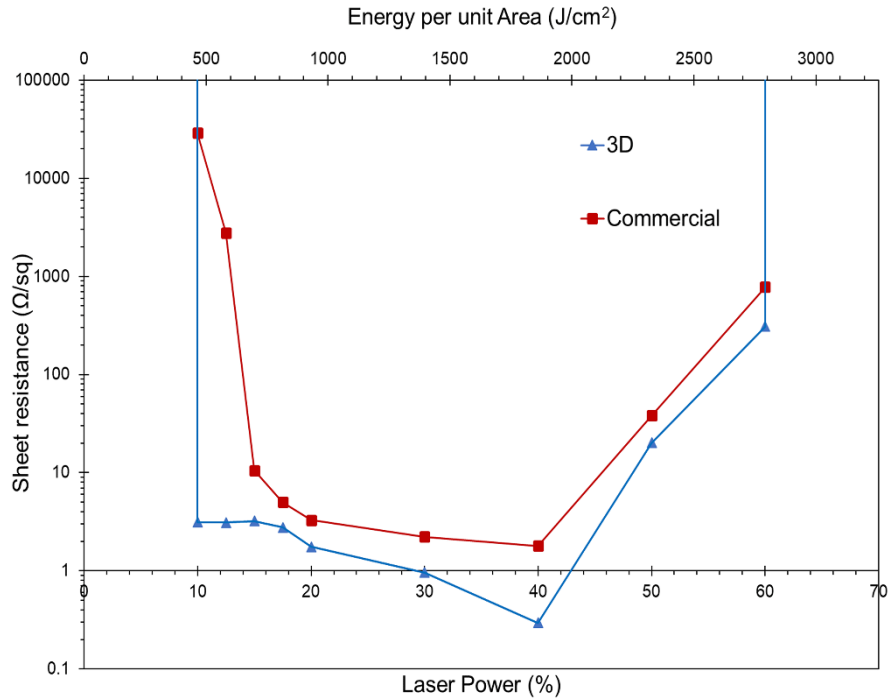


Figure 3-5. The effect of polymer on sheet resistance. The lowest sheet resistance is obtained at 40% laser power for the rectangle pattern on the 3D printed substrate.

3.4 Material Characterization

3.4.1 Resistivity and Thickness

Figure 3-6 shows optical micrographs of the cross-section of three pulse wide lines with different laser powers on 3D printed and commercial samples. As shown in Figure 3-6 (a) and (b), at 10% power, the transformation only happens at the surface of the substrates. By increasing the power to 20%, the heat starts to diffuse inside

the substrate, and the graphene layer becomes thicker (Figure 3-6 (c) and (d)). At 40% power, the largest thickness is achieved (Figure 3-6 (g) and (h)). Engraved line width also increases with increasing laser power. The width of engraved lines on 3D printed PEI is wider compared to commercial samples. By comparing the 3D printed and commercial samples at each laser power, we can see the engraved lines are about 20% to 45% wider for 3D printed than commercial samples.

The resistivity can be calculated based on Eq. 3-3 [68]:

$$\rho = R_{sh} \cdot t \quad (\text{Eq. 3-3})$$

Where ρ is resistivity (in $\Omega \cdot \text{m}$), R_{sh} is sheet resistance (in Ω/sq), and t is the thickness (in m).

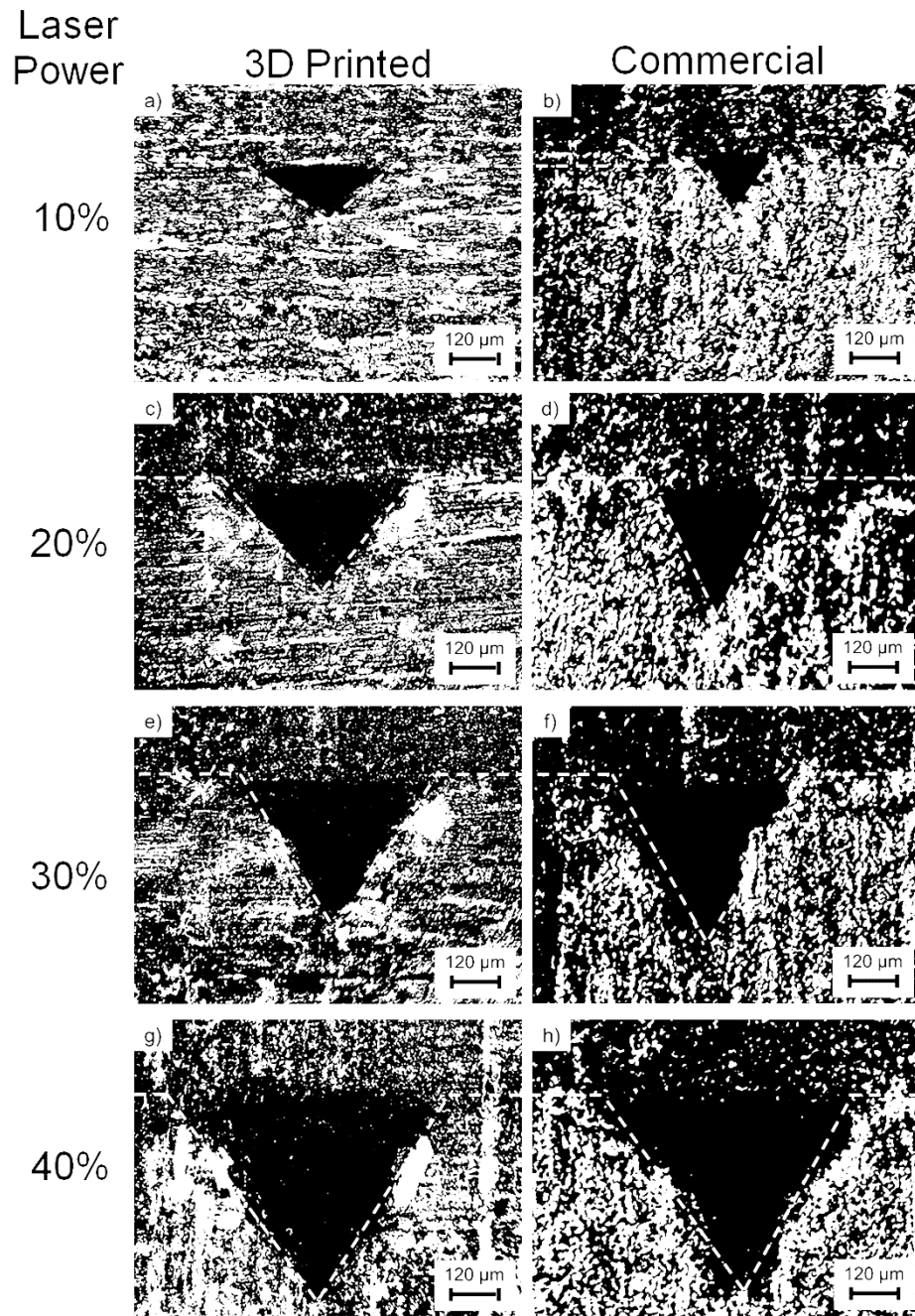


Figure 3-6. Cross-sectional optical micrographs of three pulse wide lines on 3D printed and commercial substrates for a,b) 10%, c,d) 20%, e,f) 30%, g,h) 40% laser power, respectively. Line width and depth increase with increasing laser power. The increase in the line width is clearer in 3D printed sample compared to commercial samples.

Figure 3-7 shows the correlation of resistivity and thickness with laser power for 3D printed and commercial samples. The thickness of commercial samples is higher than the 3D printed samples for all laser power except 10 and 40%. Therefore, based on Eq. 3-3, the resistivity is lower for 3D printed samples. Although the thickness is higher for 3D printed samples at 40% power, it has lower resistivity compared to the commercial samples. We can conclude that increasing laser power not only increases the graphene thickness but also improves material quality, thereby decreasing resistivity. Large thickness and low resistivity combined result in low sheet resistance.

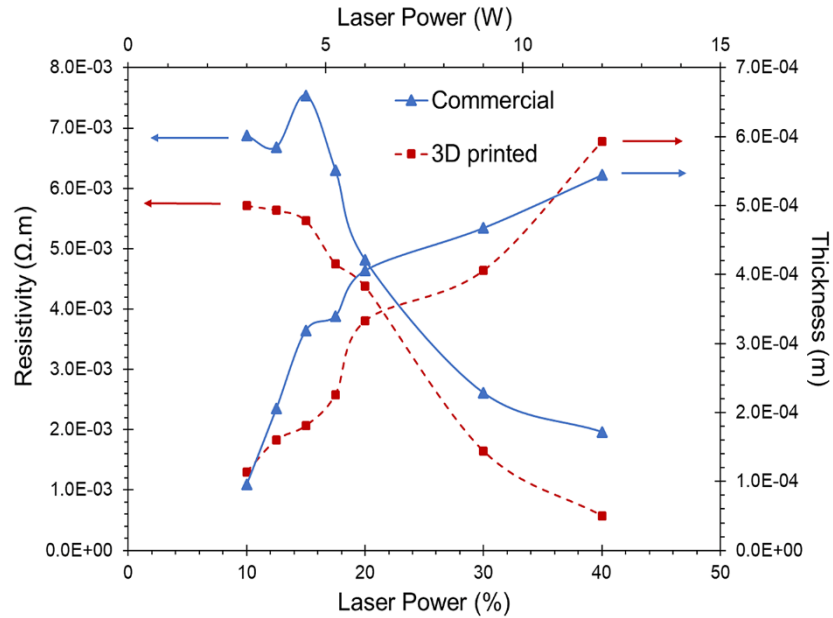


Figure 3-7. Resistivity and thickness as a function of laser power for three pulse wide lines in 3D printed and commercial samples. The increase in thickness and decrease in resistivity with increasing power combine to achieve a low sheet resistance.

3.4.2 Raman Spectroscopy

The material quality is studied with Raman spectroscopy. Figure 3-8 (a) shows the Raman spectra for rectangle pattern samples with different laser powers on 3D printed substrates. All samples indicate D and G bands at 1300 cm^{-1} and 1550 cm^{-1} , respectively. However, for 10%, 20%, and 30% samples, the intensity of the peaks is not very high. Also, the D and G bands are connected representing high-temperature annealed nano graphite [69]. At 40% power, a 2D peak appears at 2700 cm^{-1} , signifying graphenic carbon presence [28]. The low intensity of the D peak around 1350 cm^{-1} is due to low defect density in this sample, and the presence of the G peak at 1575 cm^{-1} indicates the formation of multi-layer graphene [70].

Raman spectroscopy results for commercial samples are demonstrated in Figure 3-8 (b). For all the samples, G and D bands appear at around 1300 cm^{-1} and 1550 cm^{-1} . Same as 3D printed samples, the D and G bands are not separated and form an interconnected peak that represents high-temperature annealed nano graphite. The 2D peak in commercial samples is just a broad peak, and it is not as detectable as the 2D peak in 40% power on the 3D printed substrate.

The quality of LIG varies with position relative to the laser pulse and some areas with 40% power exhibit very high quality graphene. Figure 3-9 shows Raman spectrum for 40% laser power on 3D printed sample. The spectrum is obtained from a different position on the sample and it shows sharp 2D peak at 2690 cm^{-1} .

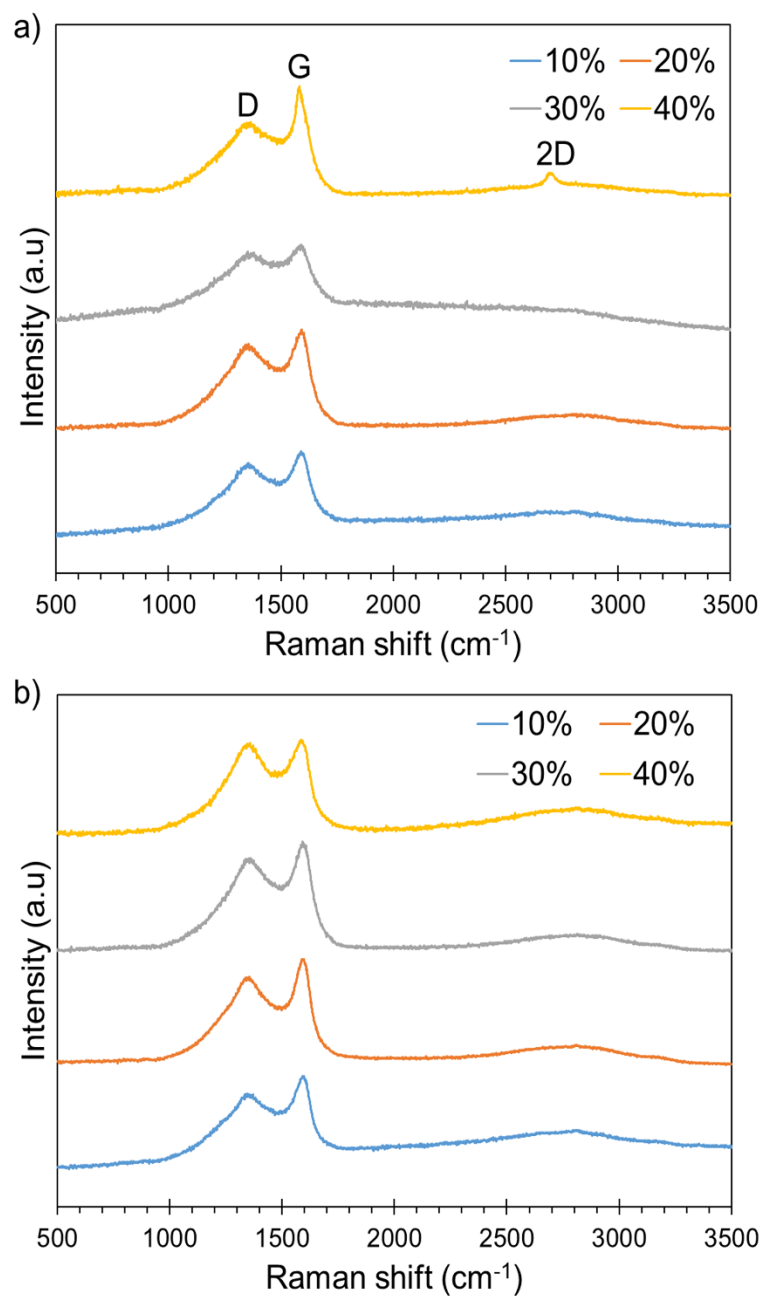


Figure 3-8. Raman spectra for rectangle patterns with different laser powers on a) 3D printed PEI and b) commercial PEI. Clear multi-layer graphene peaks can be observed at 40% power for the 3D printed PEI.

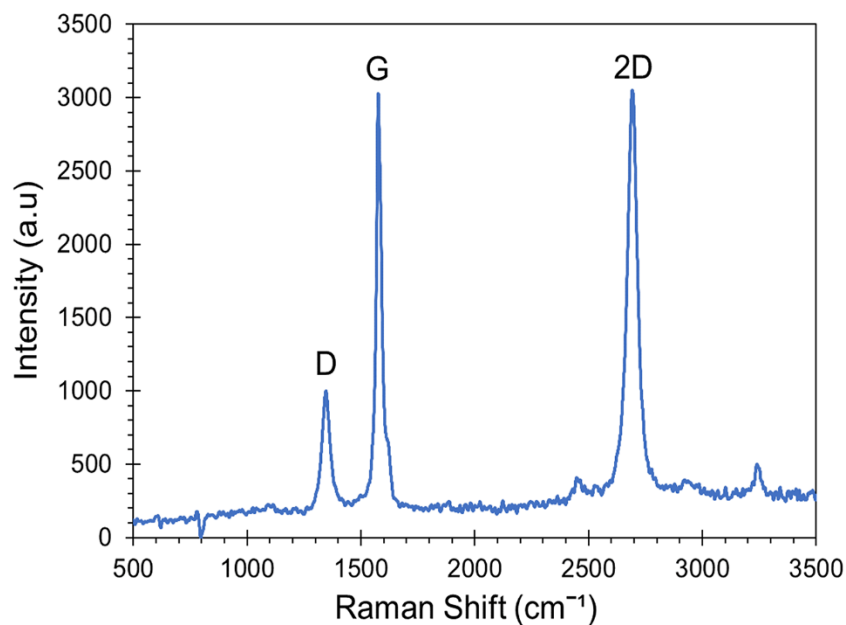


Figure 3-9. Raman spectrum for rectangle pattern with 40% laser power on 3D printed sample. The spectrum is obtained from a different position.

3.4.3 Scanning Electron Microscopy

SEM images of the LIG surface on 3D printed substrates are shown in Figure 3-10. The morphology for the 10% power sample is mostly twisted branches, and the size of particles is small (Figure 3-10 (a)). By increasing the power to 20%, particles start to grow, but there is not much difference between 10% and 20% power samples (Figure 3-10 (b)). Increasing power to 40% leads to more growth of particles, and the morphology changes to a more spherical shape. Besides, the porosity of particles is considerable compared to lower power samples (Figure 3-10 (d)). Porosity combined with low resistance is highly desirable for devices such as

chemical sensors or electrochemical energy storage. Figure 3-10 (e) to Figure 3-10 (h) shows the formation of microscale dendritic defects on the samples' surfaces. As indicated in the images, the size of defects changes with changing laser power. The biggest size defect is observed for 20% power, and the planar defect density for this sample is $8.5 / \text{mm}^2$ which is the highest among the studied samples. The defect density for 40% power is $3.6 / \text{mm}^2$, and the size of these defects is much smaller than for the other samples. At high power, there is more energy for the transformation of PEI to graphene and less time for defect growth, which explains the improvement in electrical conductivity.

Figure 3-11 shows the SEM images of engraved rectangle patterns on commercial PEI. Like the 3D printed samples, the 10% power sample is made of intertwined branches, and particles' porosity is not significant. By increasing the laser power to 20%, the branches start to grow, and the porosity is increased (Figure 3-11 (b)). The 30% power sample also shows the same trend. The big difference between commercial and 3D printed samples is the morphology of 40% power samples. Figure 3-11 (d) shows the morphology of the 40% power sample. The branches are less distinguishable and form bigger clusters.

Figure 3-12 shows the morphology of both 3D printed and commercial PEI for different laser power at lower magnification. For 10% power, the laser passes are differentiable in both samples (Figure 3-12 (a) and (b)). By increasing the power to

20%, the laser passes in the 3D printed sample are disordered, but they are still distinctive. Unlike the 3D printed sample, the surface morphology of the commercial sample is changed, and laser passes are not detectable. Higher powers change the surface morphology of commercial samples completely, and the features have irregular shapes (Figure 3-12 (f) and (h)). The features grow significantly, and the large-scale porosity is higher for the commercial samples, which may explain the higher resistivity. Also, there is no indication of microscale dendritic defects on the surface of commercial samples.

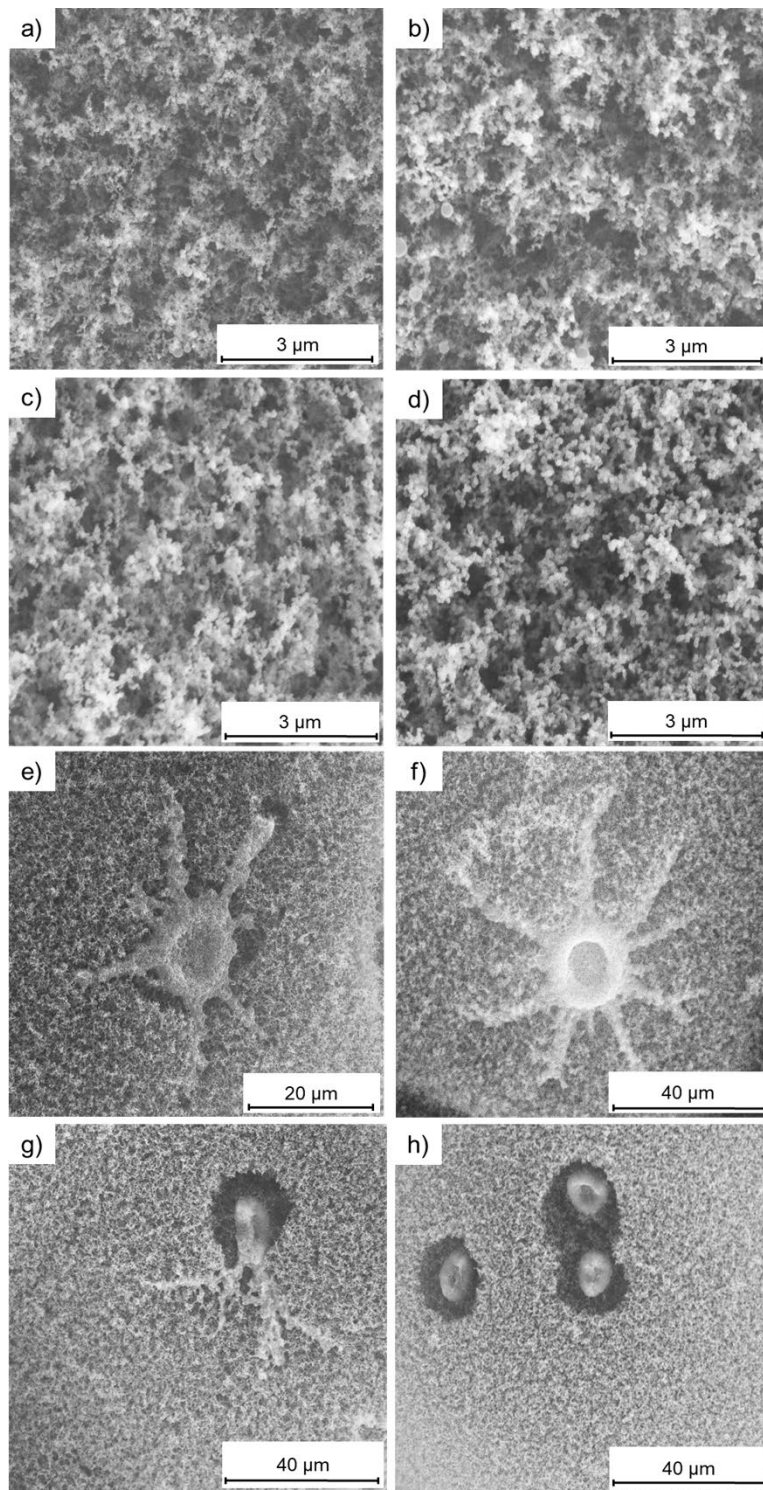


Figure 3-10. SEM images of the graphene surface in rectangle pattern samples at a) 10%, b) 20%, c) 30%, d) 40% laser power on 3D printed PEI substrate. The size of graphenic branches increases with increasing power. Surface defects are shown for e) 10%, f) 20%, g) 30%, and h) 40% laser power. Defect size initially increases from 10% to 20% power and then decreases up to 40%.

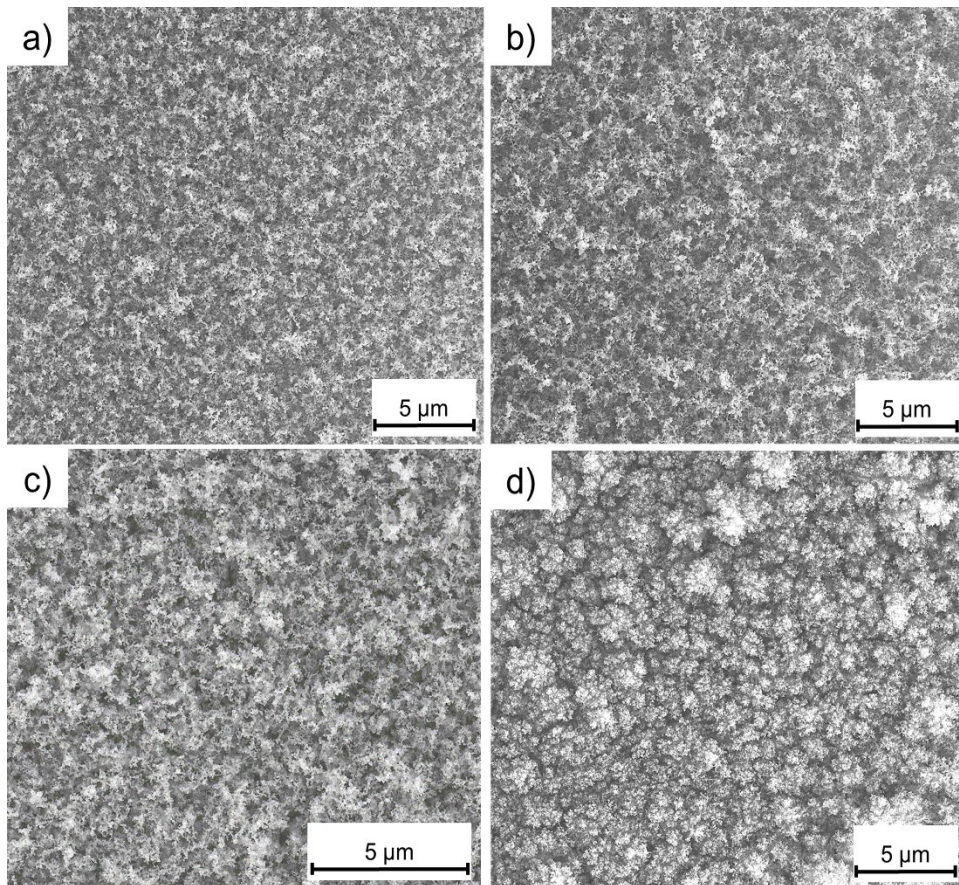


Figure 3-11. SEM images of the graphene surface in rectangle pattern samples at a) 10%, b) 20%, c) 30%, d) 40% laser power on commercial PEI substrate. The size of graphenic branches increases with increasing power.

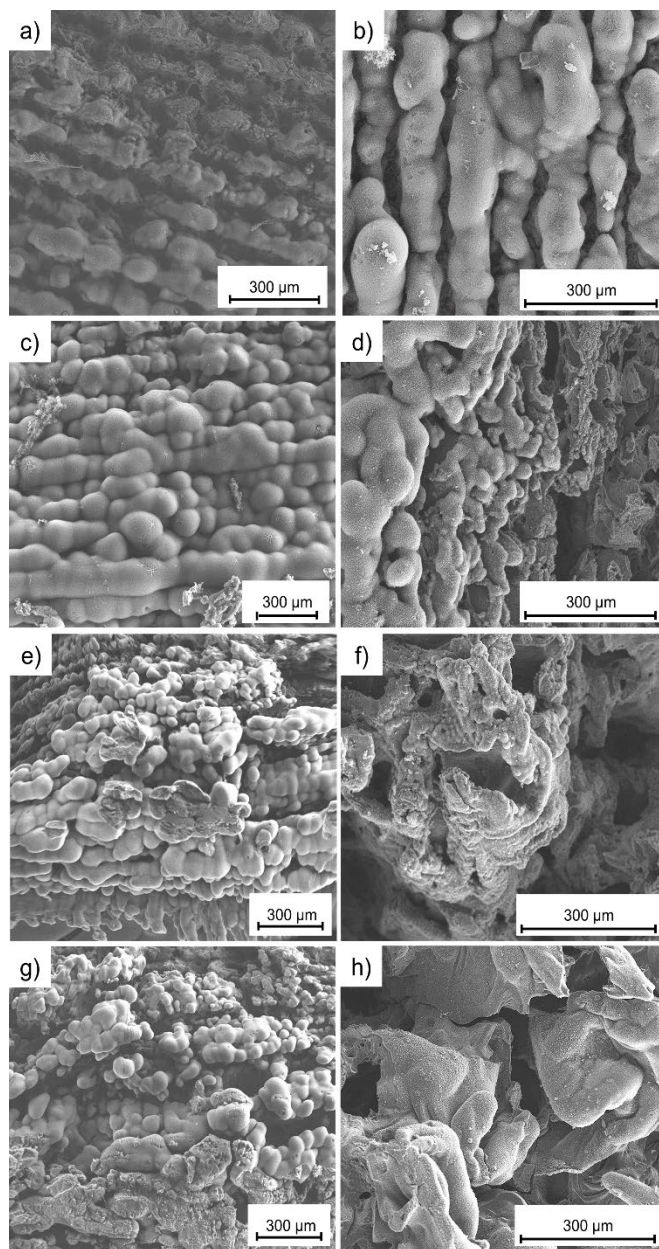


Figure 3-12. Low-magnification SEM images of the graphene surface in rectangle pattern samples at a) 10%, c) 20%, e) 30%, g) 40% laser power on 3D printed PEI substrate. SEM images of the graphene surface in rectangle pattern samples at b) 10%, d) 20%, f) 30%, h) 40% laser power on commercial PEI substrate. At 30% and 40% power, commercial samples show different morphology.

3.4.4 Thermal Analysis

Differential scanning calorimetry is a method to determine the crystallinity of polymers based on the heat of fusion measurement. Figure 3-13 shows the DSC thermograms for 3D printed and commercial PEI samples. Both samples exhibit a similar transition corresponding to the glass transition at 221°C. The DSC results show the enthalpy for 3D printed is different from commercial PEI. The specific enthalpy for the 3D printed sample is 3.11 J/g, and for the commercial sample is 0.95 J/g. Also, heating polymers (e.g. during 3D printing) can lead to the appearance of sharp endothermic peaks at the glass transition. This endothermic peak is associated with enthalpy relaxation due to physical aging after heating the samples [71]. During the 3D printing process, the filament is heated, and chains rearrange themselves into a close-packed configuration. Therefore, the physical aging appears in 3D printed samples, and the endothermic peak is significant. It can be concluded that 3D printing changes the properties of the PEI. Therefore, 3D printed and commercial PEI show different interactions with the laser.

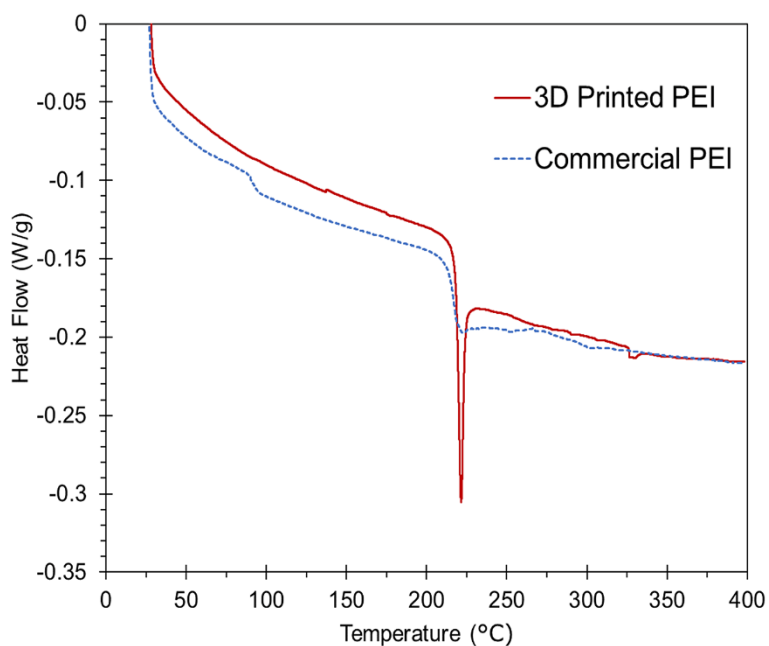


Figure 3-13. DSC thermograms of 3D printed and commercial PEI. The sharp endothermic peak at the glass transition is due to the physical aging of 3D printed PEI.

Thermogravimetric analysis studies the polymers' thermal stability by monitoring the change in the weight of the sample while it is being heated. Figure 3-14 illustrates the TG curves and DTG curves for 3D printed and commercial PEI. Both samples show good thermal stability up to 450°C under air atmosphere. The first small peak of DTG was associated with the first weight loss of the samples, followed by the second and third, as labeled in the figure. The mass change is due to main-chain scission and the release of volatile products. The weight loss in 3D printed PEI is 3.5% more than the commercial sample. Since the chemical

composition of 3D printed and commercial PEI is similar, this difference in weight loss can be due to physical aging in 3D printed samples.

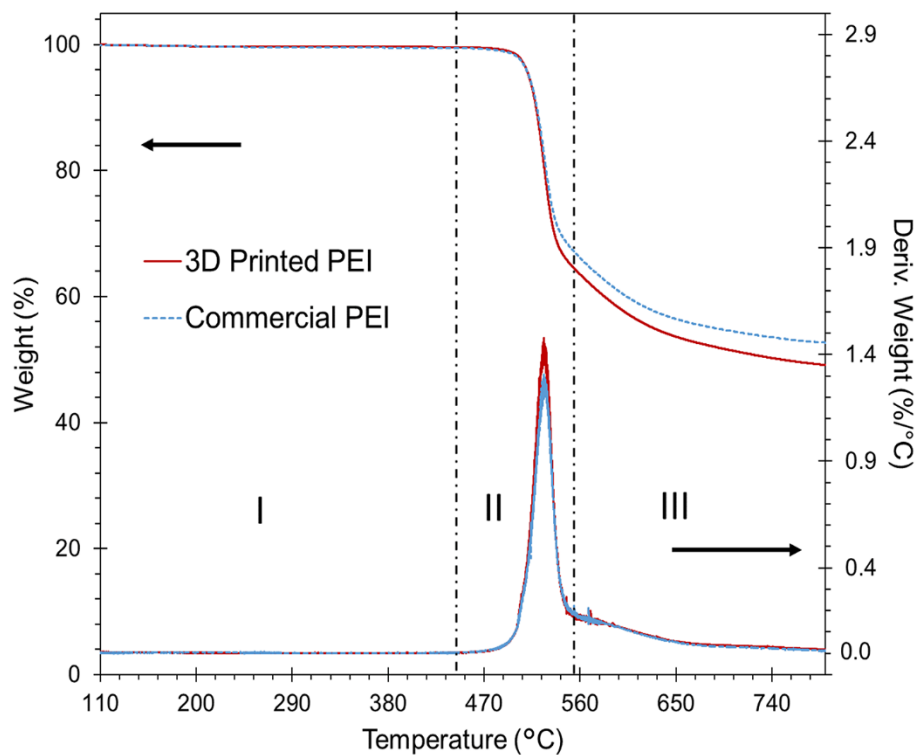


Figure 3-14. TG and DTG analysis of 3D printed and commercial PEI. The weight loss in 3D printed PEI is 3.5% more than the commercial sample

3.4.5 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy is utilized to study the chemical nature of samples on 3D printed and commercial PEI. Figure 3-15 shows the XPS survey and atomic percentages of carbon and oxygen in each sample. The curves in Figure 3-15 (a) and (b) show that the intensity of oxygen peaks is reduced to a great extent. The atomic percentage of carbon is 65% before LIG conversion, and it increases up to 80% in all samples. The atomic percentage of oxygen is reduced to less than 10% for commercial samples and 13% for the 3D printed samples.

Although the lowest sheet resistance is achieved with 40% power in both 3D printed and commercial samples, the atomic percentage of carbon is not the maximum value in these samples. The low sheet resistance in these samples is not only a function of carbon percentage but also the morphology and thickness.

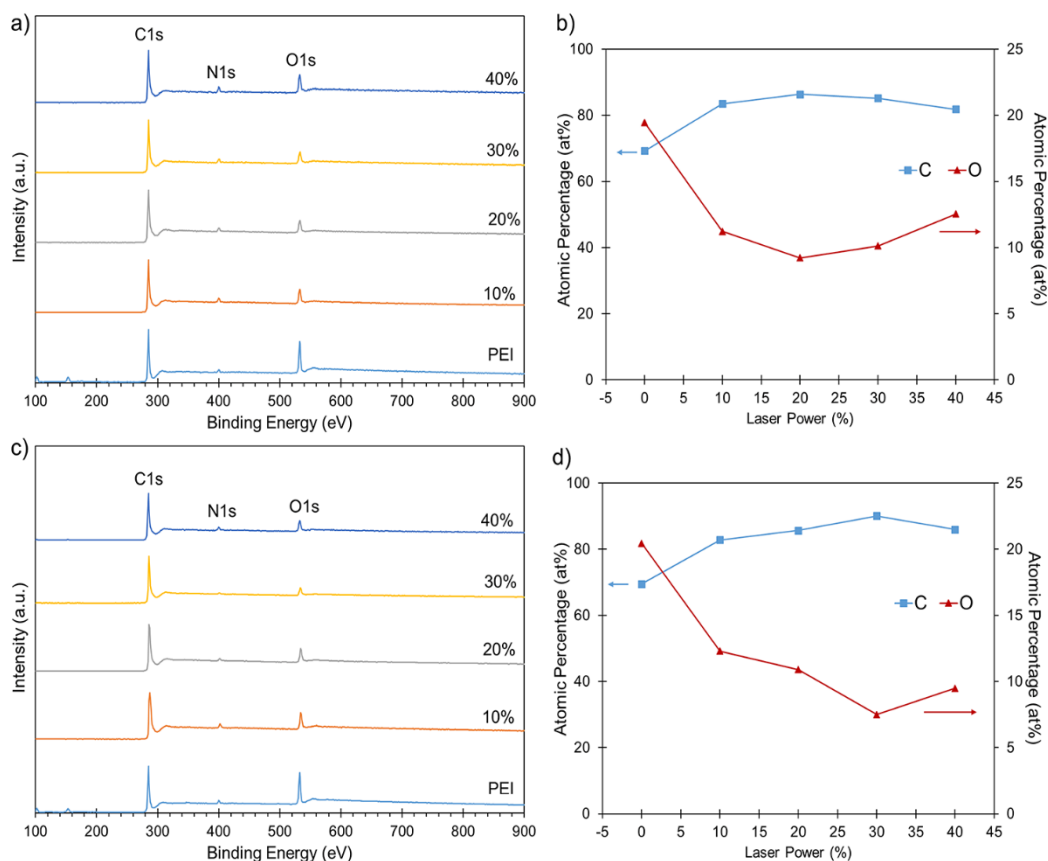


Figure 3-15. a) XPS analysis and b) atomic percentages of carbon and oxygen as a function of laser power for rectangle-patterned LIG on 3D printed PEI. c) XPS analysis and d) atomic percentages of carbon and oxygen as a function of laser power for LIG samples on commercial PEI.

3.5 Strain Gauge Design

Raster and vector modes are used to study the effect of laser mode on the engraved patterns. The laser performs a printer-like function in the raster mode and moves back and forth across the material while the laser engraves the surface. In the vector mode, the laser starts at a specific point and continues along the line until the shape

is engraved. Figure 3-16 demonstrates the difference between raster and vector modes. A strain gauge is designed with these two different modes, and the resistance is measured for each of them.

Table 3-1 shows the specification of two different designs and the measured resistance. Since the conductivity is higher for engraved patterns with raster mode, the connection pads are fabricated with this mode in both designs to enhance the conductivity. Although the laser parameter is the same for both designs, the resistance per line is lower for the active grid engraved with raster mode. In the vector mode, the designs consist of one pulse wide line, but in the raster mode, the designed lines consist of multiple overlapping lines. The back and forth movement of the laser combined with overlapping adjacent lines will lead to lower resistance in raster mode.

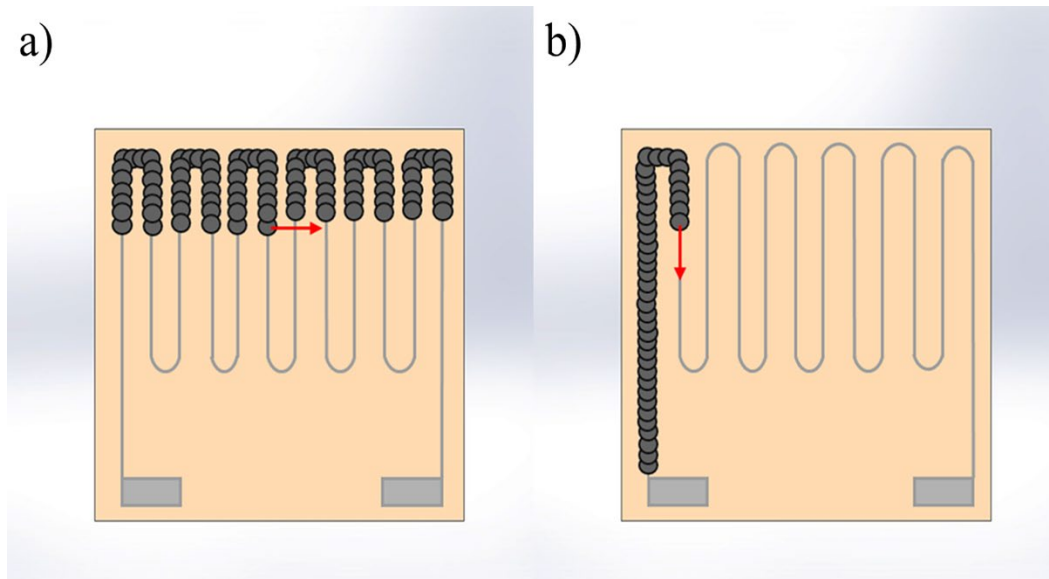


Figure 3-16. The schematic illustration of a) Raster mode and b) Vector mode. The red arrow shows the direction of the laser.

Table 3-1. The properties of designed strain gauges with raster and vector mode.

	Engraving mode		Laser Power (W)	Laser Speed (cm/s)	Resistance per line (Ω)
	Active grid	Connection pads			
Design 1	Raster	Raster	6	2.5	32 ± 0.8
Design 2	Vector	Raster	6	2.5	134 ± 0.5

3.6 Conclusion

We have demonstrated the direct conversion of a 3D printed polymer (PEI) into graphene by using a CO₂ laser. Sheet resistance was optimized by varying the laser power and pattern. Increasing power and line width reduce sheet resistance and defect density up to the point where the material is ablated. The 40% laser power gave the best result. Much lower sheet resistance (0.30 Ω/sq) was achieved on the 3D printed PEI compared with commercial sheets, as well as previous reports on 3D printed PEI/PC and PEEK. Different material characterizations were conducted on the 3D printed and commercial PEI. Although both samples had similar chemical compositions, the morphology of laser-induced samples was very different. Also, because of the rearrangement of chains during the 3D printing process, the thermal analysis of the 3D printed PEI showed different results. This technique enables the facile integration of electronics on different 3D printed geometries and structures, opening up many different applications.

CHAPTER 4. INK-JET PRINTING GRAPHENE ON NOVEL SURFACES

4.1 Introduction

Ink-jet printing is an additive manufacturing (AM) subcategory to fabricate various electronic devices, like transistors, displays, and sensors. This technique is based on the jettability of fluids through a nozzle. By applying precise digital control of the jetting, the drops land on the substrate at the desired position and form different patterns and structures. Different functional materials can be deposited directly on various substrates [24]. Multiple types of inks like metal-based inks, conductive polymers, and carbon-based inks have been developed for ink-jet printing. Metal-based inks, like silver and copper, are interesting due to their high conductivity. However, high cost and the risk of oxidation under ambient conditions are the main drawbacks of silver and copper ink, respectively [72].

Graphene is one of the carbon-based inks that has been used widely for ink-jet printing. The chemically-derived graphene inks like graphene oxide (GO) are also a promising candidate for different applications. The GO contains oxygen groups, and it is dispersible in different media. Although the dispersibility of the GO is ideal for ink preparation, it is not conductive. The GO can be transformed to reduced graphene oxide (rGO) through chemical, thermal, or photothermal routes. The obtained rGO is graphene-like material and shows high conductivity [73].

The most conventional substrates for ink-jet printing graphene and GO inks are flexible plastics. Polyethylene terephthalate (PET) and polyimide (PI) are commonly utilized for fabricating different electronic devices [44]. Electronic grade papers are another option for ink-jet printing substrate [74]. In some cases, glass and FTO glass are used as the substrate for specific applications like solar cells [75]. There are few reports on ink-jet printing on treated Si/SiO₂ substrates [48].

This chapter demonstrates the ink-jet printing of graphene oxide ink on 3D printed polylactic acid (PLA), silicon (Si), and silicon nitride (SiN) substrates. The wettability of the ink on each surface is investigated, and the drop spacing for printing uniform lines is optimized. Different reduction methods are used to convert the printed GO patterns to rGO. Printing multiple passes has been used to increase the thickness of printed patterns and improve conductivity. The integration of ink-jet printing and 3D printing has not been studied extensively before. Various geometries and structures can be used as 3D printed substrates, and conductive patterns can be applied with ink-jet printing onto them. Also, printing of graphene oxide on silicon nitride has not been done before. Printing graphene-based materials on silicon and silicon nitride can open up many applications that integrate printed materials with traditional silicon microelectronics, like ion-sensitive field effect transistors (ISFET) and graphene field effect transistors (GFET).

4.2 Experimental

4.2.1 Ink Preparation and Printing

Single-layer GO powder was purchased from Cheap Tubes. The dimensions of GO flakes were 300 nm x 800 nm x 1 nm. To make the GO ink, 100 mg of GO powder was dispersed in 10 ml of deionized (DI) water, and the solution was sonicated for 2 hours. The sonicated solution was filtered with a 0.45 micron nylon syringe filter afterward. Ethylene glycol (EG) was chosen as the additive to increase the ink's viscosity. After filtering the GO solution, 31.06 ml EG was added, and the solution was sonicated for 1 hour. Finally, the ink was filtered again to make sure there were no agglomerated particles in it. The viscosity of the ink was measured with RheoSense μ VISC Portable Viscometer at room temperature.

The 3D printed substrates were designed using CAD software (Solidworks). PLA was used as the starting filament and 3D printed by fused deposition modeling (FDM) using an Ultimaker 3 printer. The dimensions of substrates were 3 cm x 3 cm x 2 mm. The surface of the 3D printed substrates was leveled with an epoxy (UV Cure 60-7170, Epoxies, Etc.) layer. Extrusion printing of epoxy layer on PLA substrate was performed with Voltra V-One PCB printer. The printed epoxy was cured with the Light-welder PC-2 for 15 minutes. The 3D printed substrates were sonicated in DI water for 5 minutes to remove any dust. The (100) oriented Si and SiN wafers were purchased from University Wafer. Both wafers were P doped, and

the dopant was boron. Each wafer was split into smaller parts before the cleaning procedure. The surface of the wafers was cleaned with DI water rinse, followed by an ethanol rinse. The sequence was repeated 3 times and then blow-dried by air.

A custom-built piezoelectric DOD ink-jet printer was used to print GO ink on the substrates. The printer stage moved relative to the printhead, and any pattern was printable with a custom LabVIEW program (National Instruments, Austin, TX). The nozzle's orifice diameter was 60 μm , and it was purchased from Microfab Technologies, Inc. (Plano, TX). The printed patterns were dried at 70°C for 30 minutes on a hot plate. After drying, the printed patterns were imaged by optical microscopy (OMAX Trinocular Metallurgical Microscope (Model M83MP)). The thickness of printed lines was measured using profilometry (Alpha-Step D-500, KLA-Tencor). A probe station with a semiconductor parameter analyzer (Keithley 4200A) was used to measure the printed patterns' resistance. The contact angle of the ink on the substrates was measured using the sessile drop method with a KRÜSS drop shape analyzer (DSA25E). Raman spectra were obtained with a Horiba Scientific (Model: LabRAM ARAMIS) Raman Microscope using 532 nm laser excitation with a laser power of 50 mW.

4.2.2 Graphene Oxide Reduction

The ink-jet printed GO samples on 3D printed substrates were reduced with a Xenon X-1100 High-Intensity Pulsed Light System. The machine's maximum

voltage was 3000 V, and the off-time was 10 ms through the whole experiment. The amount of energy per pulse was varied with the on-time, number of pulses, and the applied voltage. The printed GO lines on Si and SiN wafers were first reduced with the xenon lamp. To improve the conductivity, thermal reduction with a vacuum furnace was also utilized. The reduction temperature was in the range of 200°C to 300°C, and the time was varied from 30 to 90 minutes. The effect of the vacuum environment on the conductivity of the reduced samples was also studied. In the final step, the samples were reduced with hydrazine hydrate (N_2H_4 , Millipore Sigma). Printed samples were placed in a small petri dish. The small petri dish was placed inside a bigger one that contained 1 ml of hydrazine hydrate. The whole setup was sealed, rested under the fume hood for 30 minutes, and then heated up to 200°C for 4 minutes. Figure 4-1 shows the schematic setup of reduction with hydrazine hydrate (HH).

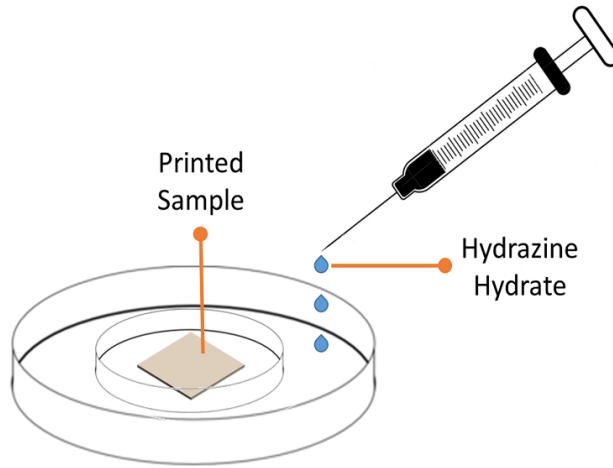


Figure 4-1. The schematic illustration of reduction setup for Si and SiN wafers with hydrazine hydrate. The large petri dish was sealed and placed under the fume hood for 30 minutes.

4.3 Printing on 3D printed PLA

The surfaces used for ink-jet printing need to be clean and smooth, without any roughness. Due to the nature of the 3D printing process, the fabricated surface is usually rough and serrated. A layer of epoxy is printed with extrusion printing to level the surface of 3D printed PLA. Figure 4-2 (a) shows the PLA substrate after printing a square pattern of epoxy on top of it. Figure 4-2 (b) demonstrates the optical micrograph of the PLA substrate. The dashed line is the boundary of the epoxy layer on the PLA substrate. It shows the difference that the epoxy layer makes to flatten the substrate. This layer improves the printability of the ink on the surface. Figure 4-2 (c) shows the optimum epoxy layer thickness on the PLA substrate. The average thickness of the epoxy layer on PLA is 90 μm . A lower

thickness will lead to a wavy surface which is not suitable for printing. A thicker layer of epoxy can alter the heat transfer properties and change the drying condition. Therefore, it is essential to optimize the thickness of epoxy. By varying the extrusion printing parameters, like the nozzle's height, the thickness of printed epoxy can be optimized. Figure 4-2 (d) illustrates the sessile droplet of GO ink on the substrate. The measured contact angle is 52° .

The viscosity of the ink is ~ 8 cP at room temperature. Although the ink's viscosity is lower than the recommended range for ink-jet printing, manipulating the applied voltage helps the droplet formation. Table 4-1 demonstrates the used bipolar waveform parameters for jetting GO ink with the ink-jet printer. These parameters are vital to prevent the satellite effect. In satellite formation, the droplet shows a long tail separated from the primary droplet and breaks into a tiny droplet. Satellite droplets will decrease the quality of printing and blur the final feature. Figure 4-3 shows the ink stream jetting from the nozzle orifice. As it demonstrates, spherical droplets are formed, and no primary droplet is observed. Also, the prepared ink is highly stable and can be used for printing for more than 3 months.

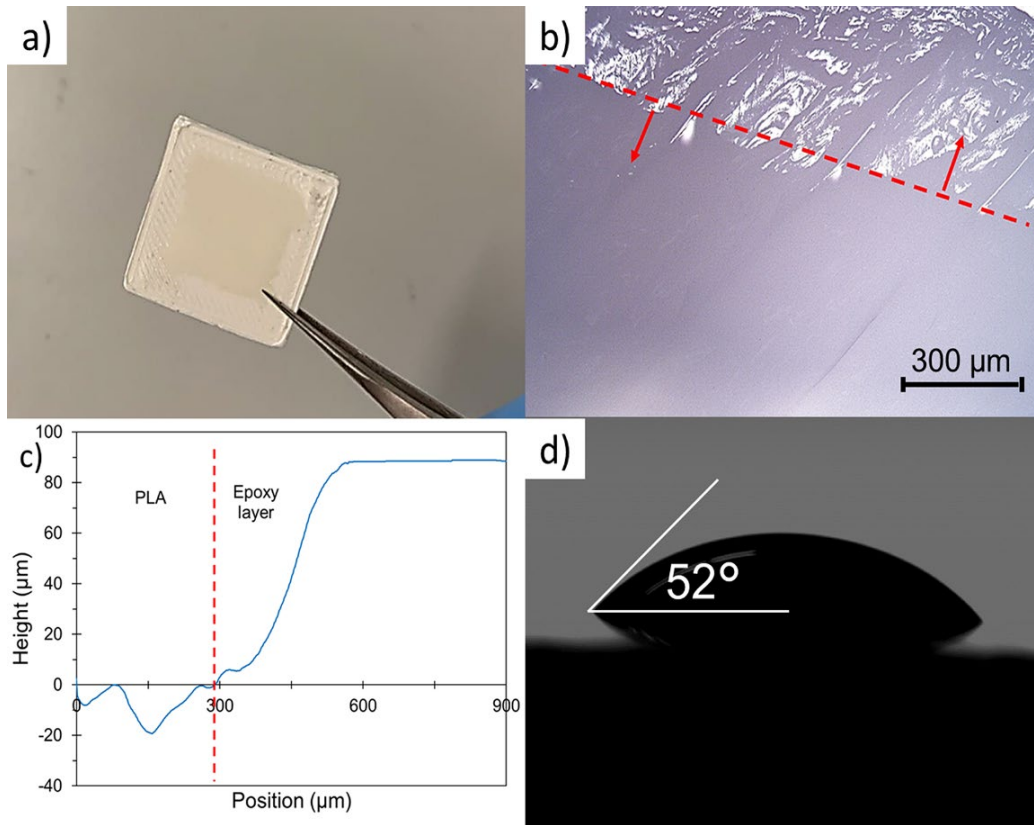


Figure 4-2. a) A digital image of 3D printed PLA substrate with epoxy on top. b) The optical micrograph of PLA substrate with epoxy layer. The dashed line shows the boundary between the epoxy and PLA. c) Profilometry scan across the 3D printed substrate and epoxy layer, and d) the GO ink's contact angle on printed epoxy layer.

Table 4-1. The used ink-jet printing parameters for jetting GO ink.

Parameter	Value
Rise time 1 (μs)	3
Dwell time (μs)	30
Fall time (μs)	3
Echo time (μs)	60
Dwell voltage (V)	26
Echo voltage (V)	-26
Idle voltage (V)	0
Rise time 2 (μs)	3

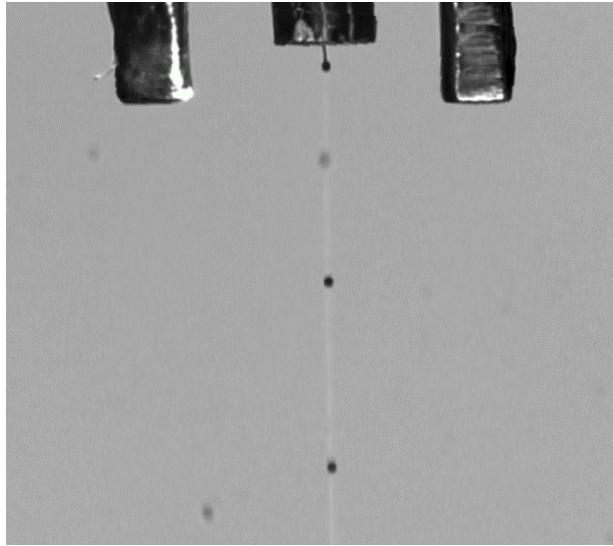


Figure 4-3. The stream of ejected GO ink and spherical droplet formation without any satellite effect.

Figure 4-4 demonstrates different behavior of printed lines on the 3D printed substrate for various values of drop spacing. The drop spacing is defined as the distance between the center of two adjacent drops landed on the substrate. When the drop spacing is too large (Figure 4-4 (a)), there is no interaction between the landed drops, and they dry individually on the substrate. When the drop spacing decreases to $90\text{ }\mu\text{m}$, some drops overlap, but there is still discontinuity in the printed line (Figure 4-4 (b)). The continuity of the lines is essential to maintain the conductivity. For the drop spacing of $80\text{ }\mu\text{m}$, the overlap, and interaction between the drops increase, but there are still gaps along the line. As Figure 4-4 (d) demonstrates, by decreasing the drop spacing to $70\text{ }\mu\text{m}$, the landed drops merge, but each maintains the rounded contact line and forms a scalloped pattern. Due to

the formation of lines, the ink's spreading is less, and the printed lines are narrower compared to the previous situations. Uniform lines of GO on the 3D printed substrates are achieved with 50 μm drop spacing. The lines have smooth edges, and there is no gap observed (Figure 4-4 (f)). The width of the printed line is around 60 μm , and its length is 2000 μm .

Due to cohesive forces, the landed droplets form an ellipsoid shape at the beginning of the line. This ellipsoid shape, known as a bulge in printing, is to minimize the surface energy of landed droplets. The difference between the shape of the printed line and the bulge at the beginning creates a pressure gradient. Therefore, the fluid flows toward the back of the line, leading to higher thickness at the bulges compared to the line itself [76]. This fact is demonstrated in the thickness measurements of printed lines in Figure 4-5. The average thickness for the initial bulge of printed GO on 3D printed PLA is 80 nm. The thickness reduces to 40 nm for the printed lines. Although the bulges create thickness variance in printed lines, they can be used as contact pads for resistance measurement. Also, the edges of printed lines are thicker than the middle due to the coffee ring effect. The evaporation rate at the printed pattern's contact lines is higher, which induces a capillary flow and drives particles toward the line's edges. The coffee ring effect can be suppressed with temperature control.

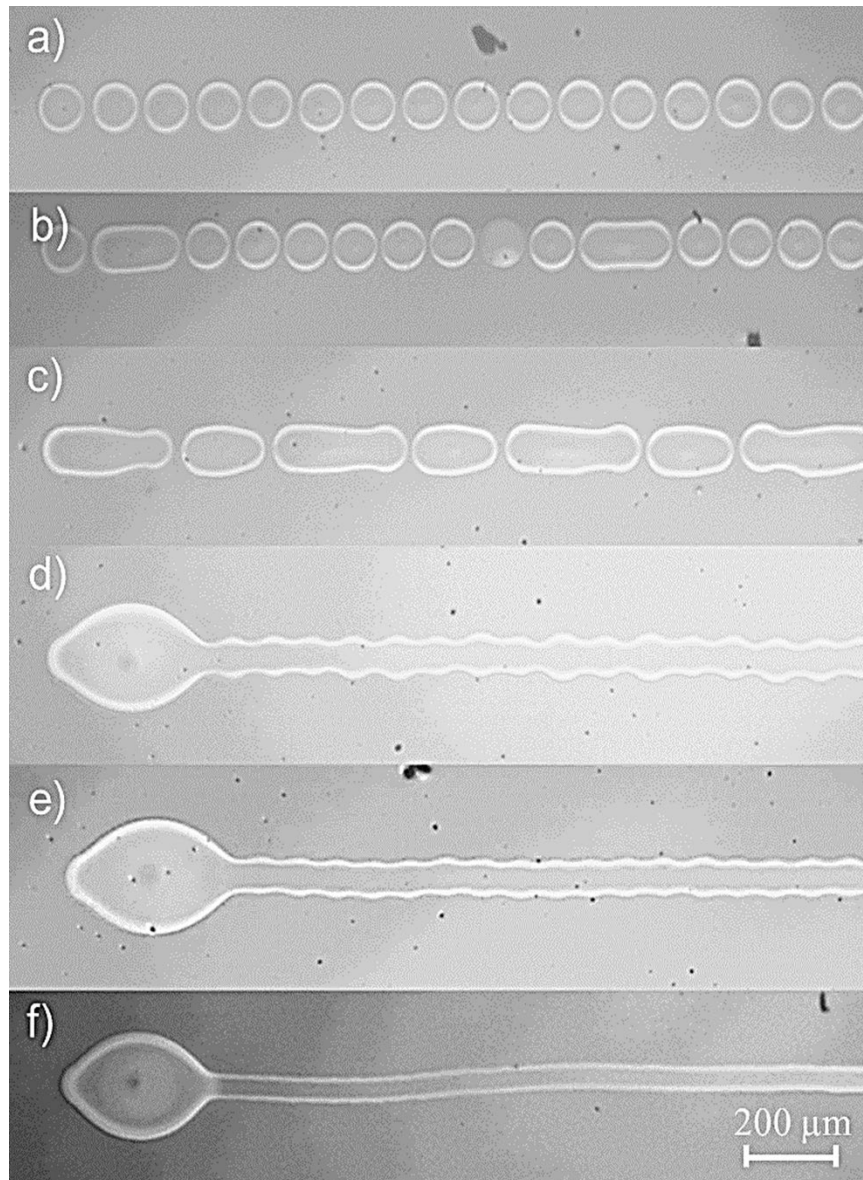


Figure 4-4. Optical micrographs of printed lines on epoxy on PLA with different drop spacing. The drop spacing is a) 100 μm , b) 90 μm , c) 80 μm , d) 70 μm , e) 60 μm , and f) 50 μm . A uniform line is achieved with 50 μm drop spacing. The lines are dried at 70°C for 30 minutes before observation under the microscope.

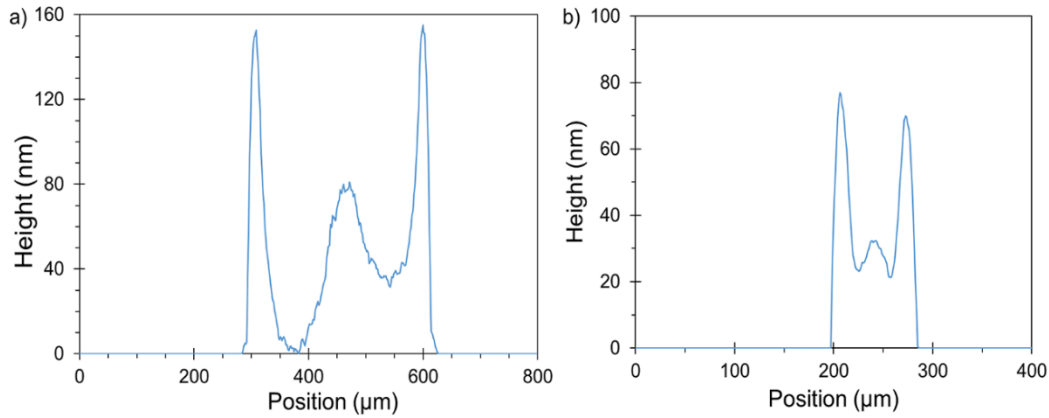


Figure 4-5. Profilometry scan across printed lines with drop spacing of 50 μm . Graph a) is the thickness of initial bulging and, graph b) is the thickness of the uniform line.

4.4 Printing on Silicon and Silicon Nitride Wafer

The prepared GO ink is also used to print on Si and SiN wafers. Printing on these substrates is challenging due to the different surface properties compared to epoxy. Also, their reflective surface acts as a mirror and makes the tracking of printed lines visually hard. Figure 4-6 shows the contact angle of GO ink on as-received and cleaned substrates. As presented in the figures, the contact angle of GO ink on the Si substrate is close to zero, and the ink spreads, which makes the printing difficult. The contact angle of the ink on SiN is around 37° , which is smaller than the GO's contact angle on epoxy on PLA substrates. The lower contact angle of the ink on the SiN substrate leads to wider lines. Rinsing the Si substrate with DI water and

ethanol increases the contact angle to 25° , but the change is not sufficient and does not change the printing properties. Rinsing of the SiN substrates does not change the surface properties, and the contact angle is very similar.

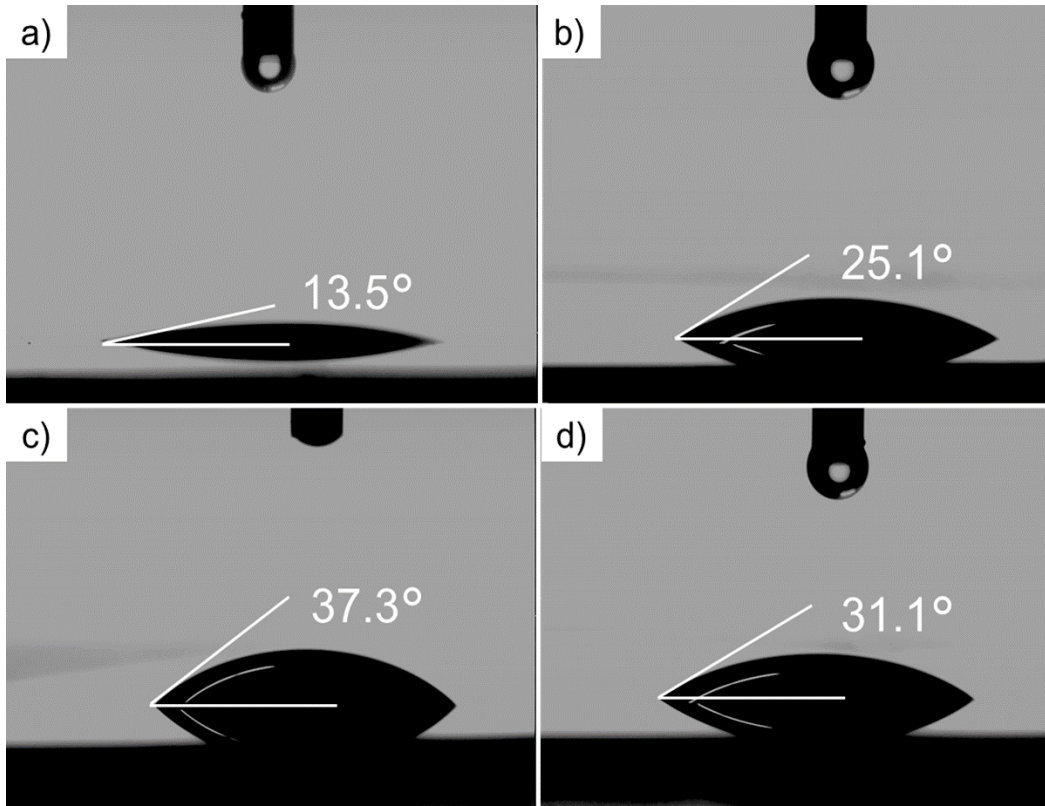


Figure 4-6. The contact angle of GO ink on Si substrate a) before and b) after the cleaning procedure. The contact angle of GO ink on SiN substrate c) before and d) after the cleaning. Rinsing the substrate with DI water improves the contact angle slightly only in the case of silicon.

Figure 4-7 exhibits different behavior of printed lines on the SiN substrate for different drop spacing. The optimum drop spacing to print a consistent GO line on SiN substrate is 100 μm (Figure 4-7 (d)). The edges of the printed lines are wavy, but it does not affect the pattern's performance. The width of the printed line is around 120 μm , and its length is 1800 μm . By increasing the drop spacing to more than 100 μm , the lines break, and they are not useable for any application. Decreasing the drop spacing to less than 100 μm leads to bulge formation along the lines. The bulges appear periodically and also at the beginning of the lines. The Laplace pressure is more prominent for 70 μm drop spacing and leads to stronger fluid flow and significant bulges.

The printed patterns on Si substrate are demonstrated in Figure 4-8. Due to the high surface energy and low contact angle, printing the lines on the untreated surface is not possible. The presented patterns are initially printed to form squares on the substrate, but they merge and turn into a circular shape to minimize surface energy. Rinsing the Si substrate with DI water and ethanol does not change its surface tension and the shape of printed patterns. Figure 4-9 shows the profilometry scan across printed patterns on Si and SiN substrates. The thickness of printed lines on SiN is much lower than on epoxy/PLA substrate. Since the contact angle of the GO ink on the SiN substrates is small, the lines are wider and, as a result, thinner. Also, the coffee ring effect can be seen in the printed lines profilometry scan. Although the contact angle of the ink on Si substrates is smaller than SiN, the circular patterns

are thicker than the lines on SiN due to the lower coffee ring effect. The thick circular patterns on Si substrates are still four times thinner than printed lines on PLA substrates.

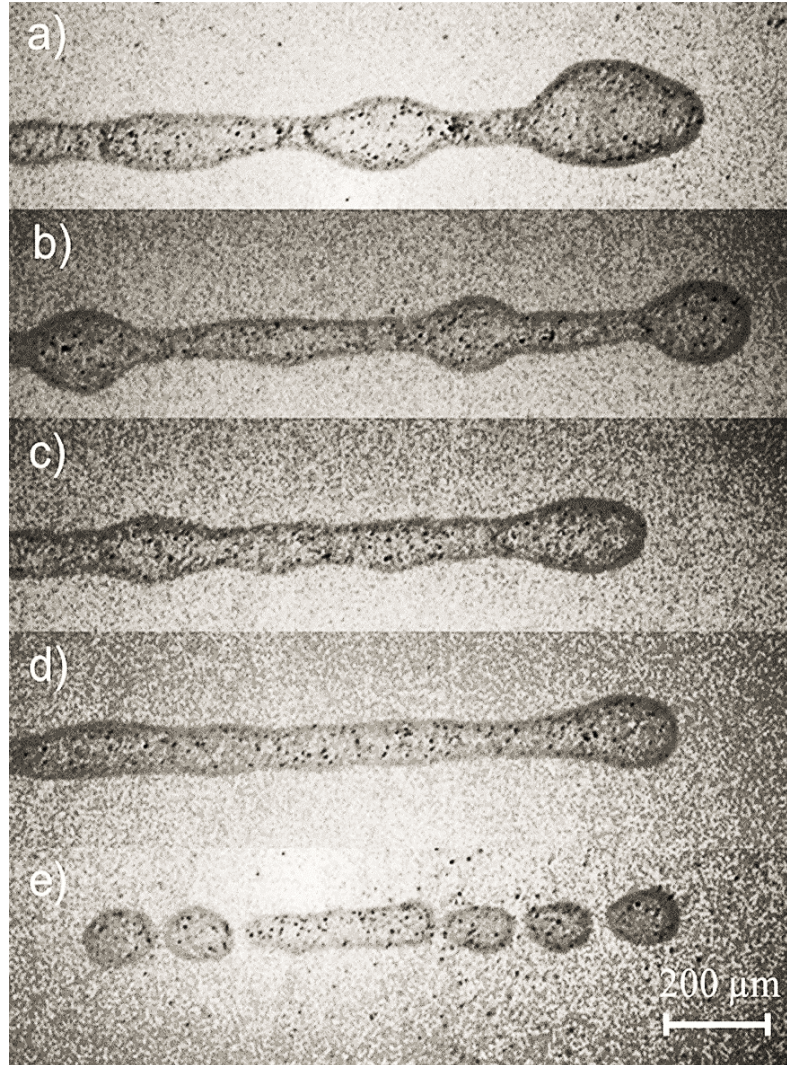


Figure 4-7. Optical micrographs of printed lines with different drop spacing on SiN substrate. The drop spacing is a) 70 μm , b) 80 μm , c) 90 μm , d) 100 μm , and e) 110 μm . A consistent line is achieved with 100 μm drop spacing. The lines are dried at 70°C for 30 minutes before observation under the microscope.

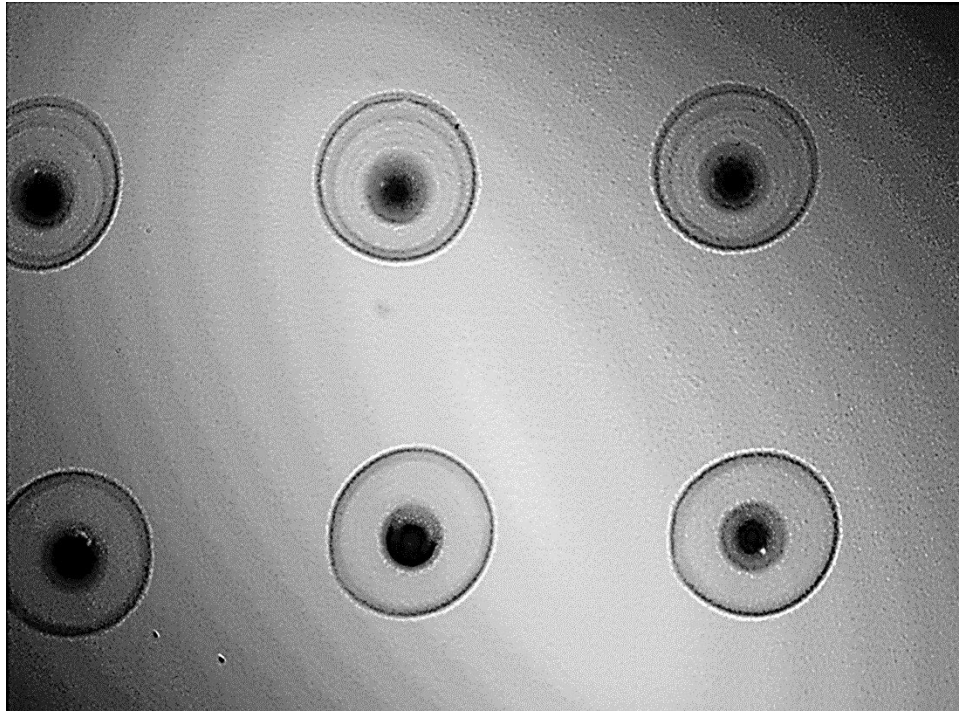


Figure 4-8. The optical micrograph of printed square patterns on Si substrate. Due to the low contact angle of the GO ink on Si, it spreads on the surface in the form of a circular pattern.

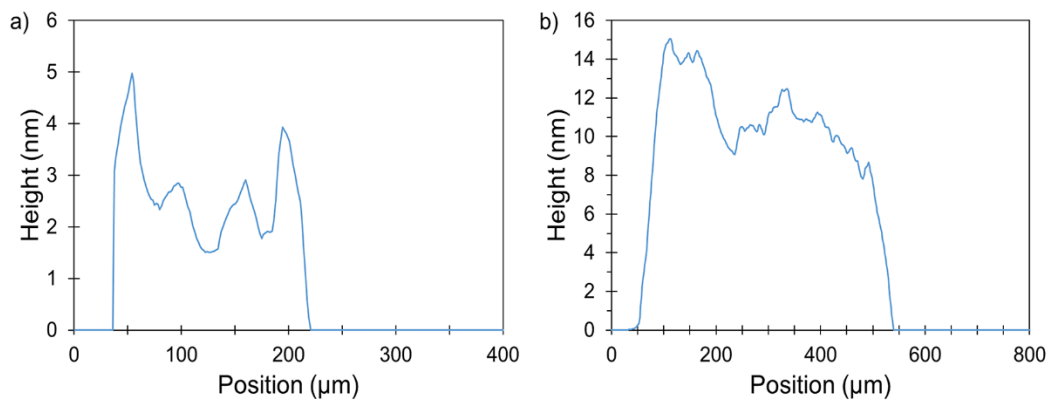


Figure 4-9. Profilometry scan across printed patterns on a) SiN substrate and b) Si substrate. The patterns are dried at 70°C for 30 minutes.

4.5 Graphene Oxide Reduction

Since the glass transition temperature for PLA is around 80°C, it is not recommended to use high temperatures for the reduction process. Also, it is not chemically resistant to strong reducing agents. Therefore, the printed lines on the 3D printed PLA substrates are reduced with the xenon lamp. The photothermal process with the xenon lamp is rapid and more suitable for substrates like PLA, which can not bear high temperatures. Figure 4-10 shows the sheet resistance of printed GO lines on PLA substrate reduced with the xenon lamp. The maximum voltage is utilized ($V = 3000\text{ V}$) to get high-quality rGO after the reduction. The off-time is the time gap between every two consecutive pulses, and it is set to 10 ms for all the samples. The duration of each pulse is on-time, and it is varied to see its effect on the sheet resistance. Also, the number of pulses is another parameter that changes the resistance of rGO. Generally, by increasing the pulse number, the amount of transferred energy to the sample increases. A higher amount of energy leads to better elimination of the oxygen group in GO and lower final sheet resistance. However, there is an optimum pulse number for each sample, and the sample starts to burn after that. Different on-times can change the optimum pulse number for each sample. The lowest achieved sheet resistance is $10\ \Omega/\text{sq}$ for the sample with 2 ms on-time after applying 3 consecutive pulses.

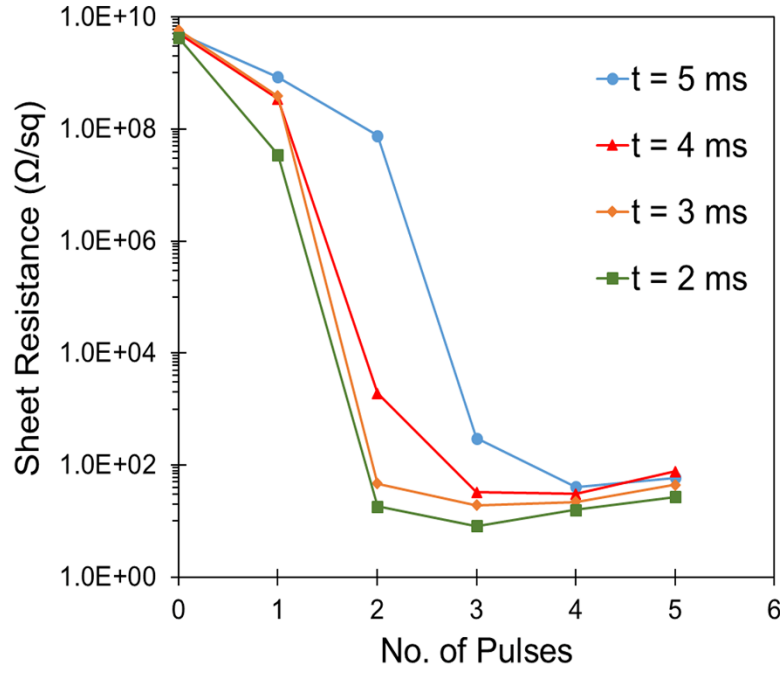


Figure 4-10. The sheet resistance of reduced lines on epoxy/PLA as a function of pulse number. The applied voltage is 3000 V, and the off-time is 10 ms for all samples.

Table 4-2 presents the sheet resistance of reduced GO on Si and SiN substrates through the photothermal route. The applied voltage is 3000 V, the off-time is 10 ms, and the on-time is 5 ms for all samples. The sheet resistance for the circular patterns on Si substrates are calculated based on the following equation [77]:

$$R_{sh} = \frac{\pi R}{2 \ln \frac{2d}{\delta}} \quad (\text{Eq. 4-1})$$

Where R is measured resistance, d is the distance between the probes and δ is the diameter of probes.

Table 4-2. Sheet resistance of photothermally reduced GO ink on Si and SiN substrate.

Number of Pulses	Sheet Resistance (Ω/sq)	
	Silicon (Si)	Silicon Nitride (SiN)
0	4.55E+11	8.28E+11
50	1.60E+08	1.73E+09
100	3.18E+08	3.22E+09
150	3.27E+08	4.47E+08
200	2.24E+08	2.66E+08
250	1.29E+08	2.01E+08

Figure 4-11 demonstrates the trend of sheet resistance change as the function of pulse numbers. In general, by increasing the number of pulses, the sheet resistance decreases. Although in PLA samples, applying 3 to 5 pulses obtains low sheet resistance, 250 pulses on Si or SiN substrates can not provide the same amount of energy for GO patterns. The final sheet resistance of the rGO pattern is 10^7 times higher than the rGO pattern on the PLA substrate. This can be a result of the lower thickness of printed GO patterns on Si and SiN substrate. The thermal conductivity

of silicon and silicon nitride is much higher than PLA, which might conduct heat away from the printed GO patterns. Moreover, the absorption coefficient is different for polymers and Si-based wafers. Therefore, the amount of applied energy to the GO can be different. The lowest sheet resistance is achieved after applying 250 pulses on both substrates.

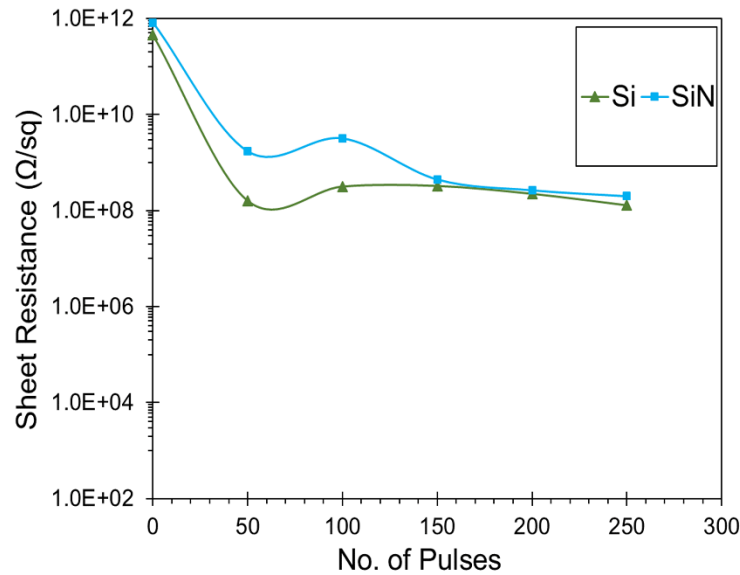


Figure 4-11. The sheet resistance of reduced patterns as a function of pulse number on Si and SiN substrates. The applied voltage is 3000 V, the on-time is 5 ms, and the off-time is 10 ms for all samples.

Another method to reduce the GO patterns on silicon is the thermal route. Thermal annealing can eliminate the oxygen groups in the GO structure and increase the conductivity. Table 4-3 shows different conditions of thermal annealing to reduce

the printed GO. Various temperatures and times have been utilized to achieve low sheet resistance for rGO. Figure 4-12 exhibits the measured sheet resistance of rGO for different cases. Based on the results, the temperature has the most significant effect on the final sheet resistance. Longer time and vacuum environment improve the reduction process for some cases, but their effect is less than temperature.

Table 4-3. The applied conditions and measured resistance of reduced GO ink via thermal route.

Case	Conditions			Sheet Resistance (Ω/sq)	
	Temperature ($^{\circ}\text{C}$)	Time (min)	Vacuum	Silicon (Si)	Silicon Nitride (SiN)
0	70	30	✗	4.53E+11	9.19E+11
1	200	30	✗	1.38E+07	9.78E+07
2	250	60	✗	3.21E+06	5.64E+07
3	250	30	✗	2.69E+06	2.85E+07
4	250	30	✓	4.73E+06	3.55E+07
5	300	30	✗	3.02E+06	4.05E+07

6	300	30	✓	3.48E+06	3.07E+07
7	300	90	✓	2.25E+06	2.39E+07

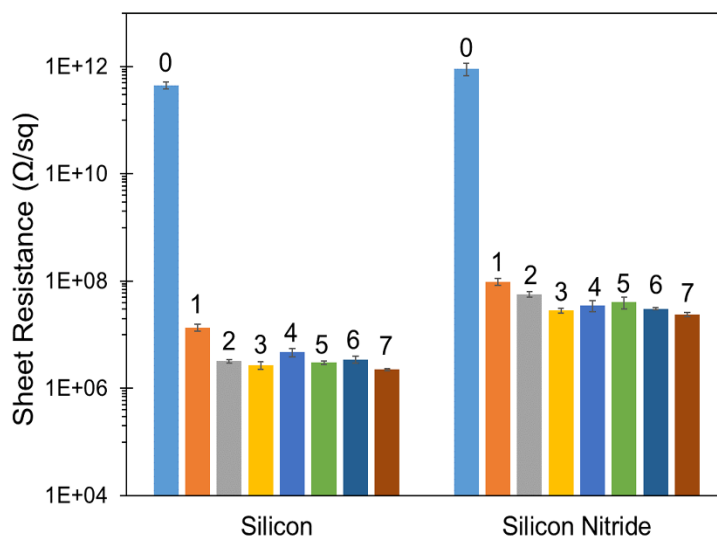


Figure 4-12. The sheet resistance of thermally reduced GO ink printed on Si and SiN substrates. The details of each case can be found in Table 4-3. Case 0 is before reducing the samples.

For the chemical route, hydrazine hydrate (HH) is used as the reducing agent. The nucleophile of hydrazine attacks the epoxide groups of GO and forms a hydrazine alcohol moiety. The formation of the alcohol moiety releases a water molecule and removes the hydroxyl groups in graphene oxide. At the end of the process, the high temperature eliminates all the residue of used hydrazine [78]. Figure 4-13

demonstrates the sheet resistance of printed GO on Si and SiN substrates before and after the reduction. By using HH vapor, a significant amount of conductivity is restored for the Si sample. The higher sheet resistance of printed rGO on SiN substrate is due to the low thicknesses. Although hydrazine hydrate is a strong chemical, it does not affect Si or SiN wafers. The sheet resistance of rGO on Si is $1.22 \times 10^6 \Omega/\text{sq}$, and on SiN is $4.63 \times 10^8 \Omega/\text{sq}$.

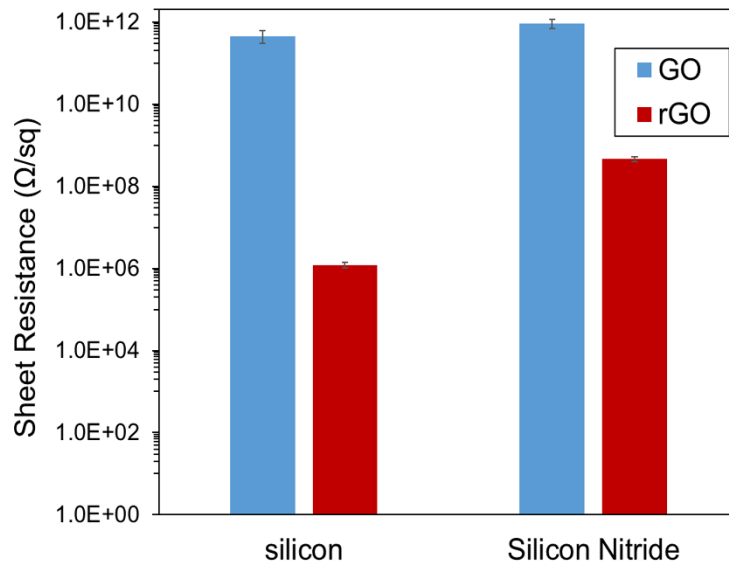


Figure 4-13. The sheet resistance of printed patterns on Si and SiN substrates, before and after reducing with hydrazine hydrate.

After investigating the properties of thin layer GO on Si and SiN substrate, multiple printing is utilized to increase the thickness of printed patterns and improve the quality of reduced GO. The printing process and parameters in multiple printing are similar to one-pass printing. The GO patterns are printed on substrates, dried at

70°C for 30 minutes, and this process is repeated multiple times. Several layers of printed GO ink increase the thickness of the final patterns. Figure 4-14 shows the profilometry scan across the multiple printed patterns on Si and SiN substrates. The printing and drying have been repeated five times (5x) for each sample. The average thickness of the GO pattern on SiN (Figure 4-14 (a)) increases to 50 nm after five times printing. The coffee ring effect is still noticeable in the sample. As shown in Figure 4-14 (b), the GO pattern's average thickness is 120 nm, and the thickness variance is higher along the surface of printed circles after multiple printing.

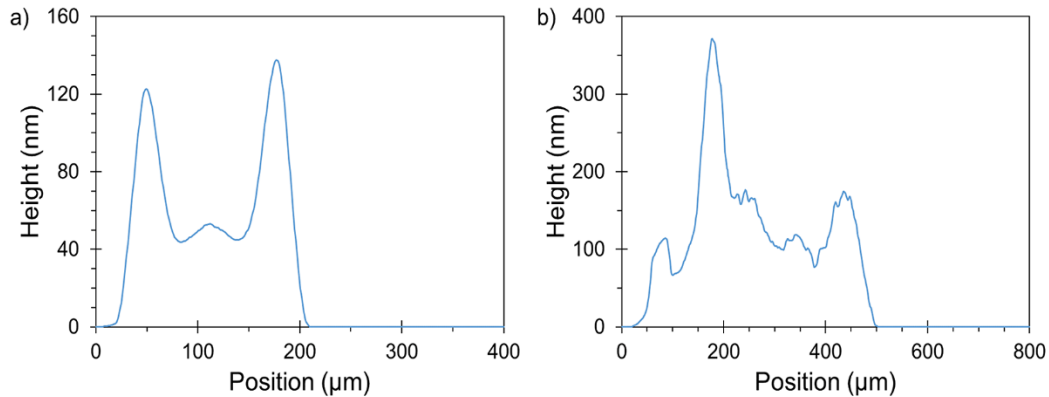


Figure 4-14. Profilometry scan across multiple (5x) printed patterns on a) SiN substrate and b) Si substrate. The patterns are printed 5 times and dried at 70°C for 30 minutes after each printing. By increasing the number of printing passes, the thickness increases significantly.

The change in thickness after multiple printing affects the sheet resistance of the reduced GO on both substrates. Figure 4-15 shows the comparison between the

sheet resistance of single and multiple printed patterns reduced with different methods. As it is predicted, the thicker samples show lower sheet resistance after reduction on both substrates. The reduced samples with the xenon lamp show more than 100 times change in the sheet resistance after multiple printing. For the thermally reduced sample on Si substrate, there is no change in sheet resistance after multiple printing. However, the thicker GO on the SiN substrate shows 10 times lower sheet resistance after thermal reduction. The reduced multiple-printed patterns via hydrazine hydrate vapor demonstrate the lowest sheet resistance.

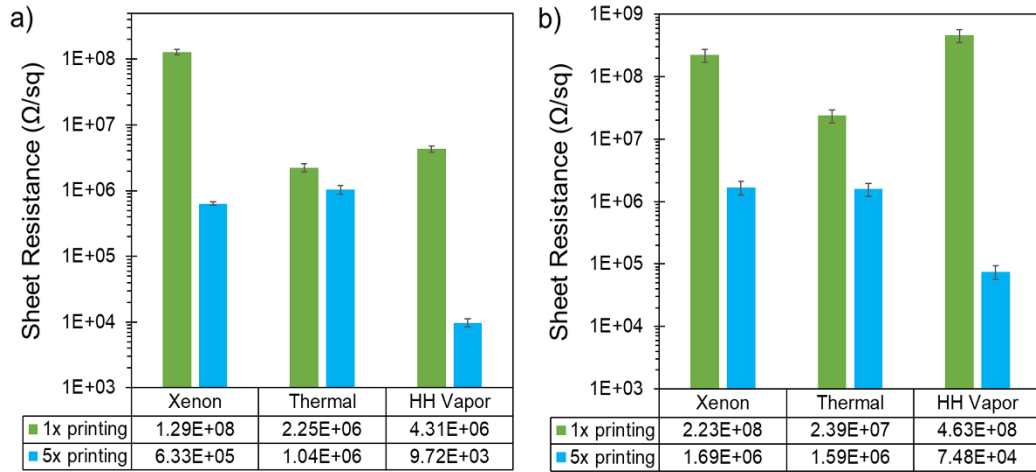


Figure 4-15. The sheet resistance of reduced GO printed for 1 and 5 times printing on a) Si and b) SiN substrate with different methods. The xenon reduction parameters: applied voltage=3000 V, on-time=5 ms, off-time=10 ms, and the number of pulses=250. The thermal reduction parameters: temperature=300°C, time=90 min, and vacuum atmosphere. The numbers in the tables are the calculated sheet resistance in Ω/sq .

Figure 4-16 shows the conductivity of printed GO patterns on 3D printed PLA and SiN wafer. The thickness of all the GO lines is around 50 nm. The printed GO is not conductive before reduction treatment. Using xenon lamp for 3D printed samples is effective and can restore conductivity. The conductivity of rGO on PLA is 2000 S/m. However, this reduction technique is the least effective method for the GO patterns on SiN wafers. The restored conductivity value of the GO pattern through the thermal route is very similar to the photothermal method, and it is not recommended for this sample. The most effective way is using hydrazine hydrate as the reducing agent. The conductivity of reduced samples with hydrazine hydrate is about 500 S/m, which is acceptable for reduced GO.

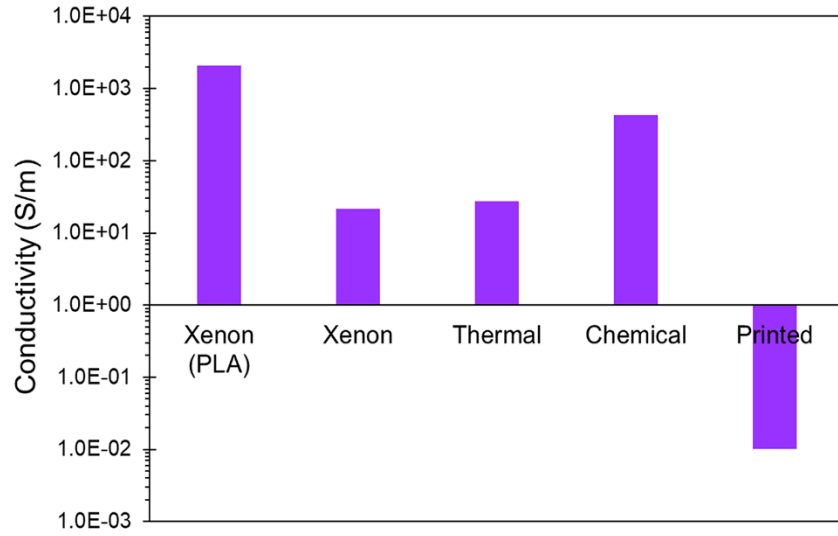


Figure 4-16. The conductivity of printed GO pattern on PLA and SiN substrates reduced with different methods. The xenon reduction parameters for PLA: applied voltage=3000 V, on-time=2 ms, off-time=10 ms, and the number of pulses=3. The xenon reduction parameters for SiN: applied voltage=3000 V, on-time=5 ms, off-time=10 ms, and the number of pulses=250. The thermal reduction parameters: temperature=300°C, time=90 min, and vacuum atmosphere. The printed column represents the conductivity of GO before any reduction treatment.

Figure 4-17 shows the Raman spectra for the GO and rGO on PLA and SiN substrate. The typical characteristic of the carbon material's spectrum contains D and G bands. The D band around 1350 cm^{-1} is due to defects in the structure. The G band at about 1550 cm^{-1} indicates the in-plane vibration of carbon atoms and multi-layer graphene formation [70]. As it is demonstrated, all the spectra contain the G and D bands. The intensity of the D band is comparable to G due to structural disorder induced from reduction. When the amount of disorder is high, the D + G

band also appears around 2950 cm^{-1} . The intensity of D + G is higher for reduced GO on SiN substrate due to using the hydrazine hydrate as the reducing agent. The chemical reduction is more intense than the photothermal method and increases the defects and disorder to a higher level [79].

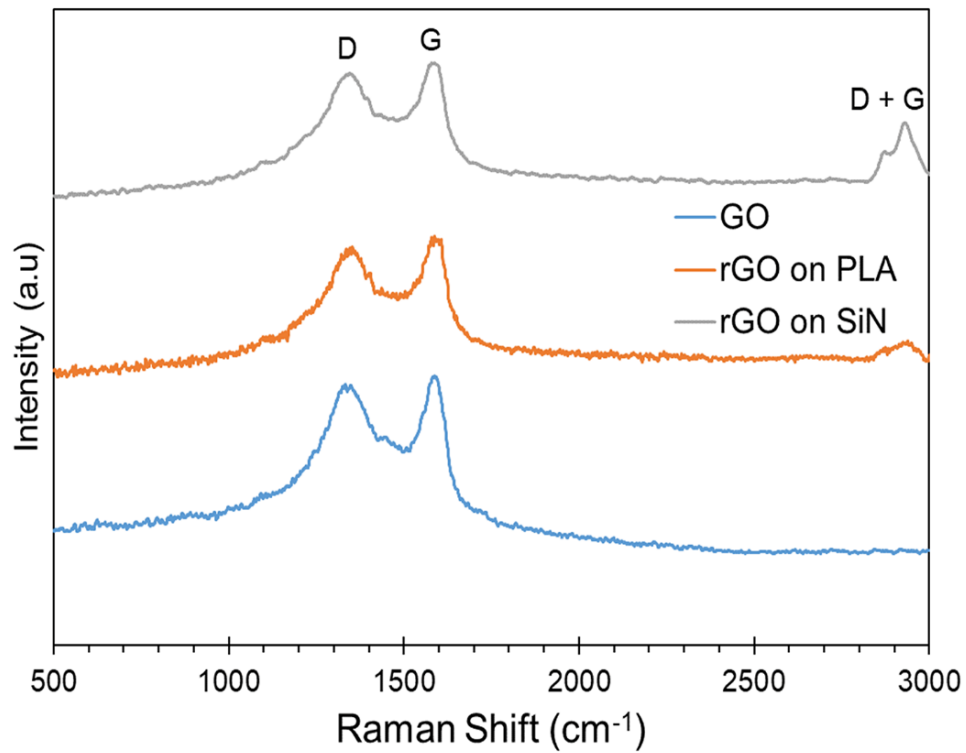


Figure 4-17. Raman spectra for printed GO pattern on PLA and reduced GO patterns on PLA and SiN substrates.

4.6 Conclusion

This chapter demonstrates ink-jet printing of graphene oxide ink on 3D printed PLA substrate. Extrusion printing of epoxy on the PLA creates a smooth surface ready for printing. Also, printing on silicon and silicon nitride is demonstrated without any surface modification. Based on the utilized substrate, the reduction method for transforming GO to rGO can be different. Highly conductive rGO (~ 2000 S/m) patterns can be obtained through xenon lamp reduction. Due to the properties of Si and SiN, the xenon flash reduction is not effective. However, with the chemical reduction, the conductivity of GO patterns can be restored. The ability to print on 3D printed substrates and SiN wafers can develop various sensing devices for different applications.

CHAPTER 5. GRAPHENE BASED ION-SENSITIVE FIELD EFFECT TRANSISTORS

5.1 Introduction

Recently, the electrical detection of chemical and biological species using different materials and devices has attracted significant attention. Field-effect transistors (FET) are one type of devices that can be modified and used to detect different stimuli. In FETs, conductivity can be controlled by applying an electric field, and small measured signals can be amplified [10]. Ion-sensitive field-effect transistors (ISFETs) are one type of FET device that can measure ion concentration in solutions. ISFETs are mainly used to measure H^+ or OH^- ions in solutions. Therefore, they are used as pH sensors [12]. An ion-sensitive material or membrane is used instead of conventional metal gates to adsorb H^+ or OH^- ions reversibly. This binding creates an electrical potential proportional to the logarithm of ion concentration, hence controls the surface potential and current of the ISFET and helps to detect pH [13].

Among different ion-sensitive materials, graphene is a promising candidate for FET fabrication due to its high carrier mobility, unique band structure, and large specific surface area. Graphene's high sensitivity and selectivity make it extremely useful for pH sensing [80]. The integration of graphene and semiconductor devices like FET and complementary metal-oxide semiconductors (CMOS) has been studied before. However, in CMOS fabrication, only a few used ink-jet printing to fabricate

the graphene as the sensing material. Graphene was printed on gold electrodes for breath analysis and humidity detection [81], [82]. In one study, a flexible substrate was used to fabricate FET, and graphene was ink-jet printed as the channel [83]. In another study, graphene was printed on Si/SiO₂ wafer as the bottom-gate, source, and drain of a MoS₂ FET [58]. However, none of these devices were used for pH detection. The integration of silicon FET with ink-jet printed graphene as the top-gate for pH sensing and other biosensing applications needs to be studied.

In this chapter, the integration of two complementary microfabrication techniques is investigated. First, a silicon JFET with open gates is designed. Then, a graphene oxide layer is ink-jet printed onto the open gate of the transistor. The printing behavior of graphene oxide ink on the JFET chip is investigated, and the I-V characteristics are measured. Finally, the JFET is used to detect the pH of different solutions. The integration of the well-established silicon fabrication technology with ink-jet printed graphene top-gate will allow the fabrication of different sensors on the same platform. This can be ideal for lab-on-chip applications and point-of-care diagnostics.

5.2 Experimental

5.2.1 Silicon chip Design and Fabrication

The JFET was designed with Tanner L-edit MEMS Design software. Figure 5-1 shows the final design of the chip. The silicon JFET chip design was according to the constraints of printed graphene oxide on silicon (Si) and silicon nitride (SiN) substrates. Each chip contained 35 devices with different dimensions. The designed channel widths were 1 and 2 mm. Various channel lengths from 10 to 200 μm were used in the design to see the effect of channel length on the I-V characteristics. The green parts on the design layout represent top side metal contact layers. The red mark in the middle is the silicon alignment marker, and the dark blue layer is the passivation opening to the channels. The chips were fabricated on silicon wafers by CMC at 3IT.Nano (Université de Sherbrooke).

Figure 5-2 illustrates the cross-section of the designed chips. The thickness of n-type silicon is $420 \pm 25 \mu\text{m}$. The p-type layer on top is boron-doped, and the thickness is 1.6 μm . Source and drain contacts are made of gold, and the bottom gate is aluminum-based. After deposition of the SiO_2 layer on p-type silicon, the whole chip is passivated with a silicon nitride layer. Finally, source and drain pads and top gates are etched, and the silicon device is ready for printing of the rGO gate. Figure 5-3 shows the fabricated chips. The designed chips on the wafer are

diced into individual dies, and the outcome is 52 chips with a dimension of 5x5 mm.

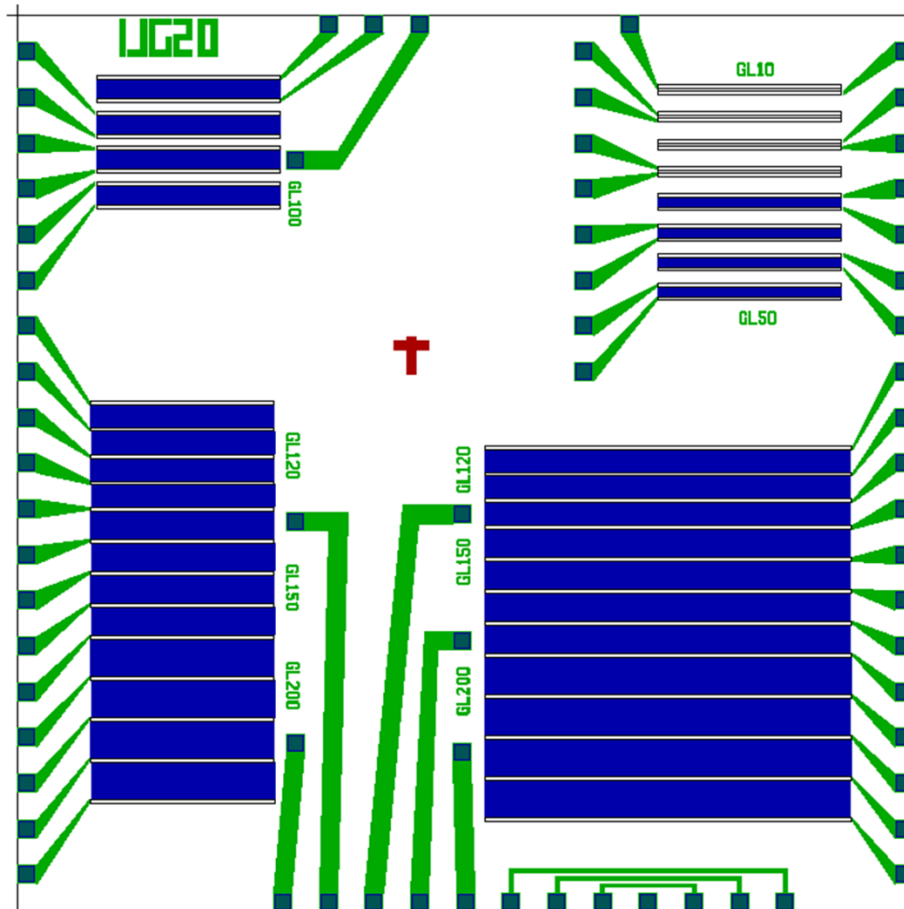


Figure 5-1. The final design of the JFET chip. The channel widths are 1 and 2 mm. The channel lengths are etched onto the substrate as labels next to devices. The green parts on the design layout are top side metal contact, the red mark in the middle is the silicon alignment marker, and the dark blue layer is the passivation opening to the channels.

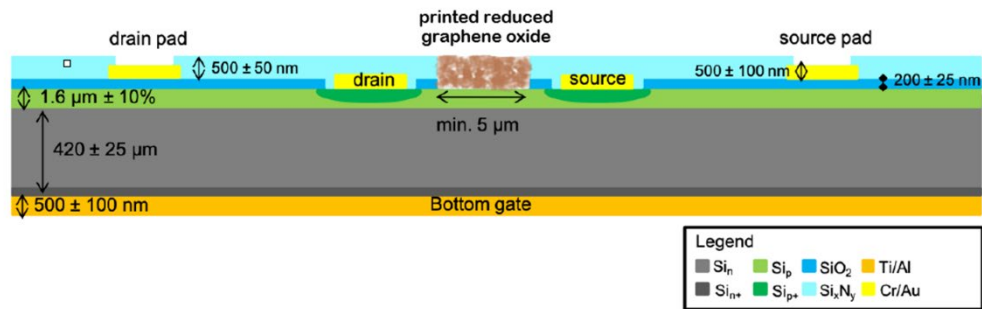


Figure 5-2. Schematic illustration of the fabricated chip with the printed reduced graphene oxide as top-gate. The minimum required dimensions are shown in the figure. © 2018 CMC Microsystems. All rights reserved.

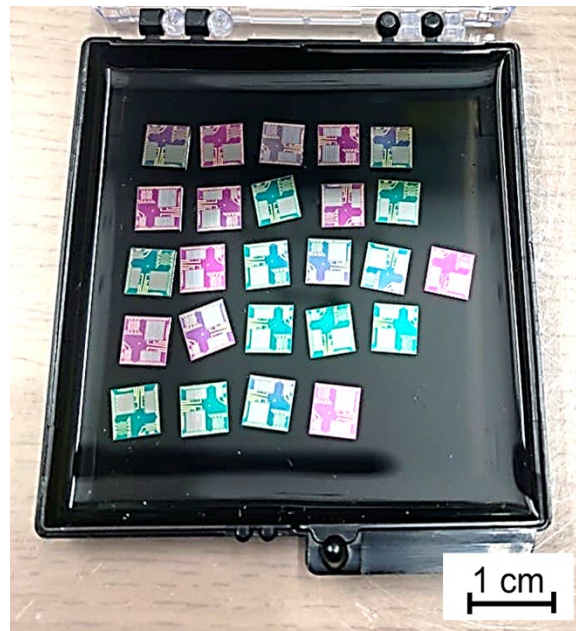


Figure 5-3. The fabricated chips by CMC at 3IT.Nano (Université de Sherbrooke). The designed chips on the wafer are diced into individual dies.

5.2.2 Printing and Characterization on the Chip

Thermal annealing was utilized to reduce the back-gate leakage and improve the JFET performance. The chips were annealed at 300°C for 30 minutes under vacuum atmosphere. A Plasmod plasma system was used to treat the surface properties of the chip before the ink-jet printing process. The air plasma power was 70 W, and the time was 4 seconds. The graphene oxide (GO) ink was used to print the top gate on the open channels of JFET. A custom-built piezoelectric drop-on-demand (DOD) ink-jet printer was used to print GO ink. The details of ink preparation can be found in section 4.2.1. Multiple layer printing was used to print thick GO top gates on the JFETs. Each GO top gate was printed ten times, and it was dried after each printing pass at 70°C for 15 minutes. The printed GO top gates were reduced with hydrazine hydrate (HH) vapor to restore the conductivity. The details of reduction can be found in section 4.2.2.

The JFET electrical measurements were done with a probe station with a semiconductor parameter analyzer (Keithley 4200A). For the I_d - V_d characteristics, the drain voltage was in linear sweep mode, and different bottom-gate voltages were applied to see the effect on the drain current. The bottom gate was linearly swept for the I_d - V_g characteristics, different drain voltages were applied, and the drain and gate currents were measured simultaneously. Three different solutions were used to see the effect of pH on the printed reduced graphene oxide (rGO) gate.

Hydrochloric acid (HCl) was diluted with deionized (DI) water to obtain the 1.5 and 4.5 pH. DI water was used as the third solution with a pH of 7. A small drop of the solution was placed on the JFET chips, and the IV characteristics were measured for each device.

5.3 Printing on JFET

Although the printing condition on Si and SiN substrates were optimized before, printing on JFET open channels can be challenging. Figure 5-4 shows the printed GO lines on the JFET. As it demonstrates, the channel is hydrophobic, and instead of uniform lines, printed lines tend to break into individual droplets. Based on contact angle measurements presented in Figure 4-6, Si and SiN substrates are hydrophilic. The hydrophobicity of JFET channels can be due to the JFET fabrication process. Therefore, to prepare the open channels for printing uniform GO lines, plasma treatment is needed. Since long plasma treatment can alter the device properties, only 4 seconds of treatment is used to improve the surface properties. Also, longer treatment times will decrease the contact angle to about 0° , and it is not possible to control the printed lines.

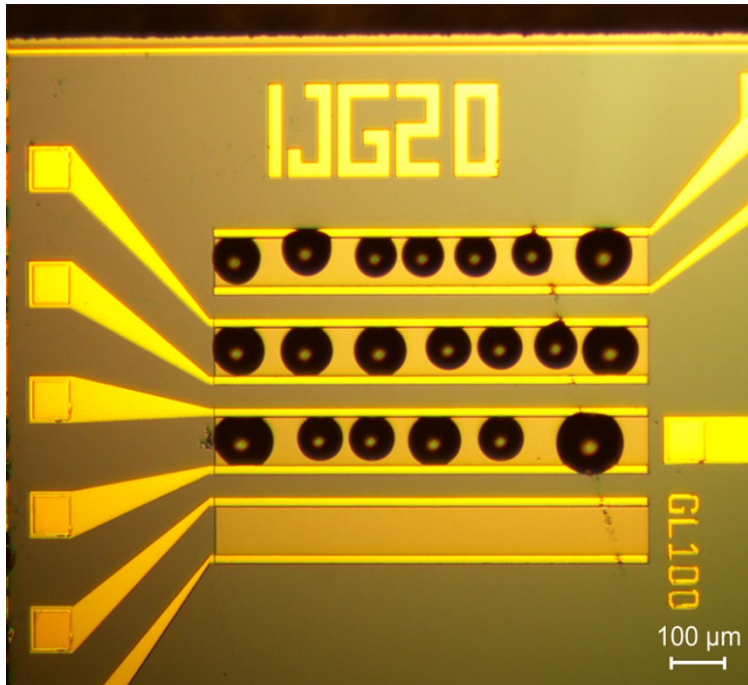


Figure 5-4. Optical micrograph of printed GO lines on the open channel of the JFET before any surface treatments. Instead of continuous lines, individual droplets are formed.

Figure 5-5 (a) shows the GO printed line on the plasma-treated JFET channel. The picture is taken with the ink-jet printer camera, right after printing the line and before the drying process. The plasma treatment changes the contact angle of GO ink on the channel, and uniform lines are formed after printing. Figure 5-5 (b) demonstrates the GO lines after drying. The printed lines are dried on the ink-jet printer stage at 70°C for 15 minutes. The dried line has a low thickness, and it is not easy to identify it on the JFET channel. A thicker GO top-gate is needed for the final application; therefore, multiple layer printing is utilized to increase printed lines' thickness.

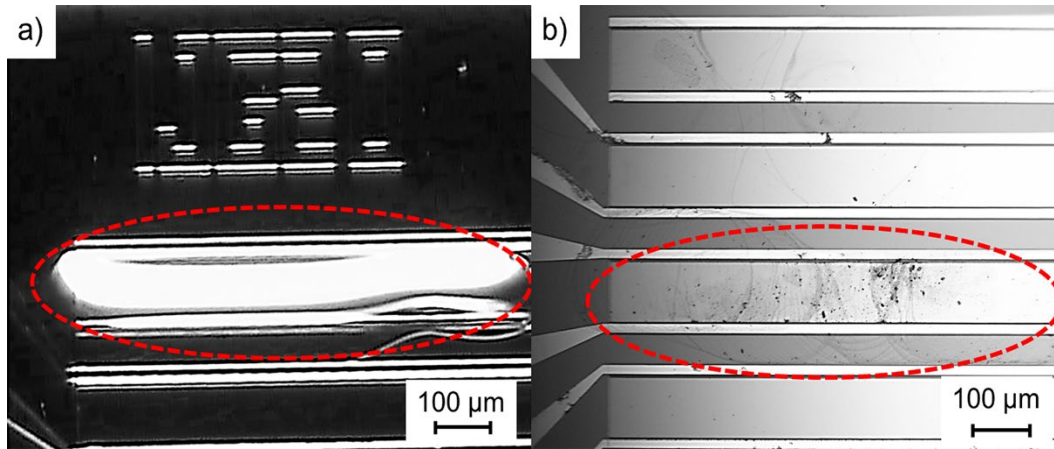


Figure 5-5. a) The printed GO line on the JFET channel after plasma treatment, and b) the GO lines after drying at 70°C for 15 minutes. The red circles show the boundaries of printed lines.

The optical micrograph of multiple printed GO lines is shown in Figure 5-6 (a). The lines are printed ten times (10x) and dried after each printing pass. Several layers of printed GO ink increase the thickness of the final patterns and improve the conductivity of rGO. Figure 5-6 (b) shows the rGO lines after the reduction process. The printed lines on the open channels are reduced with HH vapor. The resistivity of rGO top-gates is around 0.003 $\Omega\cdot\text{m}$. The lines show consistency after reduction, which is essential for the applications.

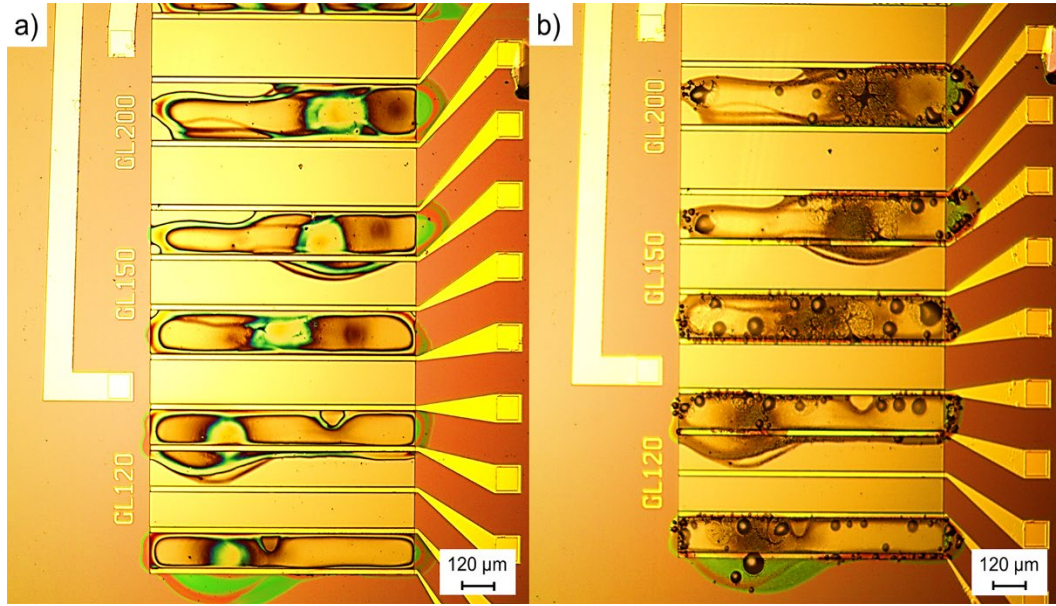


Figure 5-6. The optical micrograph of multiple (10x) printed GO lines a) after drying process and b) after reducing with HH vapor.

5.4 JFET I-V Characteristics

The output characteristics and transfer curves are measured for all the devices to characterize the performance of the JFET. The output characteristics (I_d - V_d curves) are obtained by sweeping the drain voltage from 0 V to -5 V for different applied back-gate. The transfer curves (I_d - V_g curves) are measured by sweeping the back-gate voltage from 1 V to -1 V for different drain voltages. The extracted parameters from these curves are I_{on}/I_{off} , $I_{DS,Sat}$, V_p , and saturation region. I_{on}/I_{off} is the ratio between on-state current and off-state current. High I_{on}/I_{off} is the indication of good performance. $I_{DS,Sat}$ is the drain saturation current when the gate voltage is zero. V_p or pinch-off voltage is the gate voltage that leads to minimum conduction in the

channel, and the drain current is close to zero when $V_g = V_p$. In the saturation region, the JFET is turned on. In this region, the drain current is controlled by the gate voltage, and changing the drain voltage does not affect the drain current.

Figure 5-7 (a) and (b) show the measured I-V characteristics for the JFET with 100 μm channel length and 1 mm channel width without annealing. As Figure 5-7 (a) demonstrates, $I_{DS,\text{Sat}}$ is 152 μA for the device. The pinch-off region starts at $V_g > 3$ V, and the saturation voltage is -1.5 V when $V_g = 0\text{V}$. $I_{\text{on}}/I_{\text{off}}$ can be calculated from I_d - V_g curves in Figure 5-7 (b). $I_{\text{on}}/I_{\text{off}}$ for this device is around 2, which is low for the JFET. The large gate leakage is one of the reasons for this low ratio. The gate current is dominant in most of the operating region and deteriorates the JFET performance

5.4.1 Annealing Effect

After measuring the I-V characteristics with back-gate biasing, the annealing treatment is used to improve the JFET performance. Figure 5-7 (c) and (d) show the I_d - V_d and I_d - V_g curves for an annealed chip at 300°C for 30 minutes under vacuum environment. Again, the channel length is 100 μm , and the channel width is 1 mm. $I_{DS,\text{Sat}}$ is 378 μA , and the saturation voltage is -2 V for the annealed chip. The $I_{\text{on}}/I_{\text{off}}$ is 4.5, which is two times higher than the non-treated device. The annealing process also decreases the gate leakage, and the drain current is dominant

over a wider gate voltage range in I_d - V_g curves. Based on the results, the annealing treatment is necessary to have a better performance in the JFETs.

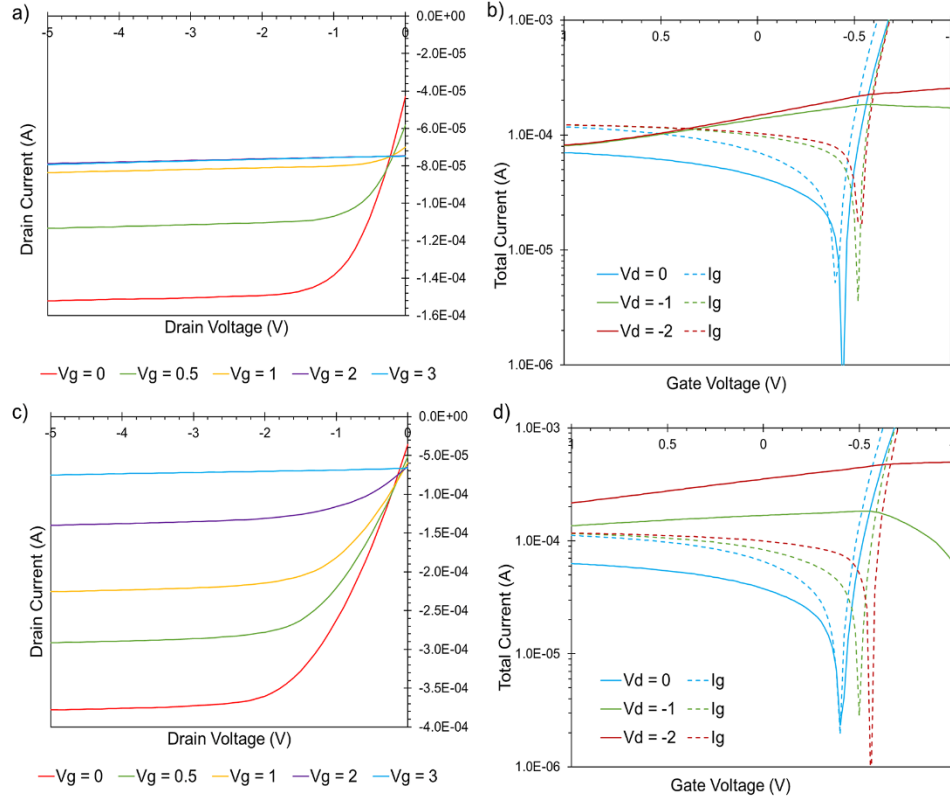


Figure 5-7. a) Output characteristics and b) transfer curves of an unannealed JFET. c) Output characteristics and d) transfer curves of annealed JFET.

The chips were annealed at 300°C for 30 minutes under the vacuum atmosphere. The channel length is 100 μm , and the width is 1 mm for all samples.

5.4.2 Channel Length Effect

One of the parameters that affects the I-V characteristics is the channel length. The designed JFET consists of different channel lengths to see the effect. For the long-channel devices, $I_{DS,Sat}$ is inversely proportional to the channel length, and longer channel lengths lead to lower $I_{DS,Sat}$ [84]. Hence I_{on}/I_{off} is also different for different channel lengths. Figure 5-8 shows the I-V characteristics for 50 μm and 200 μm devices. The channel width is 1 mm for both devices. $I_{DS,Sat}$ is 213 μA for 200 μm channel length, and it is 525 μA when the channel length is 50 μm . I_{on}/I_{off} is 2 for the long channel device and 5.4 for the short channel device. The gate current leakage is similar in all devices.

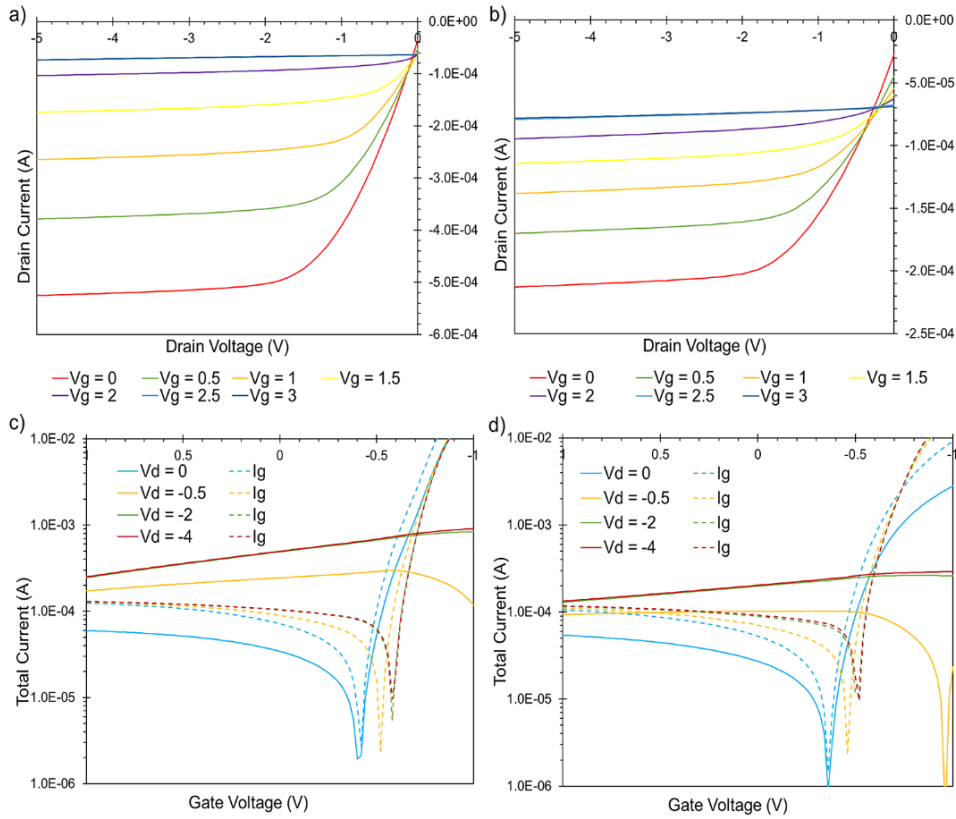


Figure 5-8. Output characteristics of JFETs with a) 50 μm and b) 200 μm channel length. Transfer curves of JFETs with c) 50 μm and d) 200 μm channel length. The channel width is 1 mm for all of the devices. The chips were annealed at 300°C for 30 minutes under a vacuum atmosphere.

5.4.3 Reduced Graphene Oxide Top-gate

The GO top-gate is printed on the open channels of the JFET as the soft material to detect pH of different solutions. The printed GO lines are reduced before measuring the I-V characteristics. Figure 5-9 (b) and (d) show the output characteristics and transfer curves for 120 μm channel length with rGO top-gate. The printed rGO does not change $I_{\text{on}}/I_{\text{off}}$ of the devices significantly. $I_{\text{on}}/I_{\text{off}}$ with rGO top gate is 2.6 and

without rGO is 2.5. The gate leakage is similar, and the operating gate voltage is between 1 V and -0.5 V in both devices. $I_{DS,Sat}$ is 460 μA for the device with rGO top-gate and 680 μA without rGO top-gate.

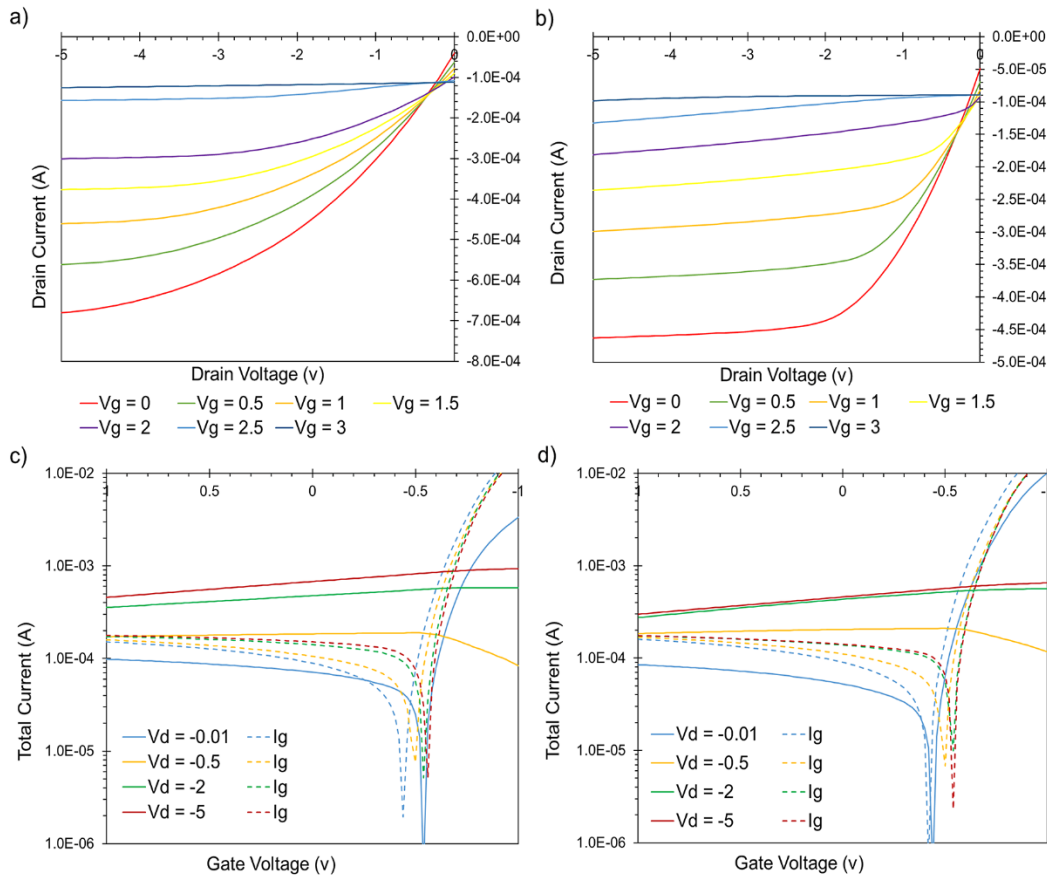


Figure 5-9. Output characteristics of JFETs with back-gate bias a) without rGO top gate and b) with rGO top gate. Transfer curves of JFET c) without rGO top gate and d) with rGO top gate. The channel length is 120 μm , and the width is 1 mm for all of the devices.

5.5 pH Detection

Three different solutions are used to characterize the sensitivity of JFET to pH. Figure 5-10 shows the effect of different pH on I_d - V_d characteristics of JFETs with and without rGO top-gate. The channel length is 150 μm , and the channel width is 1 mm for all devices. In both cases, with increasing solution acidity, $I_{DS,\text{Sat}}$ decreases. When there is no rGO top-gate (Figure 5-10 (a)), the pinch-off voltage also decreases with changing the pH of solutions.

Output conductance is used as the metric to show the change in the devices for different pH. The output conductance is calculated as following [85]:

$$g_0 = \left. \frac{\partial I_d}{\partial V_{ds}} \right|_{V_{gs}} \quad (\text{Eq. 5-1})$$

Figure 5-11 shows the change in output conductance for JFET with and without the rGO top gate. The output conductances are extracted from I_d - V_d curves, with the help of Eq. 5-1. As Figure 5-11 (a) demonstrates for JFETs without rGO top gate, when the solution's acidity increases, the conductance first increases and then decreases. Also, with increasing the gate voltages, the conductance decreases. Figure 5-11 (b) shows the conductance change in percentage from pH =7. When the pH changes to 4.5, the conductance increases about 10 percent for all samples and decreases when the pH is 1.5. Although the JFET without the rGO top gate shows sensitivity to different pH, there is no specific trend in the graphs. Since the

change in conductance is not monotonic, it is impossible to use interpolation and predict the pH of an unknown solution. For instance, when the measured conductance is around 0.0004 S, and the gate voltage is 0 V, the solution's pH can possess two different values. Figure 5-11 (c) shows the output conductance for JFET with rGO top gate. The range of extracted conductance for these devices is lower than the JFETs without the top gate. Unlike graph (a), the conductance decreases when the solution is more acidic. Also, for the larger gate voltages, the conductance is higher. For different applied gate voltages, the change in conductance is linear, and all of them follow the same trend. Figure 5-11 (d) shows the descending trend for conductance change in percentage with decreasing pH to 1.5. Not only the JFETs with rGO top gate show sensitivity to different pH, but this graph can also be used to interpolate measured conductance and determine the pH value for unknown solutions.

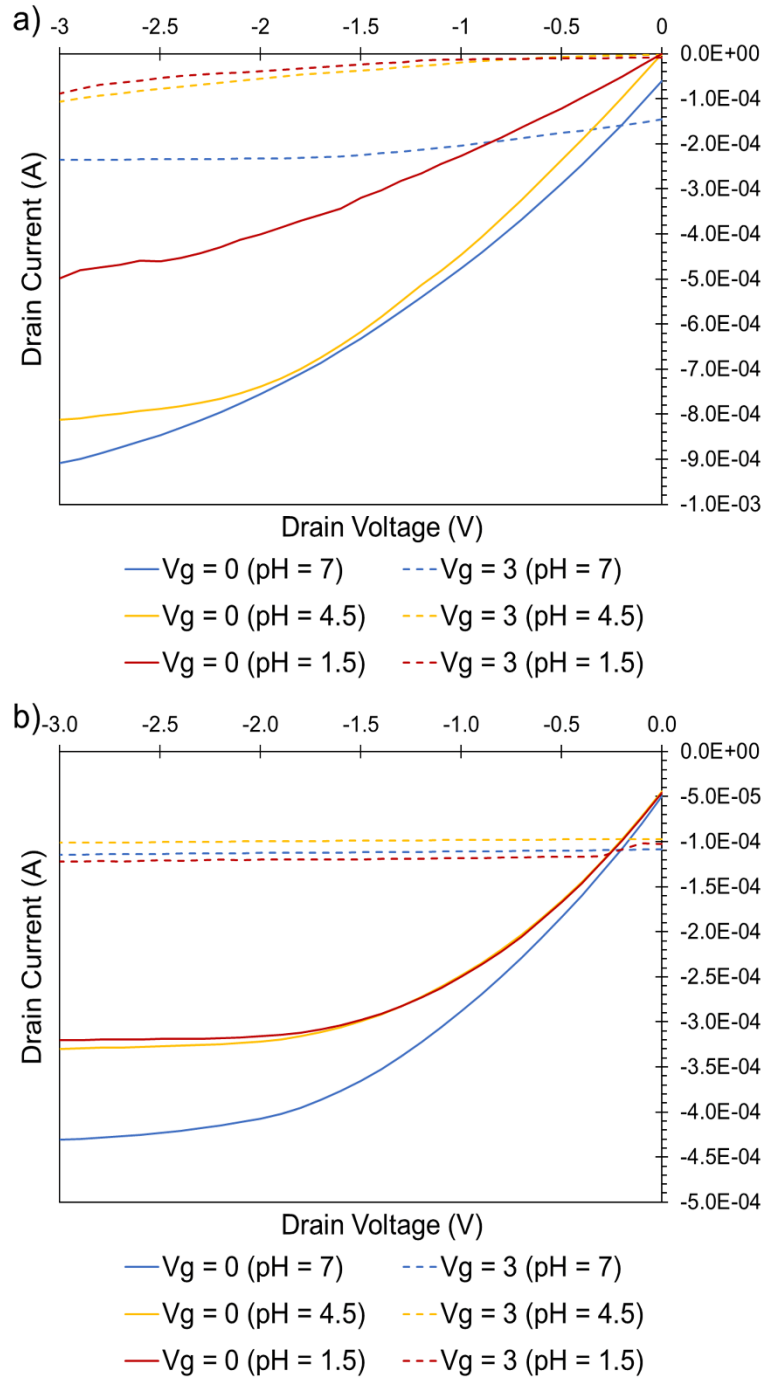


Figure 5-10. Effect of different pH on I_d - V_d characteristics of JFETs a) without and b) with printed rGO top-gate. The channel length is 150 μm , and the channel width is 1 mm for all devices.

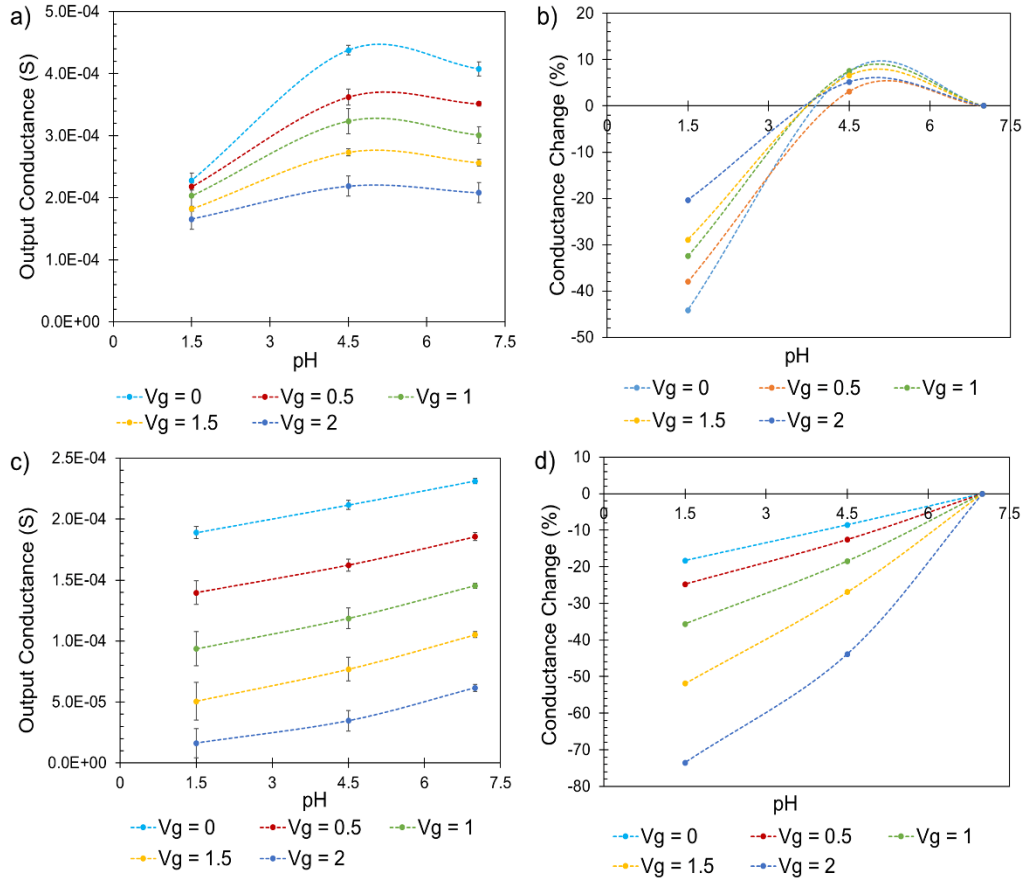


Figure 5-11. a) Output conductance and b) conductance change as a function of pH for JFET without top-gate c) Output conductance, and d) conductance change as a function of pH for JFET with rGO top-gate. The JFET with rGO top-gate shows the same trend for different gate voltages.

Different channel lengths are utilized to see the effect on pH detection. Figure 5-12 shows the saturation current for different channel lengths as a function of pH. As it was discussed in section 5.4.2, shorter channel length leads to higher $I_{DS,Sat}$. Also, for the same channel length, with increasing the acidity, $I_{DS,Sat}$ decreases.

Another parameter that shows the sensitivity of JFET to different pH is transconductance. The equation to calculate transconductance is as follow [85]:

$$g_m = \left. \frac{\partial I_d}{\partial V_{gs}} \right|_{V_{ds}} \quad (\text{Eq. 5-2})$$

Figure 5-13 shows extracted transconductance as a function of pH for different channel lengths in JFET with rGO top gate. The transconductances are extracted from I_d - V_g curves for saturated drain currents. The transconductance value is higher for shorter channels, and with increasing the channel length, the transconductance gain decreases. Also, for a specific channel length, higher acidity leads to lower transconductance gain. By using interpolation, the pH of different solutions can be predicted.

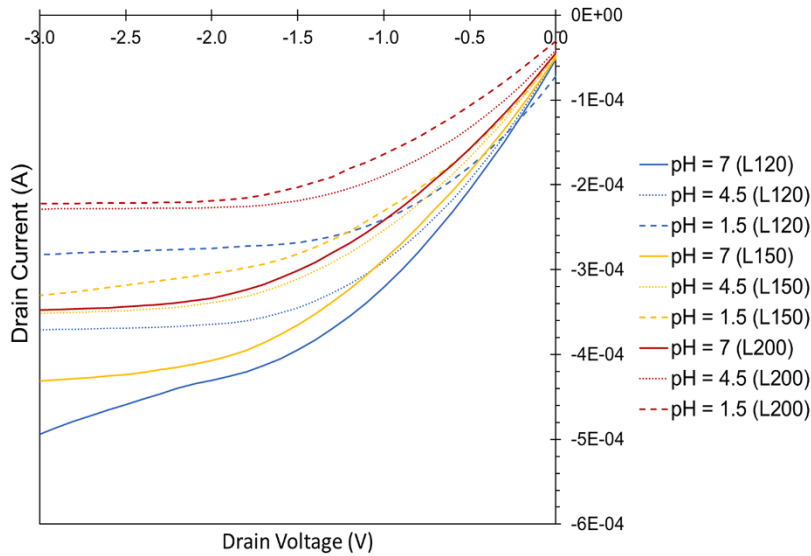


Figure 5-12. Drain saturation current for different channel lengths with rGO gate as a function of the solutions' pH.

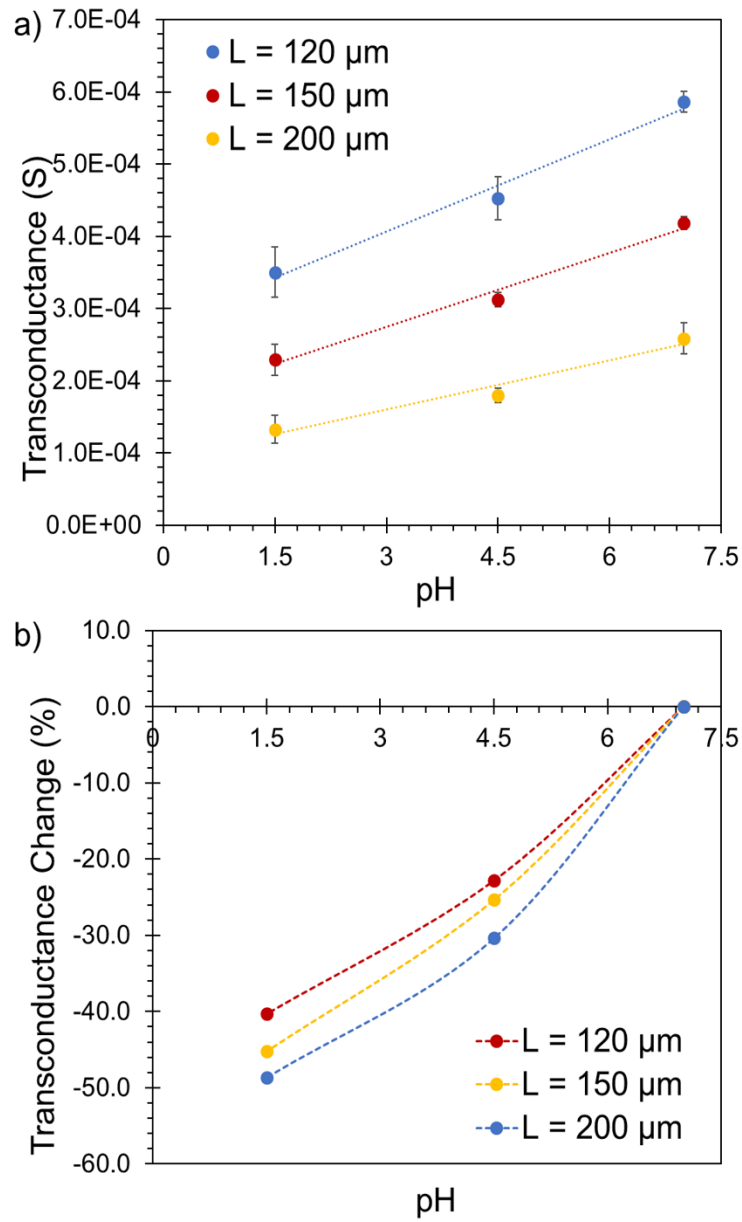


Figure 5-13. a) Extracted transconductance and b) transconductance change as a function of pH for different channel lengths in JFET with rGO top-gate. The channel width is 1 mm for all devices.

To test the durability of the rGO top-gate, the pH measurement is performed ten times, and the change in transconductance is recorded each time. Figure 5-14 demonstrates the change in transconductance after each testing cycle. The tested device has 200 μm channel length and 1 mm width. A solution with a pH of 1.5 is used to perform the test. As demonstrates in Figure 5-14, there is a jump after the first measurement, and after that, the transconductance does not change significantly anymore. Although the used solution is very acidic, the rGO top gate is very stable for pH measurements.

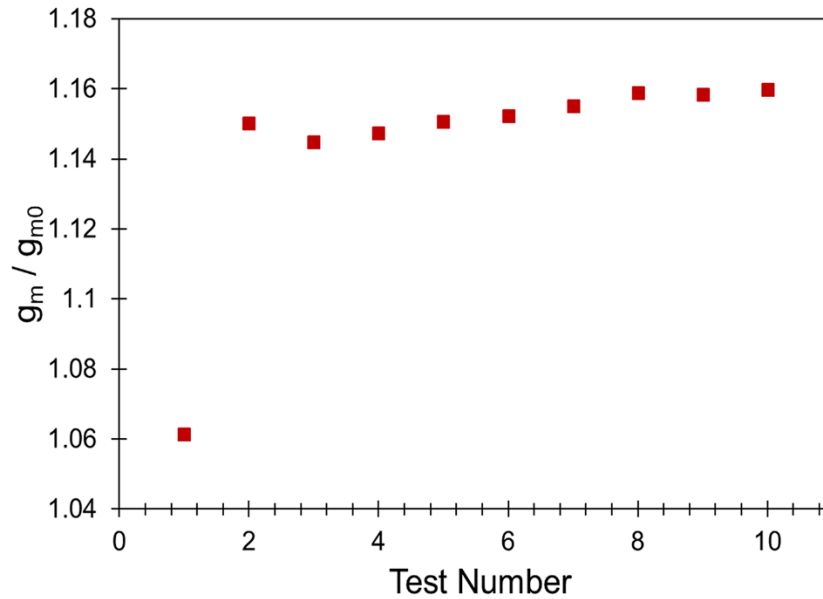


Figure 5-14. The change in transconductance after 10 times testing for JFET with rGO top gate. The channel length of the device is 200 μm , and the channel width is 1 mm.

5.6 Conclusion

This chapter demonstrates the integration of two complementary microfabrication techniques. JFET chips with open gates are designed based on ink-jet printing constraints. rGO is used as the soft material and ink-jet printed onto the open gates of the transistor. The I-V characteristics of JFET are measured for different conditions. The results show that heat treatment can improve the performance of JFET. Also, short channel devices are proved to perform better. Finally, the JFET is used to detect the pH of different solutions. The JFET without top-gate shows some sensitivity to pH, but it is not enough for a pH sensor. The rGO top-gate shows sensitivity to pH and the extracted data can be used to predict the pH of unknown solutions. The integration of the well-established silicon fabrication technology with ink-jet printed graphene top-gate will allow different sensors to be fabricated easily next to each other on the same silicon platform. These compact sensor arrays will be ideal for lab-on-chip applications and point-of-care diagnostics.

CHAPTER 6. CONCLUSION AND FUTURE WORK

In this chapter, the conclusions from this work are summarized. Then, suggestions are made for future work that could specifically build on the results of this thesis.

6.1 Conclusions

In this thesis, graphene-based devices are fabricated with low-cost methods on different surfaces. The integration of graphene with 3D printed structures through the LIG or ink-jet printing techniques provides flexibility and high conductivity. Also, the ability to fabricate different graphene patterns makes it ideal for various applications. The integration of ink-jet printed graphene with semiconductor devices like silicon-based field effect transistors opens up many sensing applications.

In chapter 3, 3D printed polyetherimide is converted into graphene by using a CO₂ laser. Different parameters are investigated to optimize the sheet resistance of obtained graphene. The same technique is used for a commercial polyetherimide, but the results are different. The lowest sheet resistance is achieved by using 40% laser power, and it is around 10 times lower for 3D printed polyetherimide. The material characterizations show that the morphology of obtained graphene on different substrates is different. However, the chemical composition of different

samples is similar after conversion. Also, because of the rearrangement of chains during the 3D printing process, the thermal analysis of the 3D printed polyetherimide shows different results.

In chapter 4, graphene oxide (GO) ink is ink-jet printed on novel substrates like 3D printed polylactic acid (PLA), silicon (Si), and silicon nitride (SiN) wafers. A layer of epoxy is printed on the 3D printed PLA to smooth the surface. Also, printing on silicon and silicon nitride is demonstrated without any surface modification. The printing condition on each surface is optimized, and different reduction methods for transforming GO to reduced graphene oxide (rGO) are utilized. Ink-jet printed rGO patterns with a conductivity of 2000 S/m can be obtained through xenon flash lamp reduction on 3D printed PLA. Due to the properties of Si and SiN, the xenon flash reduction is not practical. However, by using hydrazine hydrate as the reducing agent, GO patterns' conductivity can be restored up to 500 S/m.

In chapter 5, the integration of two complementary microfabrication techniques is demonstrated. Junction field effect transistor (JFET) chips with open gates are designed based on ink-jet printing constraints, and rGO is ink-jet printed onto the transistor's open gates as the sensing material. Different characteristics like I_{on}/I_{off} and $I_{DS,Sat}$ are extracted from I-V curves to see the effect of different conditions. The results show that heat treatment can improve the performance of JFET. Also, short channel devices are proved to perform better. Finally, the JFET is used to

detect the pH of different solutions. The change in output conductance and transconductance shows the sensitivity of rGO top-gate to pH.

6.2 Future work

Due to the low sheet resistance of obtained laser-induced graphene on 3D printed PEI, there are several ways to use it in a device. The designed strain gauges can be tested in a strain sensor setup. The ability to use this technique for strain sensor fabrication allows testing different patterns for strain gauge. In addition to the serpentine strain gauge, an interdigitated pattern could be used to detect the applied strain. Since the substrate is fabricated by 3D printing, different structures with complex 3D designs can be built with graphene conductors. Also, The engraved patterns have the potentials to be used as supercapacitors and electrochemical sensors.

In the GO printing process, the ink formulation can be optimized to suppress the coffee ring effect. Also, symmetric printing can be utilized to remove the bulges in printed lines. One idea in this field is to print strain sensors on the 3D printed substrate. PLA is very flexible and a good option for strain sensor fabrication. Also, more complicated 3D printed structures can be 3D printed as substrates. The cubic substrate with rGO conductors is a suitable device for pressure sensors. Although

the flash reduction process is optimized, further optimization can lead to higher conductivity of reduced graphene oxide.

In the pH detection process, instead of the back-gate sweep, the voltage can be applied to the solution on the rGO top-gate. A silver/silver chloride electrode is needed to apply the voltage to the solution, and a microfluidics setup can be designed to contain the solution. In that case, the back-gate can be biased to improve the performance of the transistor. The fabricated pH sensor can be modified with various functionalizations, for example to use it as an insulin detector. Due to the large surface area and unique structure, the functionalization of graphene is possible. Functionalizing of rGO with insulin specific aptamer can be done through immersion or ink-jet printing. With few modifications, the device could also detect different gasses like NH_3 , NO_2 , and H_2 .

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