CMOS Compatible Carbonization of Polymer for Electrochemical Sensors

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To the Graduate Council:

I am submitting herewith a dissertation written by Mohammad Aminul Haque entitled "CMOS Compatible Carbonization of Polymer for Electrochemical Sensors." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Electrical Engineering.

Nicole McFarlane, Major Professor

We have read this dissertation and recommend its acceptance:

Andre Zeumault, Garrett S. Rose, Nickolay V Lavrik

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(Original signatures are on file with official student records.)
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I am extremely grateful to my advisor Dr. Nicole McFarlane for all of her valuable suggestions, guidance, and support during my Ph.D. I am specially grateful to her for giving me the opportunity to work at Oak Ridge National Laboratory on materials processing.

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Abstract

Carbon-based electrodes that are integrable with CMOS readout electrodes possess great potential in a wide range of cutting-edge applications. The primary scientific contribution is the development of a processing sequence which can be implemented on CMOS chips to fabricate pyrolyzed carbon microelectrodes from 3D printed polymer microstructures to develop lab-on-CMOS monolithic electrochemical sensor systems. Specifically, optimized processing conditions to convert 3D printed polymer micro- and nano-structures to carbonized electrodes have been explored in order to obtain sensing electrodes for lab-on-CMOS electrochemical systems. Processing conditions have been identified, including a sequel of oxidative and inert atmosphere anneals to form pyrolyzed microstructures on metallized substrates. Developed processing sequence was optimized to improve shape retention alongside maintaining an electrical insulation over the metallized substrate and around the carbonized precursors. It has been demonstrated that oxidation of titanium metal layer can be exploited to develop electrically insulating titanium oxide around the pyrolyzed precursors in a self-aligned manner. Nonetheless, substantial shrinkage of 3D printed polymeric precursors is unavoidable during their carbonization process. Moreover, primary steps of carbonization produces catalytically active titanium oxide which causes further reduction of carbon and serious artifacts in the carbonized microstructures. As such, an optimized processing sequence has been developed to reduce these detrimental effects of titanium oxide on reserving the shape of pyrolyzed polymers. The processing sequences were characterized in terms of their influence on the growth of titanium oxide and dimensional changes in the 3D printed polymers. Besides, the degree of carbonization of pyrolyzed precursors was evaluated using impedance and Raman spectroscopy. Electrical current-based localized Joule heating was used to overcome incomplete pyrolysis and analytical
approximation and FEM-based COMSOL simulation were performed to determine the required processing conditions and potential outcomes. Increase in electrical conductivity of partially pyrolyzed polymer was observed by increasing anneal time within CMOS compatible temperature windows and by increasing ambient temperature of the partially pyrolyzed polymer. Using a high electrical bias and elevated ambient temperatures, an estimated average temperature of 727 °C was obtained within the active section of the precursor using localized Joule heating. This approach experimentally verified the feasibility of achieving complete carbonization of 3D printed precursors using CMOS compatible partial pyrolysis followed by localized Joule heating.
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Chapter 1

Introduction

An electrochemical sensor transforms electrochemical information (either of only one sample component or the entire sample composition) into a signal that can further be inspected to analyze the sample environment or the sample itself. It usually contains a receptor and a transducer. The receptor converts the sample information into a physical or chemical signal having a specific sensitivity. The transducer converts this signal to a user-readable value that can be further analyzed to interpret the sample information. Electrochemical sensors are extensively used in a wide-range of applications, such as the healthcare sector, environmental inspection, and food quality monitoring. In environmental monitoring, they can be used for arsenic, mercury, H\textsubscript{2}O\textsubscript{2} (in melamine strip testing), trinitrotoluene (TNT), and toxic metal ions detection [16, 101, 63, 103, 138, 124]. In food quality inspection, they can be used for detection of bisphenols, food colourant, potentially carcinogenic Ochratoxin A (OTA), and Olaquindox [67, 35, 90, 126]. In the healthcare sector, electrochemical sensing has been helpful in applications, such as ATP, glucose, lactate, DNA sensing, bacteria, and virus biomarkers [74, 5, 19, 117, 22, 85]. Development of wearable non-invasive electrochemical sensors have particularly attracted attention due to their applications in pH monitoring, lactate, amino acids, antioxidants, and metabolites detection [78, 56, 83, 18, 123]. Therefore, development of compact, cost-effective, highly sensitive electrochemical sensor has been a significant research focus over the past few decades.

The working principle of a glucose sensing system using a working electrode can be explained as follows, the electrodes are first activated with an enzyme (glucose oxidase...
(GOx)) and a co-enzyme (horseradish peroxide (HRP)). Oxidation of glucose using GOx produces gluconic acid and hydrogen peroxide (H₂O₂) as a byproduct. HRP helps in reducing (H₂O₂) in a solution that is enriched with electrolyte. The working electrode of the electrochemical cell provides electrons for the reduction to take place and this electron transfer is sensed by the readout electronics. The reactions involved in the system are outlined below

\[
\text{Glucose} + 0_2 \xrightarrow{\text{GOx}} \text{Gluconic acid} + H_2O_2
\]  

(1.1)

\[
H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O
\]  

(1.2)

The enzyme mediated technique for glucose can be extended to other analytes such as neurotransmitters (eg. serotonin and dopamine). Therefore, biocompatible electrodes play an important part in neurotechnology as a bidirectional interface. They are useful in both sensing signal from the nervous periphery and delivering signal to the system through stimulation. They work like wiretaps into the neural systems to provide external signal readout thereby providing insightful information about the structure and function of the nervous system [31, 106]. Thus, they can help the treatment of motion and sensory disorders existing in different patient groups, such as chronic pain, spinal cord injury, epilepsy, bacterial diseases, cancer, and heart diseases. For instance, electromechanical prosthetic devices can monitor electrical signals from cerebral cortex or nervous systems thereby recording intent of limb motion [20, 37]. As such, modern therapeutic systems can stimulate the nervous system to treat chronic pain [60], spinal cord injury [45], and epilepsy [34].

The improvement of applicable interfaces between microelectronic circuits and biological systems using different kinds of electrodes has gained attention in research community in recent times. An ideal electrode needs to be small enough to be integrable with sensing electronics and highly sensitive to the target nervous system. However, care needs to be taken to avoid damage to the neural tissue system upon insertion of the electrode. Recent progress in nanofabrication methods and tools have facilitated developing nanometer sized, high density electrode interfaces. Recent research trends are shifting towards the use of
nanoparticles and nanowires as functioning electrodes. Fig. 1.1 shows a few prominent works in neuroelectrode research implementing standalone and arrays of carbon-based electrodes. These carbon-based interfaces are of particular significance due to their applications in implantable biosensors and other biomedical applications.

Development of complementary metal-oxide-semiconductor (CMOS)-based large scale integrated circuits for system-on-chip applications has enabled complex signal processing at a reasonable cost. They can record, process, and generate desired signals for specific applications. Thus, they can not only record neural activity, but also change the activity with stimulating electrical signal. A widely used approach in implantable biosensing devices is based on integration of fabricated micro or nano electrodes with electrochemical characterization methods [95, 17]. 3D printing has also recently been widely implemented in designing cutting-edge electrochemical sensing systems [96, 113, 28]. Therefore, development of fabrication techniques enabling integration of highly sensitive and densely packed electrodes with readout electronics for data analysis are of growing significance.

1.1 Motivation and research goals

Conventional implementation of carbon micro and nanostructures for electrochemical sensing application usually includes processing sequence that is not compatible with widely used complementary metal-oxide-semiconductor (CMOS) signal processing circuitry. The main reason for this is the high processing temperature for carbonized electrode fabrication. Such high temperature can easily degrade the performance of CMOS electronics. Therefore, heterogeneous integration of carbon-based electrodes with CMOS electronics has gained extensive research efforts [15, 14, 76]. Furthermore, carbonization of 3D printed polymer microstructures has shown promise in this regard compared to more traditional methods such as vertically aligned carbon nanofibers (VACNFs) using plasma enhanced chemical vapor deposition (PECVD) [131, 75, 2, 134]. Inspired by the recent progress in research of two-photon polymerization-based (2PP) stereolithography [36, 89] and its efficient application in electrochemical biosensing, this work aims to develop microelectrodes by pyrolyzing precursors 3D printed using 2PP for integration on CMOS chips (Fig. 1.2). In this work,
**Figure 1.1:** (a) Microwire arrays [108]: 1. Microwire cubes within the housing that was used to collect data from monkey cortex, 2. A bundle of closely fitted microwires. b SEM image of a working carbon microelectrode [59]. (c) An array consisting of 16 arrays of carbon fibers with diameter of \(\approx 26 \, \mu m\). Blue box shows a carbon fiber and red box shows the exposed tip of a carbon fiber [39]. (d) A gold nano-electrode with diameter of \(\approx 100 \, nm\) on a tip made of tungsten [54].

**Figure 1.2:** Monolithic CMOS platform including carbonized electrodes and readout electronics.
several processing sequences have been developed to fabricate 3D carbon microelectrodes that are promising for lab-on-CMOS electrochemical sensors, while also producing electrical insulation of the surrounding metal in a self-aligned fashion. The specific challenges addressed in this work are as follows:

- Carbonization of polymer usually requires temperature of 900 °C or above. However, CMOS electronics experience significant structural and functional changes if the temperature goes beyond 525 °C [109].

- Although the carbon microelectrodes themselves need to be connected to the readout electronics, all metalization in the microelectrode surrounding need to be insulated so that electrochemical analytes do not react with them.

- Carbonization of polymer microstructures usually entails significant change in shape and size of the structure [7, 110]. Thus, retention of the desired shape of carbonized microelectrode needs to be ensured. It is expected that these structural changes would restrict use of various design and processing conditions in order to obtain optimized carbon microelectrodes for specific applications.

Exploiting polymer precursors conventionally used in two-photon polymerization, a processing sequence has been demonstrated to fabricate carbonized microelectrodes within a CMOS-compatible temperature window. Also, this processing sequence has been optimized taking into consideration the physiochemical changes experienced by the microstructures. To overcome partial pyrolysis obtained from CMOS-compatible high temperature processing, current-driven localized heating (conventionally known as Joule heating) through the partially carbonized conductive polymer structure has been utilized to convert partially pyrolyzed polymer to a completely carbonized polymer. Analytical approximation and finite element-based COMSOL simulation have been conducted to determine optimum processing conditions and potential outcome. Finally, experimental observation showed the feasibility of using this approach to achieve irreversible change in conductivity resulting from localized Joule heating in a 3D printed partially carbonized structure. Design, processing sequence, and outcome of the processing in terms of material and electrical characterizations have been discussed in this dissertation.
1.2 Dissertation Outline

The rest of this dissertation is organized as follows. Chapter 2 presents the literature review over printed electrode sensors including various printing technologies and carbon-based sensors. Chapter 2 is an extensive literature review which discusses the pyrolysis of 3D printed polymer within a CMOS-compatible temperature window alongside structural and electrochemical characterization. The working principle of the processing tools and their importance in the developed processing sequence to maintain CMOS compatibility is also explained in chapter 2. To overcome the issue of partial pyrolysis found in literature, chapter 3 proposes a process development using localized Joule heating toward obtaining completely pyrolyzed polymer in a CMOS-compatible environment. To overcome limitations observed in chapter 3, localized Joule heating alongside analytical simulations and estimated temperature within the heated structure is proposed in chapter 4 and chapter 5 summarizes the novel experimental findings of this research while also indicating potential future research paths in this technology.
Chapter 2

Literature Review

Portions of this chapter have been published as:


2.1 Printed Electrode Sensors

For the purpose of electrochemically sensitive electrode fabrication, screen printing is the most commonly used technology. While this offers fast production, it is limited to 2D printing and design complexity. Thus, additive manufacturing-based printing technology has taken the lead in sensor fabrication due to the advantage of generating fast prototypes at lower production cost and ability to design complex electrodes. In this method, the primary step usually includes designing model layer-by-layer in a computer aided design (CAD) software before importing the designed file in the printing instrument for printing. Few of the frequently used printing technologies used so far are: inkjet printing, AFM dip-pen nanolithography, and extrusion based printing. Inkjet printing normally uses thermoplastic and wax materials, solvent inks, UV-curable inks, and dye sublimation inks for printing. Solvent inks usually consist of inexpensive volatile organic compounds. UV-curable inks consist of acrylic monomers that is cured by exposing to strong UV light using mercury-vapor lamp or UV LED. Dip-pen nanolithography (DPN) uses small organic
molecules, such as alkanethiols and mercaptohexadecanoic acid for printing. These materials were used because they can form well-ordered self-assembled monolayers (SAM). Later on, sol-gel precursors, colloidal nanoparticles, polymers, and biomolecules (proteins and oligonucleotides) were used for printing using dip-pen nanolithography [38]. Extrusion-based printing uses thermoplastics (such as PolyLactic Acid, Thermoplastic PolyUrethane, and Nylon), ceramics, and concrete. Another approach is to achieve carbonized electrode through pyrolysis which has been discussed later in section 2.2, since that is the focus of the research discussed here.

Some of the most significant works on using inkjet printing for sensing applications in the twentieth century were conducted in [57, 84, 46]. Inkjet printing was used for precise deposition of enzyme and subsequent immobilization onto a sensing ion sensitive field effect transistor (ISFET) device [57]. Printing was controlled by pulses [57]. The droplet positioning was controlled using a microscope [57]. Inkjet printing was also used to deposit mediator solution (instead of enzyme) whereas working carbon electrodes were fabricated using screen printing on a PVC substrate [84]. Functionality and tetrathiafulvalene (TTF) -coupling of enzyme were verified by comparing with a calibration curve in a three-electrode system. Concentration was changed by multiple cycles of deposition using the print head [84]. A combination of screen printing (for working lactate electrodes on PVC substrate) and inkjet printing (for conducting membrane deposition) to develop a 3-electrode electrochemical cell. Vinyl ink insulation was followed by attachment of conducting track terminals to the working electrode lead [46]. A low-cost recyclable paper-based 3-electrode platform was fabricated where working electrode and counter electrode were directly inkjet-printed whereas quasi-reference Ag/AgCl electrode was formed by electrochemically depositing AgCl over inkjet-printed Ag electrode [70] (Fig. 2.1(a)). Furthermore, surface modification, such as chemical reaction or electropolymerization of electrode was performed to prepare electrode for specific sensing application [70]. Fully inkjet-printed conducting polymer-based flexible electrodes were recently developed to record ECG signals [10]. Circular electrode disks were prepared by depositing single or multiple layers of conducting polymers on the substrate followed by connection to the contact pads. Signals were obtained by simply placing human fingers on the electrodes and then collected using toothless alligator clips and copper foil [10].
Figure 2.1: (a) An inkjet-printed three electrode platform with probes connected. Analyte solution was put inside the reaction well [70]. (b) Inkjet-printed PEDOT:PSS electrodes on paper substrate on the left and individual electrodes on the right [10].
The ability to tailor size, shape and structural composition down to tens of nms makes AFM DPN a unique technology ranging its application from medical to electronics engineering. To fabricate a light sensor, metal electrodes were first patterned on silicon chip using photolithography followed by E-beam deposition. Then perchloric acid promoted polymerization of DPN patterned conducting polymers was obtained to form solid photosensitive material. Photosensitive experiment was conducted by placing the ink-coated tip in between electrodes and measuring resistance under dark and bright conditions [119] (Fig. 2.2). A micro-/nanoarray of pH sensitive fluorescent chemosensors were fabricated on a glass substrate using direct-write parallel DPN [73]. To observe the pH sensitivity, fabricated array was immersed in varying pH (3.5-9.5) buffer solutions simultaneously measuring in situ fluorescence response with one channel detection (=550 nm) [73].

Extrusion-based printing is one of the most widely used 3D printing method nowadays. Extrusion-based printing was used to fabricate a PDMS embedded hydrogel strain sensor [121]. The sensor was probed to a multimeter to measure varying resistance as a function of bending while the sensor was attached to finger with an adhesive tape [121]. A soft pressure sensor was developed using extrusion based 3D printing having three extrusion heads to print insulation and conductive layers, and pressure sensitive ionic liquid (IL) layer [30]. The multi-layer sensor had five stretchable layers: top and bottom insulation layers, one pressure sensitive layer, and two multi-walled carbon nanotube based electrode layers creating taxels at the electrode cross-sections. While a pressure sensitive taxel zone is under an applied electric field, a compressive force reduces resistance of the intermediate pressure sensitive layer thereby changing the output voltage response of the sensor [30] (Fig. 2.3).

2.2 Sensor fabrication using pyrolysis of precursors

One of the earliest works of precursor carbonization was conducted in [107]. They formed polymer patterns on appropriate substrates using micro-molding in capillaries (MIMIC) and micro-transfer molding (µTM) [107]. These structures were then carbonized to develop carbon-rich structures [107]. They also measured the resistivity of carbonized wires using silver paint at the ends of wires to establish electrical connections and of carbonized thin
**Figure 2.2:** Optical micrograph conducting polymer. It was patterned between an electrode gap to develop a photodetector [119].

**Figure 2.3:** (a) A soft pressure sensor printed using extrusion-based printing (b) Experimental condition when pressure is applied on one of the taxels [30].
films using four-point probe [107]. Surface morphology of such carbon films were studied by by pyrolyzing both positive and negative photoresists [58]. Inspired by these reports on photoresist-derived carbon for MEMS applications, changes in physical and electro-mechanical properties of Parylene C during pyrolysis of up to 1200 °C were explored by the authors in [64]. The ability to coat Parylene film smoothly on surface at room temperature as well as its history of implementation in MEMS application motivated them to choose this specific material [129, 64]. In their thermal gravimetric analysis from 20 °C to 1200 °C, they observed the most substantial weight loss in between 500 °C and 600 °C whereas the presence of catalytic platinum (Pt) caused an additional weight loss at lower temperature [64]. Since suspended micro/nano structures do not interact to the substrate through Van-der-waal’s force, uniformed and controlled fabrication of suspended structures of desired shapes and dimensions were attempted (Fig. 2.4) [71]. Photoresist on silicon substrate was patterned by UV/EB (electron beam) and then pyrolyzed in a quartz-tube [71]. Pyrolysis can also be used in synthesizing doped wide b and gap silicon nitride for nanodevice applications as was done in [133]. Aluminum containing precursors were solidified, crushed into powders, and finally catalysis-assisted pyrolyzed at 1300 °C [133]. Two fabrication methods to obtain freestanding multi-level 3D carbon microstructures from polymer precursors were developed (Fig. 2.5) [62]. In the first method, various layers were sequentially spin-coated, soft-baked, and developed [62]. In the second method, partial exposure of the top resist layer was performed after spin-coating and soft-baking of bottom resist layer followed by one final developing step [62]. Change in volume, shape, and thickness were observed due to pyrolysis [62]. Although previous approaches developed carbon structures on a single pristine substrate, a method was later developed to fabricate micropatterned carbon nanofiber on both silicon and plasma or UV light-treated carbon film on silicon wafer [114]. The polymer precursor was deposited on the substrate by electrospinning using an electrically charged polymer solution jet [114]. Next, a soft baking step and lithographic patterning were performed to generate patterned nanofiber surface [114]. Finally, pyrolysis was performed to obtain carbon nanofibers [114]. Instead of pyrolyzing precursors, SU8 nanowires were pyrolyzed for obtaining microelectrodes [23]. For this, nanowires were first developed from
Figure 2.4: An SEM image of a carbon microwire. The wire was suspended between carbon posts. [71]
Figure 2.5: Process sequence to fabricate multi-level microstructures from SU-8 photoresist. Method I: (a) Cross-linking of first photoresist by exposure followed by post exposure bake, (b) spin-coating of the second SU-8 photoresist, (c) Cross-linking of second SU-8 photoresist layer using aligned exposure followed by baking, and (d) development of all layers of SU-8 photoresist. Method II: (e) Using exposure to cross-link anchors followed by baking, (f) Using aligned partial exposure for cross-linking of overhangs followed by baking, and (g) developing unexposed SU-8 photoresist. [62]
plasma treatment of photolithographically patterned SU-8 photoresist (Fig. 2.6) [23]. Photonoimprint lithography (P-NIL) was used to develop carbon microstructures to go beyond the resolution of traditional photolithography (Fig. 2.7) [93]. Their processing included successive spin coating of nanoimprint resist and photoresist [93]. P-NIL was performed by a Nano Imprint Module-equipped mask aligner followed by cross-linking through mercury lamp exposure [93]. Residual photoresist was removed using oxygen plasma treatment and reactive ion etching [93]. Finally, a two-step carbonization process carbonized the photoresist [93]. In contrast to aforementioned processes where pyrolysis has been conducted mostly in presence of forming gas or inert atmosphere, a two-step carbonization sequence in Ar and H₂ (10%)/Ar (90%), respectively, has been developed in [50, 128] to obtain porous carbon layer. Prior to pyrolysis, photoresist was spin-coated and lithographically patterned (optional) on a silicon substrate [50, 128]. Recently shrinkage of pyrolyzed suspended microwires was modeled to develop a methodological guideline for shrinkage evaluation (Fig. 2.8) [12]. For this, hanging microwires were formed in between vertical pillars using two photon polymerization (TPP) method [12]. Next, a two-step (for thermal stability and carbonization) pyrolysis was performed to carbonize the samples. Samples were characterized using SEM, Raman spectroscopy, and energy dispersive X-ray spectroscopy (EDS) followed by theoretical modeling to quantitatively determine the dependence of change in pyrolyzed structures on TPP process variables [12].

Some early fundamental electrochemical characterizations of the carbonized structures were conducted in [55]. The authors created a thin layer of photoresist on silicon wafers (using both manual and automated approaches) followed by heating in nitrogen to achieve carbonization [55]. To conduct electrochemical measurements in presence of Fe(CN)₆⁴⁻/Fe(CN)₆³⁻, a glass electrochemical cell was used containing working, counter, and reference electrodes [55]. Electrical connection to carbon was made using alligator clip [55]. A VersaStatTM potentiostat (controlled by a model 270/250 software) was used to sweep potential in order to conduct cyclic voltammetry and compare with conventional glassy carbon electrode [55]. In a similar but more extensive work, pyrolysis of photoresist was done in different environmental conditions [99]. Both carbonized photoresist and SiO₂ were exposed to electrolyte for electrochemical analysis using a potentiostat. In addition to that,
Figure 2.6: Multilayer processing sequence. (A) Schematic showing CNW structures of multiple heights. (B) Array of multiple height SU8 pillars. (C) An array of SU-8 pillars after treating with plasma. (D) Pyrolyzed 3D carbon nanowire microstructure array. (E) A schematic showing carbon structures with SU-8. (F, G) SEM images showing pillars of SU-8 pillars developed over CNW microstructures. (H) SU8 pillars developed in between carbonized microstructures. [23]
Figure 2.7: Schematic of the fabrication process. (a) Nanoimprint resist as well as photoresist were coated over the substrate, (b) imprint a predesigned glass mold to replicate the pattern onto the photoresist followed by UV exposure, (c) remove the glass mold to observe the patterned resist, (d) etch away residual nanoimprint resist using oxygen plasma treatment, (e) use of CF$_4$+oxygen reactive ion etch to etch away the residual photoresist top layer, and (f) carbonize the polymer precursors in a forming gas and high temperature environment. [93]
Figure 2.8: (a) Femtosecond laser setup to print SU-8 microwires, showing the microscope objective and SU-8. (b) A schematic showing the fabricated structure. [12]
a probe head consisting of four tungsten probe tips was connected to the surface followed by current measurement as a function of applied voltage. From this, sheet resistance was determined using Ohm’s law [99]. A broader range of redox systems (Fe^{2+}, Fe(CN)_{6}^{4-}, [Ru(NH3)_{6}]^{3+}, ascorbic acid, dopamine, oxygen, chlorpromazine) were characterized by the same group using similarly developed pyrolyzed photoresist films (PPF) in their later work [100]. Two photoresists were pyrolyzed on silicon and fused silica wafers followed by electrochemical characterization in a custom-made cell exposing an area of 0.24 cm² [115]. A bioanalytical systems BAS 100 potentiostat was used to run cyclic voltammetry in Fe^{+2}/Fe^{+3} cyanide and ruthenium hexamine systems [115]. Photoresist was pyrolyzed to develop a microchip capillary electrophoresis device for dopamine detection in [48]. A quartz plate was used as substrate to spin-coat positive photoresist followed by baking and UV-treatment prior to pyrolysis [48]. An attempt was made to obtain high aspect ratio C-MEMS microstructures in order to overcome the strictness of having good sidewall angle control (Fig. 2.9) [125]. Positive and negative photoresists were used for structure fabrication on metallized substrates using photolithography process and subsequent carbonization [125]. Electrochemical measurements were done in a ~6.4 cm² area within a three-electrode Teflon cell [125]. Electrical characteristics and shrinkage of pyrolyzed positive and negative photoresists were explored by the same group in [92]. To expedite mass production of carbon-based electrodes for microchip electrophoresis devices, pyrolyzed photoresist films were developed with dual-electron electrochemical detection [33]. The electrodes were developed from conventional photolithography and subsequent pyrolysis of a positive photoresist [33]. Amperometric response and cyclic voltammetry data were collected, and further processed using a CHI 802A electrochemical analyzer whereas an analog-to-digital converter was used in conjunction with LC-4CE potentiostat to collect data before finally analyzing using Chromgraph software [33]. A thin film of diluted photoresist was pyrolyzed to obtain carbon-based optically transparent electrodes (C-OTEs) [26]. It allowed to cast a film thin enough to show transparency after pyrolysis [26]. Electrochemical experiments were conducted using Ferrocyanide and hydroxymethylferrocene as oxidation-reduction couples under test [26]. An impedance biosensor was developed through aptamer-modified pyrolysis of precursor [61]. Silicon wafer was used for oxidation and then spin-coating, and pyrolysis of photoresist
Figure 2.9: SEM images of (a) and (b): An array of SU-8 post before pyrolysis. (c) and (d) An array of carbonized posts. [125]
Counter electrode and metal interconnect were formed by photolithography followed by application of negative photoresist for passivation [61]. After aptamer immobilization, electrochemical characterization was performed in a three-electrode system [61]. A sensor was developed to detect dopamine and oxygen implementing fast scan cyclic voltammetry [136]. Following the application of adhesive hexamethyldisilazane (HMDS), positive photoresist was deposited and lithographically patterned on fused silica substrate [136]. The patterned electrode arrays were then pyrolyzed in a quartz tube furnace [136]. Insulation was achieved by applying again HMDS followed by deposition and photolithographic deposition of negative photoresist [136]. Wires and epoxy were used to establish external connections to the microelectrodes [136]. Electrochemical experiments were conducted using a biopotentiostat based two-electrode setup [136]. The same research group later developed a microelectrode array using pyrolyzed photoresist to detect dopamine release [135]. This time pyrolyzed photoresist was more extensively used in forming working electrode, interconnects, and bonding pad thereby surplussing any metallization step [135]. Silicon nitride was deposited over the silicon substrate followed by photolithographically patterned photoresist and pyrolysis insulation of microelectrodes was achieved through a selective “half-etch”-wet etch-“full etch” strategy with a functional yield of up to 90% [135]. High aspect ratio microelectrodes were developed by coating micropipets with parylene C using chemical vapor deposition [80]. These pipets were then pyrolyzed to form carbonaceous electrode followed by multiple depositions of parylene C for insulation [80]. Cyclic voltammetry was performed in Ru(NH$_3$)$_6$Cl$_3$ with KCl and in dopamine hydrochloride with phosphate buffered saline buffer to observe performance of microelectrodes [80]. More recently free-standing microelectrodes with electro-active carbon surface have been fabricated using 3D printing and pyrolysis, and tested for dopamine detection [131]. Metal wires were anchored on silicon wafer followed by vertical bending using an additional chip. 3D printing was done using two-photon photolithography after a negative photoresist layer IP-S was created on the metal wires. Carbonization was achieved through pyrolysis by rapid thermal processing which created a glassy carbon-like surface [131].

Most recently, it has been possible to scale neurosensing electrodes down to nanometer size by exploiting 3D printing using two-photon polymerization and subsequent pyrolysis
For this, photoresist was added to the tip of immobilized metal wires on the silicon chip followed by direct laser writing using two-photon lithography to obtain submicrometer scale structures [11]. Carbonization and subsequent insulation were performed using rapid thermal processing and atomic layer deposition of $\text{Al}_2\text{O}_3$, respectively [11]. Finally, disk shaped nanoelectrode was achieved by focused ion beam milling under scanning electron microscopy at the tip [11].

Table 2.1 shows the most important parameters used in the literature for single-step pyrolysis of precursors whereas Table 2.2 shows the most important parameters used in the literature for two-step pyrolysis of precursors.

### 2.2.1 Materials used as precursors for pyrolysis

In one of the first demonstrations of polymer carbonization suitable for microelectromechanical system (MEMS), furfuryl alcohol-phenol was used as precursor to carbonize [107]. Among the photoresists used later, AZ-4330 and SU-8 are the most widely used photoresists. Two positive photoresists, AZ-4330 and OIR-897, and a negative photoresist (XPSU) were used for pyrolysis followed by surface study in [58]. Two positive photoresists, AZ-4330 and OCG-825, also termed as novolak resins, were used to produce carbon films on diam silicon wafers [55] whereas only AZ4330 was used in [99, 100]. AZ4330 was also used for spin-coating and pyrolyzing on to a fused quartz plate in order to develop carbon films for sinusoidal voltammetry [48]. To develop optically transparent carbon electrode, positive photoresist was diluted [26]. This would increase viscosity of the resist thereby enabling thin enough deposition of the photoresist to produce optically transparent film after pyrolysis [26].

Negative tone photoresist SU-8 was also widely used for pyrolysis [71, 62, 114, 23, 115]. Specifically, freestanding carbon microstructures [62], nanofiber layer [114], and carbon nanowire forests [23] were used using SU-8. Alongside conventional lithography, SU-8 photoresist was also used for two photon polymerization (TPP) and subsequent pyrolysis in [12]. Both positive (SP1827 and AZ4620) and negative (Iron (III) oxide modified SU-8) photoresists were used to fabricate high aspect ratio C-MEMS structures [125]. Although SU-8 produced carbonaceous structures with aspect ratios, positive photoresist failed to
Figure 2.10: Fabrication of 3D-printed carbon nanoelectrodes. [11]
Table 2.1: Processing conditions used in single-step pyrolysis of precursors.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (Torr)</th>
<th>Anneal environment</th>
<th>Heating rate (°C/min)</th>
<th>Reference</th>
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<tr>
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<td></td>
<td>He</td>
<td>5</td>
<td>[58]</td>
</tr>
<tr>
<td>20-1200</td>
<td></td>
<td>N₂</td>
<td>10</td>
<td>[64]</td>
</tr>
<tr>
<td>1300</td>
<td>75×10⁻³</td>
<td>N₂</td>
<td></td>
<td>[133]</td>
</tr>
<tr>
<td>900</td>
<td></td>
<td>N₂</td>
<td>5</td>
<td>[114]</td>
</tr>
<tr>
<td>600-1100</td>
<td></td>
<td>N₂</td>
<td></td>
<td>[55]</td>
</tr>
<tr>
<td>600-1100</td>
<td>10⁻⁵, 10⁻⁷, 760</td>
<td>Vacuum, N₂, forming gas (95% N₂, 5% H₂)</td>
<td>20</td>
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<td>forming gas (95% N₂, 5% H₂)</td>
<td>10</td>
<td>[100]</td>
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<tr>
<td>600-1100</td>
<td></td>
<td>forming gas (95% N₂, 5% H₂)</td>
<td>1-5</td>
<td>[115]</td>
</tr>
<tr>
<td>1000</td>
<td></td>
<td>forming gas (95% N₂, 5% H₂)</td>
<td>10</td>
<td>[48]</td>
</tr>
<tr>
<td>900</td>
<td></td>
<td>N₂</td>
<td></td>
<td>[80]</td>
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<td>[33]</td>
</tr>
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<td>forming gas (95% N₂, 5% H₂)</td>
<td>4</td>
<td>[135]</td>
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<tr>
<td>1000</td>
<td></td>
<td>forming gas (95% N₂, 5% H₂)</td>
<td>5</td>
<td>[80]</td>
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**Table 2.2:** Processing conditions used in two-step pyrolysis of precursors.

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<th>Anneal environment</th>
<th>Heating rate (°C/min)</th>
<th>Reference</th>
</tr>
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<td>N₂</td>
<td></td>
<td></td>
<td>[71]</td>
</tr>
<tr>
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<td>N₂, forming gas (95% N₂, 5% H₂)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>N₂</td>
<td></td>
<td>3</td>
<td>[62]</td>
</tr>
<tr>
<td>900</td>
<td>N₂</td>
<td></td>
<td>10</td>
<td>[23]</td>
</tr>
<tr>
<td>350</td>
<td>N₂</td>
<td></td>
<td>5</td>
<td>[93]</td>
</tr>
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<td>N₂</td>
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<td></td>
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<td>Ar</td>
<td>[50]</td>
</tr>
<tr>
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<td>Ar</td>
<td>1</td>
<td>Ar, 10% H₂/90% Ar</td>
<td>[128]</td>
</tr>
<tr>
<td>900</td>
<td>Ar</td>
<td>1</td>
<td>Ar, 10% H₂/90% Ar</td>
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</tr>
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<td>1</td>
<td>Ar, 10% H₂/90% Ar</td>
<td></td>
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<tr>
<td>900</td>
<td>Ar</td>
<td>1</td>
<td>Ar, 10% H₂/90% Ar</td>
<td></td>
</tr>
<tr>
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<td>N₂</td>
<td></td>
<td>5</td>
<td>[12]</td>
</tr>
<tr>
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<td>N₂</td>
<td></td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>N₂, forming gas (95% N₂, 5% H₂)</td>
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<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>N₂</td>
<td></td>
<td>10</td>
<td>[92]</td>
</tr>
<tr>
<td>600-1000</td>
<td>N₂, forming gas (95% N₂, 5% H₂)</td>
<td>10</td>
<td></td>
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</table>
do so due to non-uniform heating and development, inconveniently long development time, presence of bubbling and peeling, and viscosity of the resist observed in multiple approaches [125].

Since Parylene C can be smooth coated through CVD deposition alongside its low permeability, it has been used as precursor for pyrolysis in [64]. Parylene C was also used to analyze electrical properties and shrinkage of precursor [92]. More recently, parylene C was used for coating quartz pipets using chemical vapor deposition (CVD) and then pyrolyzed to obtain microelectrodes in [80].

To synthesize doped Si₃N₄ nanowires, liquid-phased polyalumínasilazanes was derived from the reaction between commercially available silizane-based precursor polyureamethylvinylsilazane and aluminum isopropoxide [133]. After solidification and subsequent crushing, polyalumínasilazane powder was pyrolyzed in presence of nitrogen to obtain Al-doped Si₃N₄ nanowires [133]. Concentration of Al controlled the doping level as well as the shape and sizes of the nanomaterial [133].

AR-UL-01 and AR-UV-01 were used as nanoimprint resist for lithography and photoresist, respectively, and subsequent pyrolysis in [93]. Similarly, SPR-220-7 photoresist was used for patterning and subsequent carbonization in [50, 128]. Shrinkage due to pyrolysis was also studied using a positive photoresist AZ9260 as precursor [61]. They observed 15%-19% final thickness of pyrolyzed film relative to initial non-pyrolyzed photoresist as well as rounded cross section compared to rectangular photoresist resulting from photoresist reflow during pyrolysis [61].

A neurotransmitter detector was fabricated by pyrolyzing negative tone photopolymer IPS. This photopolymer was layered on a metal anchor immobilized on silicon wafer, and SU-8 developer was used for developing 3D printed structures [131]. IP-S photoresist was also used for two-photon polymerization and subsequent pyrolysis in [11]. Table 2.3 shows the most frequently used materials for pyrolysis to fabricate microelectrodes.
Table 2.3: Materials used in pyrolysis of precursors.

<table>
<thead>
<tr>
<th>Photoresist</th>
<th>Reference</th>
<th>Year</th>
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<tr>
<td>furfuryl alcohol-phenol</td>
<td>[107]</td>
<td>1997</td>
</tr>
<tr>
<td>Positive photoresist</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OIR-897 [58]</td>
<td>2001</td>
<td></td>
</tr>
<tr>
<td>SPR-220-7 [50, 128]</td>
<td>2013, 2014</td>
<td></td>
</tr>
<tr>
<td>SP1827 [125, 92]</td>
<td>2005, 2005</td>
<td></td>
</tr>
<tr>
<td>AZ4620 [125, 92]</td>
<td>2005, 2005</td>
<td></td>
</tr>
<tr>
<td>AZ P4330-RS [26]</td>
<td>2006</td>
<td></td>
</tr>
<tr>
<td>AZ9260 [61]</td>
<td>2008</td>
<td></td>
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<tr>
<td>Negative photoresist</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XPSU [58]</td>
<td>2001</td>
<td></td>
</tr>
<tr>
<td>NANOTM SU-8 100 [71]</td>
<td>2006</td>
<td></td>
</tr>
<tr>
<td>polyimide [115]</td>
<td>2002</td>
<td></td>
</tr>
<tr>
<td>Iron (III) oxide modified SU-8 [125]</td>
<td>2005</td>
<td></td>
</tr>
<tr>
<td>Polymer</td>
<td></td>
<td></td>
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<tr>
<td>Parylene C [64, 80]</td>
<td>2004, 2011</td>
<td></td>
</tr>
<tr>
<td>Polyureamethylvinylsilazane [133]</td>
<td>2007</td>
<td></td>
</tr>
<tr>
<td>AR-UL-01 [93]</td>
<td>2012</td>
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</table>
2.3 Sensor fabrication using Carbon based nanomaterials-CNT/CNF

Carbon nanotubes and graphene have been a major research focus over the last two decades. Other allotropes of carbon are: double-walled CNT, graphenated CNT, nanobuds, graphene nanoribbons, graphene nanoplatelets, carbon foam, nanodiamonds, and fullerenes. The ground state electronic configuration of carbon is \(1s^22s^22P_x^12P_y^12P_z^0\) (Fig. 2.11(a)). There are six electrons around the carbon nucleus (Fig. 2.11(b)). Among them, four electrons are valence electrons. These valence electrons can form sp, sp\(^2\), and sp\(^3\) hybridization. Formation of sp\(^2\) hybridization is shown in Fig. 2.11(c). When one carbon atom shares sp\(^2\) electrons with surrounding three carbon atoms, monolayer graphene is formed [132]. The structure of single-walled carbon nanotube (SWCNT) can be visualized as a rolled-up tube-shaped shell of graphene sheet. Honecomb lattice form these graphene sheets and they represent a single atomic layer of crystalline graphite. A multi-walled carbon nanotube (MWCNT) is a stack of graphene sheets where they are rolled-up in concentric cylinders. Apart from these two basic structures, depending on the formation, there are three different types of carbon nanotubes, namely armchair carbon nanotubes, zigzag carbon nanotubes, and chiral carbon nanotubes (Fig. 2.12) [104]. Nanotubes usually have a large length-to-diameter ratio thereby generating a nearly one-dimensional structure [27, 104]. The length of nanotubes can be tens of micrometers whereas their diameters can be as small as 0.7 nm [77]. MWCNTs are wider and they are considered as multiple SWCNTs stacked one inside other. However, the diameter of MWCNT has to be less than 15 nm and the structures having larger diameters are called carbon nanofibers (CNFs). Also, CNFs may consist of graphene sheets of varying shapes thereby generating more edge plane defects compared to CNTs. This property of CNF can potentially provide more sites for electron transfer when in contact with electroactive analytes [4, 51].

Carbon based materials play a central role in electrochemical biosensing. For example, carbon nanotubes, and graphene can be used for glucose, antigen, and other biological molecule detection [130, 91]. Multiwalled carbon nanotubes (MWCNTs) have shown promise through increased electroactivity in a mimicked orthopedic environment for new bone
Figure 2.11: (a) Electronic configuration of carbon (b) atomic structure of carbon atom. (c) sp\(^2\) hybridization [132]

Figure 2.12: (a) Armchair carbon nanotube (b) Zigzag carbon nanotube (c) Chiral carbon nanotubes [104].
growth electrochemical sensor [116]. Intensity and shift-dependent fluorescence emission of single walled carbon nanotubes (SWCNTs) was used to detect active alkylating drugs (melphalan and DNA–SWNT complex) and reactive oxygen species [49]. Alteration in photoluminescence of SWCNT was also used to sense and monitor glucose concentration in blood [6]. Furthermore, SWCNT-based nanonet design was implemented to develop flexible and implantable strain sensors in orthopedic applications where microstress in bone exhibits change in resistance [52] (Fig. 2.13(a)). SWCNT also showed potential in neural interfacing when used in coating Ti-nitride electrodes for stimulating and recording neural activity [9].

Fig. 2.13(b) shows a graphene microelectrode for recording neural signals that was biocompatible and nontoxic [13]. Silver nanoparticle (Ag NP)-modified graphene oxide (GO) showed enhanced antibacterial activity compared to both Ag NP and GO, and thus has potential applications in wound dressing [69]. Researchers have also found that GF (Graphene foam, a 3D microporous network consisting of single or multiple layers of graphene sheet templated foam) electrode can reduce the dopamine detection limit up to 25 nM [25]. A hybrid lead (Pb\(^{2+}\)) sensor was developed using graphene oxide and graphene quantum dots (GQDs). It had 0.6 nM detection limit while also having Pb\(^{2+}\) detection ability from other ions [97]. A NO\(_2\) gas sensor was developed using carbon quantum-dot (CQD) in [127] (Fig. 2.14(a)). The fluorescence of CQD-functionalized aerogels was quenched in presence of NO\(_2\) while no quenching was observed when the sensor was exposed to pure nitrogen (N\(_2\)). Graphene quantum dot was used in hydrogen peroxide detection where detection limit was 0.12 µM [53]. Such detection capability is helpful in detecting H\(_2\)O\(_2\) in cervical cancer cells and in human serum samples.

Carbon nanofiber-based sensing systems were used in detection of NADH, glucose, serotonin, hydrogen peroxide, 5-hydroxytryramide, and carbon nanotube-based detectors were used to sense ethanol, dopamine, norepinephrine, glutamate, uric acid, bisphenol A, and ascorbic acid [3, 98, 75]. Researchers have previously explored the feasibility of integrating carbon nanospikes and nanofibers with CMOS electronics [111, 112, 2]. A glucose biosensor was developed in [2] using custom designed CMOS potentiostat and vertically aligned carbon nanofibers (VACNFs). To synthesize the VACNF fiber forests on silicon wafer, DC plasma-enhanced chemical vapor deposition (PECVD) was employed over nickel (Ni) dots [2]. A
Figure 2.13: (a) 3D diagram of strain sensor using patterned SWCNT [52] (b) Neural microelectrode fabricated using graphene. [13]

Figure 2.14: (a) Fluorescence quenching of carbon quantum dot-functionalized aerogels for NO$_2$ sensing [127]. (b) VACNF growth for impedance sensing [134].
similar approach was followed in [134] (Fig. 2.14(b)) to develop VACNF in order to develop a cell impedance sensor. PECVD was also used in growth of carbon nanospikes [111, 112]. However, one advantage in growing carbon nanospikes is that, unlike VACNF growth, carbon nanospike growth does not require any catalyst thereby facilitating bath fabrication with greater reproducibility. Furthermore, carbon nanospikes were used in detecting hydrogen peroxide where detection limit was 0.2 mM [112].

2.4 Summary

A literature review on printed electrode sensors has been presented. The two principal types of processing methodologies used for fabrication, namely, printing of conducting material and pyrolysis of precursors, have been highlighted. Discussion of printing conducting material includes inkjet printing, dip-pen nanolithography, and extrusion-based printing. Besides, processing technologies used for pyrolysis of precursors are highlighted as well as the materials used for these technologies. Also, notable research in the field of carbon-based sensors including carbon nanotubes, graphene, and carbon nanofibers has been reviewed.
Chapter 3

CMOS-compatible Carbonization of Polymers

Portions of this chapter have been published as:


3.1 3D printing and carbonization of polymer

3.1.1 Substrate metallization using E-beam evaporation

Bare silicon as well as metallized silicon and silica substrates were used to fabricate and process structures. To obtain metallized substrates, electron beam evaporation (VE-240, Thermionics) was used to deposit metal films on 100 mm diameter silicon and fused silica wafers. In this method, vacuum systems are used to deposit thin layers of materials onto the substrates. Here a well confined beam of high energy electrons are directed towards the target high purity material. This beam of electrons heats up the source material to melt and then evaporate. Within an E-beam evaporator, multiple source materials can be rotated to guide them in the path of electron beam. This helps in depositing multiple materials without breaking the vacuum [65].

Inside an E-beam evaporator, electron gun produces the beam of electrons, and the crucible contains the source material. The electron gun contains the filament (source of electrons) and a magnet to steer the electron beam towards the crucible. When the filament heats up (up to 2500 °C), the filament glows, electron beam is generated, and high energy electrons leave the filament surface. A high voltage electrode accelerates these electrons and the magnet steers and focuses the electron beam towards the source material. The filament current can be changed to adjust the power level. Some materials like titanium can melt at lower power and may potentially change state at higher power. On the other hand, some materials like gold require higher power just to melt. The crucible itself can be made of tungsten, copper or even ceramic material. The evaporation system used here can house four source material in four separate crucible within the hearth. The hearth is cooled by flowing water and thereby prevented from melting. Following the metal deposition, wafers were diced into 12.5 × 12.5 mm² chips using an Accretech dicing saw (SS10, Accretech).

3.1.2 3D printing using two photon polymerization

3D polymer structures were additively fabricated using two-photon polymerization on bare silicon as well as on metallized silicon and silica substrates. For this, a commercially available
Two-photon polymerization tool (Photonic Professional GT, Nanoscribe GmbH) was used. Two photon polymerization is performed in a dielectric material. A dielectric material works as an insulator and it can be polarized when an electric field is applied across it. When an electric field is applied across it, the charges do not flow like a conductor but shift their positions slightly. Positive charges tend to shift towards the negative terminal and negative charges tend to shift towards the positive terminal. This polarization depends on the strength of applied field and it is expressed as,

\[ P = \epsilon_0 \chi_0 E \]  

(3.1)

where, \( \chi_0 \) is electric susceptibility of the dielectric material and it determines how easily the dielectric field is polarized under an electric field, \( \epsilon_0 \) is electric permittivity of free space, \( P \) is the induced dielectric polarization density and \( E \) is the applied electric field. This shows a linear relation between the applied electric field and induced polarization. When a light beam falls on a dielectric material, the electric field causes polarization within the dielectric material. This induced polarization depends on the intensity of the beam since electric field is related to the intensity \( I \) by \([87]\),

\[ E \propto \sqrt{I} \]  

(3.2)

The linear relation between polarization and intensity is violated when light intensity is high enough so that electric field is greater than or comparable to the interatomic field (in orders of hundreds of MV/m). This non-linearity is expressed in terms of higher order of susceptibilities as \([1]\),

\[ P = \epsilon_0 \chi^{(1)} E + \epsilon_0 \chi^{(2)} E^2 + \epsilon_0 \chi^{(3)} E^3 + ... \]  

(3.3)

Now such high electric field can be achieved only by applying nanosecond or femtosecond laser pulses only. Different high order effects can be observed, such as optical mixing, second harmonic generation, and two-photon absorption. In contrast to single photon absorption where materials absorbs a photon only when energy of the photon is greater than or equal to the energy band gap of the material, two photon absorption occurs when energy band gap
between the two energy states involved is equal or less than the sum of two photons absorbed. It is a third order process that involves an intermediate state helping the transition of electron from the lower to the higher energy state. However, lifetimes of such virtual transition states are in the order of femtoseconds. Therefore, an atom temporarily at that virtual state must have available photon to be able to jump to the higher energy state within this short period of time. This is possible if there is abundant number of photons available at that time around that excited atom. In order to increase the number of available photons thereby increasing the probability of photon absorption, both spatial and temporal compressions of photons are required. Spatial compression can be achieved by using high numerical aperture objective to focus the laser beam. Temporal compression is achieved by using nanosecond or femtosecond pulsed laser. A combination of both the compression schemes give the best results in obtaining two photon absorption [140].

In traditional photopolymerization, entire irradiated (visible or UV) area goes through a polymerization reaction to create a crosslinked polymer structure. On the other hand, two-photon polymerization is confined to the focal volume of the laser beam. This enables achieving submicron resolution beyond the diffraction limit (diffraction limit, \( d = \frac{\lambda}{2n \sin \theta} = \frac{\lambda}{2NA} \), where \( d \) is the resolvable feature size, \( \lambda \) is the wavelength of light, \( n \) is the refractive index of the light traversing medium, \( \theta \) is the angle subtended by the optical objective lens and \( NA \) is numerical aperture). Besides, most of the UV (ultraviolet)-curable resins work as transparent material to infrared (IR) light. Therefore, polymerization can take place inside the material as well as on its surface. Also, such polymerization can further be leveraged by using a three-dimensionally movable stage thereby printing a 3D structure predefined by a computer aided design (CAD) model.

A regular photopolymerization process can be divided into three steps, initiation process, propagation process, and termination process [140]. In the initiation process, photoinitiators (PIs, molecules that can generate reactive ions or free radicans when exposed to visible or UV radiation) absorb two photons, elevate onto the excited states, and then decompose into radicals (R).

\[
P^I + h\nu \rightarrow P^I^* \rightarrow R \cdot + R\cdot
\]
In the propagation process, radicals and monomers (M) combine into monomer radicals (RM)

\[ R \cdot + M \rightarrow RM \cdot \xrightarrow{M} RMM \cdots \rightarrow RM_n \cdot \] (3.5)

Finally, two monomer radicals are combined thereby terminating the photopolymerization process.

\[ RM_n \cdot + RM_m \cdot \rightarrow RM_{n+m}R \] (3.6)

Vendor supplied liquid photopolymer (IP-S, Nanoscribe GmbH) was used to 3D print polymeric precursors. Initially, cylindrical and cone-shaped polymers structures of various sizes and aspect ratios [110, 102] were printed. In particular, cone and pillar polymer structures with sizes specified in Table 3.1 were 3D printed. These sizes were chosen to entail a wide enough range of heights and diameters in order to be able to explore the effects of processing sequences on sizes of 3D printed structures.

In the initial experiments, a single layer of Ti (100 nm) was deposited on the substrates using e-beam evaporation method. These metallized substrates were then used for fabricating polymer structures. However, some stability issues were observed during 3D printing on these metallized substrates. Cavitation (formation of bubbles) was observed during two-photon-polymerization-based 3D printing when the focused laser beam was scanning over the Ti-metallized substrate (Fig. 3.1). Fig. 3.1(a) shows the formation of bubbles as laser scans the photopolymer solution and Fig. 3.1(b) shows the outcome of such structures after developing. Some of the structures were loosely bound to the substrate whereas some structures floated away during writing. This behavior could be explained by the substantial absorption of laser beam energy in the near infrared region (NIR) in the Ti film and this, in turn, generated heat and/or shock waves [29, 66]. Generation of these waves affected the cross-linking of polymers. This adverse phenomenon lead to poor adhesion of the polymer structures, thereby making a Ti-coated substrate unsuitable for two photon polymerization. To address this issue, a 50 nm gold layer was deposited on top of the Ti layer. E-beam evaporation was used to deposit gold on the Ti-metallized wafer. This would increase reflectivity (and subsequently, reduce laser absorption) of the
Table 3.1: Design dimensions of polymer cones and pillars fabricated using.

<table>
<thead>
<tr>
<th>Shape</th>
<th>Label</th>
<th>Diameter (µm)</th>
<th>Height (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cone</td>
<td>C55</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>C515</td>
<td>5</td>
<td>15</td>
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<tr>
<td></td>
<td>C1010</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>C1515</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>C2020</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Pillar</td>
<td>P55</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>P520</td>
<td>5</td>
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<tr>
<td></td>
<td>P1010</td>
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<td>10</td>
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<tr>
<td></td>
<td>P1515</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>P2020</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

Figure 3.1: Cavitation observed during two-photon polymerization on titanium-coated silica substrate. (a) Bubbles forming during direct laser writing as seen on the computer screen. (b) Optical microscopy images showing unstable/broken structures on metallized substrate.
substrate in NIR. Finally, the two-layer-metallized chips were used to successfully fabricate polymer structures as can be seen in Fig. 3.2. Both the objective lens and specimen were immersed in the immersion oil to increase the resolving power of microscope. Without using immersion oil, light rays reflecting from the sample get diffracted at the air interface and can miss the objective causing information loss. Therefore, a high refractive index (around 1.515 [88]) immersion oil is used to increase the numerical aperture of the objective lens. An SEM (Merlin, Zeiss) was used to image the precursors before and after various steps in the processing sequence. Two of the most common methods in SEM imaging are using secondary electrons and backscattered electrons. Most of the SEM images used in this work utilized secondary electrons for imaging. Once two photon polymerization writing of the structures was completed, the uncrosslinked IP-S was removed by soaking in an SU-8 developer for 20 min followed by rinsing with isopropanol and blow drying with filtered nitrogen.

Fig. 3.3 shows sample SEM images of conical and pillar structures from Table 3.1. Fig. 3.3 (a) and (b) show cone and pillar, respectively, with base diameter of 5 µm and height of 5 µm whereas Fig. 3.3 (c) and (d) show cone and pillar, respectively, with base diameter of 20 µm and height of 20 µm. These images show that larger structures can be more accurately printed with sharper edges compared to the smaller ones. This needs to be noted that resolution and accuracy depend on voxel size, which is the unit volume where polymerization takes place. The default voxel size was 1 µm in x and y directions and 3 µm in z direction. Although these values can go as low as 500 nm, this voxel size was not required to be modified in this work. Also, smaller structures are generally imaged with larger magnification, which also makes any defect and/or imperfection more easily visible compared to the larger ones.

3.1.3 Dry etch

Dry etching means the process of patterning a wafer by removing thin film using resist as a mask. A general working principle of reactive ion etching tool can be described as follows, first a high vacuum is created inside the etching chamber followed by insertion of an etching gas. When an RF power of 13.56 MHz is applied across the electrodes, the chamber generates a plasma within it. The etch gas interacts with the plasma to generate
Figure 3.2: Scanning electron microscopic image of as-printed conical structure fabricated by 3D printing using 2-photon polymerization on a metallized silica substrate. (a) one single structure (b) a typical conical pillar array. Center-to-center distance and other geometrical parameters can be easily be varied using CAD software.
Figure 3.3: Sample scanning electron microscopic images of as-printed conical and pillar structures from Table 3.1 fabricated by 3D printing using 2-photon polymerization on a metallized silica substrate to show change in printing accuracy as feature size changes. (a) Cone C55 (b) Pillar P55 (c) Cone C2020 (d) Pillar P2020.
reactive species. These reactive species can be ions, radicals, and monomers. When the electric field is high enough, they are accelerated towards the wafer surface to react with the target etch material. Following a number of complicated etching and deposition reactions, byproducts are absorbed away from the wafer surface. The reaction steps for silicon etching using CF₄ can be mentioned as an instance. First, CF₄ is dissociated into CF₃· and F· radicals in the plasma. The CF₃· radicals are adsorbed on the target silicon surface to react with Si and form SiF₄ byproduct. SiF₄ is then desorbed from the surface while etching process continues. When etching takes place in both vertical and horizontal directions due to Brownian motion of the radicals, it is called isotropic etching. Thus undercut can be produced and cannot accurately replicate patterning. Anisotropic etching takes place in vertical direction facilitating close replication of mask pattern.

The most important parameters to evaluate dry etching are [86],

- Etch rate of the target film, underlying film and mask.
- Selectivity between target and underlying films and selectivity between target film and mask.
- Critical dimension after etching
- Etch profile or taper angle, θ

The entire process of dry etching depends largely on generating plasma. Plasma is effectively an ionized gas, where the densities of electron and ion are equal thereby being electrically neutral from macroscopic point of view. Inside a plasma, collisions between an incoming electron and an atom can be broadly divided into two groups:

- elastic collisions
- inelastic collisions

Elastic collision takes place when incoming electron has a low energy resulting only change in kinetic energy. The electron loses some energy and the atom gains a slight velocity. Higher energy of incoming electron causes inelastic collision resulting various possible outcomes:
• **Excitation:** An electron transfers energy to another atom thereby energizing it to go to an excited state. The excited atom stays in the excited state for about $10^{-8}$ s. Then it comes back to the previous state causing photon emission. This phenomenon causes glow in the plasma.

• **Ionization:** When the colliding electron can provide energy higher than the ionization energy of an atom, outermost electron from the atom escapes leaving a positive ion behind.

• **Dissociation:** When the colliding electron has an energy higher than the molecule’s binding energy, the molecule get dissociated generating highly reactive particles or radicals.

• **Electron attachment:** This occurs when the colliding electron gets attached to the atom creating a negative ion.

A reactive ion etcher (Plasmalab System100 ICP RIE, Oxford Instruments) was used for the timed sputter etching of metal layers in argon (Ar) plasma. Usually 75 seconds of sputter etching was able to remove the unwanted gold layer after 3D printing. The idea was to form an electrically insulating titanium oxide ($\text{TiO}_x$) on the chip surface everywhere except the carbonized electrode. Gold layer was only required for stabilising the 3D printing process, and it needed to be removed to oxidize titanium. Therefore, the Au layer was sputter etched in an Ar plasma to expose Ti prior to the oxidative anneal. Low chamber pressure is required to obtain high energy ions since lower pressure allows longer mean free path for ions thereby providing higher kinetic energy for sputtering. The required sputter etch recipes would operate in pressures in the range of 2-10 mTorr. However, purely CCP mechanism can go as low as 50 mTorr pressure. Therefore, a combination of both Capacitively Coupled Plasma (CCP) and Inductively Coupled Plasma (ICP) mechanisms were used in the RIE tool to achieve the desired chamber pressure.
3.1.4 Thermal Processing

In analogy to carbon fiber production and previous work on the carbonization of 3D printed polymer microstructures, this work exploited the basic idea of a sequence of stabilizing and carbonizing anneals. These anneals were performed in oxidative and inert atmospheres, respectively [7, 24]. Rapid thermal processing (RTP) allows to treat the precursors in high temperature within a fast processing time with a high temperature ramping rate. Historically, high temperature furnace is used for pyrolysis. However, since RTP is mostly used in wafer processing and the objective of this work was to make processing sequences more compatible to CMOS, RTP was chosen as the thermal processing tool in this work.

In rapid thermal processing, a bank of lamps are used to optically heat one wafer at a time. For this, the wafer is placed in a cold-wall chamber with quartz windows. The temperature of the wafer is monitored using a pyrometer (in the RTP tool, thermocouples were used to monitor the temperature). Inside the chamber, wafer is heated front and/or backside by lamps using radiative heating. Temperature within the chamber can range from 150 °C to 1500 °C with a ramping rate of up to 200 °C. The temperature hold time can range from ms to minutes depending on processes. The chamber is designed in such a way to reflect the power from chamber walls thereby exposing the entire wafer to uniform heat.

The oxidative and inert atmosphere anneals were carried out, respectively, in pure oxygen at 450 °C for 10 min and in Ar at 500 °C for 15 min using a rapid thermal processing tool (RTP, EasyTube® 3000, First Nano). Therefore, the entire processing sequence included 3D printing of precursors, sputter etching of gold, initial oxidation and final carbonization. The processing sequence shown in Fig. 3.4 was used in the initial experiments.

3.1.5 Observations and Process Optimization

This sequence provided the desired outcome in some instances. However, these results were not initially consistent. Several types of pronounced artifacts and reproducibility issues were also encountered. For example, Fig. 3.5 shows polymer pillar and cone structures on a silicon substrate before ((a) and (b)) and after ((c) and (d)) a sequence of oxidative and carbonizing anneals shown in Fig. 3.4. Based on the usual carbonization method, these
**Figure 3.4:** Initial processing sequence (Sequence I) used to obtain carbonized electrodes from structures 3D printed using 2-photon polymerization [41].

**Figure 3.5:** SEM images of pillar and cone structures on a silicon substrate before and after anneal. (a) and (b) As fabricated pillar and cone structures. (c) and (d) Structures after successive anneals in O$_2$ and Ar under conditions illustrated in Fig. 3.4 [41].
structures were expected to show presence of carbon in Raman spectroscopy. However, structures in Fig. 3.5(c) and (d) did not show the presence of any carbon according to Raman spectroscopy. Raman spectroscopy only showed presence of background fluorescence. Based on these observations, the conclusion was that this issue was due to the overoxidation of the polymer in the RTP tube since the temperature of the structure itself could exceed the set point temperature during an exothermic oxidative reaction in the tube with radiative heating. Therefore, the conclusion was that using rapid thermal annealing for stabilizing anneal might be causing this overoxidation. Although Raman spectroscopy alone could not identify the nature of the residual material that formed cone and pillar structures shown in Fig. 3.5(c) and (d), similar observations were reported previously when attempting to carbonize smaller nanoscale objects, such as DNA molecules without an additional aluminum oxide coating [139].

Fig. 3.6(a) and (b) show SEM images of structures with base diameter of 5 µm and height of 5 µm (C55 and P55 in Table 3.1) after oxidation at 350 °C for 15 minutes in RTP, whereas Fig. 3.6(c) and (d) show SEM images of structures with base diameter of 20 µm and height of 20 µm (C2020 and P2020 in Table 3.1) after oxidation at 350 °C for 15 minutes in RTP. It is clearly visible that smaller structures get more damaged compared to the larger ones. Similar outcomes can be observed in Fig. 3.7((a), (b), (c), and (d) correspond to C55, P55, C2020, and P2020, respectively, in Table 3.1) where structures were oxidized at 450 °C for 10 minutes in RTP. C55 and P55 got totally damaged, and C2020 and P2020 barely maintained their structures after higher oxidation temperature. This is convincing to believe that this overoxidation adversely affects smaller structures more than larger structures. Therefore, more precise temperature control is required to achieve optimal oxidation and stabilization of the precursor.

In several cases, successful carbonization was achieved with microscale cone structures 3D printed on metallized silica substrates. Thus, Fig. 3.4 could actually produce carbonized structures, although the outcome was not consistent. Fig. 3.8 shows examples of typical artifacts in 3D printed cone structures on metallized silica substrates after processing sequence I illustrated in Fig. 3.4. Fig. 3.8(a) shows one single carbonized structure whereas Fig. 3.8(b) shows an array of such structures. The structure in Fig. 3.8 shows
Figure 3.6: SEM images of cone and pillar structures after oxidation at 350 °C for 15 minutes in RTP. (a), (b), (c) and (d) correspond to the outcomes of oxidation of structures Cone C55, Pillar P55, Cone C2020 and Pillar P2020, respectively, of Table 3.1.
Figure 3.7:  SEM images of cone and pillar structures after oxidation at 450 °C for 10 minutes in RTP. (a), (b), (c), and (d) correspond to the outcomes of oxidation of structures Cone C55, Pillar P55, Cone C2020, and Pillar P2020, respectively, of Table 3.1.

Figure 3.8:  SEM images of cone structures printed on a silica substrate with Au/Ti/Cr metallization after successive anneals in O₂ and Ar under conditions illustrated in Fig. 3.4. (a) shows one single structure whereas (b) shows an array of such structures [41].
significant shrinkage of the cone structure after annealing which is qualitatively consistent with observations reported in previous studies [110, 68]. Raman spectroscopy (Fig. 3.9) verified the presence of carbon in the structure shown in Fig. 3.8. In the Raman spectroscopy, presence of background fluorescence is also observed alongside the carbon peaks. In addition to the significant shrinkage, pronounced wrinkles on the surface were formed in the case of structures on Ti reducing core carbon [more extensively near the base of the structure, Fig. 3.8(a)] which was not present in the case of silicon substrates. Also, these wrinkles were mostly concentrated on the base of the structure and closer the metallized substrate. Therefore, it can be concluded that the wrinkles originate during the anneal in the presence of metal layers, likely due to their catalytic role in a pyrolytic conversion. In this processing sequence, Ti was used as the metal, and therefore, catalytic role of titanium oxide was the potential cause of forming the wrinkles. However, the metal layers in the proposed processing sequence are required to provide electrical connection to the carbonized electrode and simultaneously form an insulating metal oxide on the surface surrounding carbonized structures. This indicates that process sequences needed to be modified for shape retention of the precursors. Therefore, the process sequence was optimized to achieve better retention of the shape and reduce artifacts during carbonization.

It is reasonable to assume that pyrolysis of organic precursors in the presence of titanium oxides can lead to higher fraction of volatilized products and decreased volume of the carbonaceous material. The proposed hypothesis is as follows: during initial heating, the polymer starts to liquify at \( \approx 300 \) °C. Under an optical microscope, this change can even be visually observed during oxidation. Next, in between 350 °C and 400 °C, chemical reactions in the partially pyrolyzed polymer are catalyzed by the presence of already formed titanium oxides leading to additional volatilization. Also, during this process, any additional water is driven off and common organic molecules break down. Fig. 3.10 illustrates these hypothetical phenomena occurring during the polymer carbonization in the presence of catalytic metals and/or metal oxides.

To minimize undesirable catalytic effects and optimize the oxidation step, the processing sequence was divided into two oxidation substeps (Fig. 3.11)). These substeps were required to ensure both stabilization of precursor and oxidation of titanium. The first step served
Figure 3.9: Raman spectroscopy of the cone structure on metallized silica substrate in Fig. 3.8(a) processed using process sequence 1.
Figure 3.10: Hypothetical processes occurring during anneals of polymers in the presence of metals on a silica substrate. At $\approx 300$ °C, the polymer starts to liquify. Between 350 °C and 400 °C, catalytic reactions take place in presence of titanium oxide leading to substantial volatilization of precursor [41].
Figure 3.11: Two processing sequences used in this work to reduce artifacts while carbonizing the 3D printed polymer structures on a metallized substrates. In sequence II-A, sputter etch and second oxidation take place before Ar anneal. In sequence II-B, Ar anneal and sputtering take place before second oxidation [41].
to initialize the oxidation of the polymer precursor and stabilize it prior to sputter etching Au. As such, sputter etching will not reduce material damage in a stabilized precursor. The expectation was that, once the precursor is stabilized, its continued anneal during the second oxidation substep would not be associated with unwanted catalytic processes even if Ti metal or its oxide is present on the surrounding surfaces. It would require multiple processing runs to verify the hypothesis. After experimenting with various recipes, the following protocol was established that provided high reproducibility and minimized occurrence of artifacts. During the first oxidation, the material was oxidized, but the presence of gold did not allow the precursor to be affected by the catalytic effect of titanium. The first oxidation step involved heating the chip and holding it at 340 °C for 10 min on a heated stage in the presence of air. At 340 °C, gold was not also oxidized. Typically, the second oxidation step consisted of heating the chip on the heated stage and holding it at 420 °C for at least 15 min. Stabilizing (oxidizing) anneals were performed on a heated stage (LTS420E-P, Linkam Scientific) in the ambient atmosphere. When oxidizing anneal was done on a heated microscope stage, the heating rate was 40 °C/min. Since RTP caused overoxidation in the previous experiments, this modified processing sequence avoided the use of RTP for oxidative anneal. Finally, carbonization was achieved by annealing the structures in Ar at 500 °C for 10 min in RTP. This modified sequence (sequence II-A in Fig. 3.11) produced carbonized structures with better shape retention compared to the structures shown in Fig. 3.8. Also, both pillar and cone structures showed better shape retention compared to Fig. 3.8. However, the wrinkles that were observed previously were still present in these structures after the final step (Fig. 3.12).

In the next iteration of the processing sequence (sequence II-B in Fig. 3.11), the first two anneals were performed in air and Ar, respectively, prior to sputter etching Au. Oxidative anneal was performed in air whereas carbonizing anneal was performed in Ar. It was expected that as the precursor material becomes more completely carbonized, it also becomes progressively more resistant to subsequent oxidation and volatilization. Therefore, this modified processing sequence wanted to achieve carbonization of polymer before it is exposed to catalytic titanium oxide. Besides, adverse catalytic effects would be less likely during the first two anneals since Ti remained covered with Au. Indeed, sequence II-B illustrated
Figure 3.12: SEM images of polymer cone (C1010 in Table 3.1) and pillar structures (P2020 in Table 3.1 in Table I) processed using sequence II-A shown in Fig. 3.11). (a and b) as printed structures; structures after the following consecutive steps: (c and d) oxidation at 340 °C for 10 minutes on a heated stage, (e and f) sputter etch for 75 seconds and second oxidation at 420 °C for 15 minutes on a heated stage, and (g and h) anneal in Ar at 500 °C for 10 minutes in RTP.
in Fig. 3.11 allowed to obtain structures with better shape retention and reduced artifacts (Fig. 3.13). However, significant shrinkage was still observed compared to the footprint of the 3D printed precursors. It is worthy to note that the footprint of the structures that underwent first anneal occupy a small fraction of their respective original footprints indicating that a significant amount of shrinkage occurs in the first oxidation phase [Fig. 3.13(a)–(d)]. When observing under an optical microscope, this shrinkage process can be observed in real-time. The surface around the structures also becomes rough due to dewetting and/or recrystallization of Au during the high temperature anneal and ring-like artifacts become more prominent [Fig. 3.13(e) and (f)]. The ring-like footprints encompassed more area as the process sequence progressed. These ring-like artifacts are likely to be related to the layer-by-layer nature of the 3D printing. During 3D printing, the layers are formed one after another, and these layers tend to reflow around the structures during annealing. The subtle ripples on the surfaces of as-printed structures become more pronounced as the precursor shrinks during anneals and the footprint of as-printed structures exceeds significantly the footprint of the annealed structures. The surface roughness is reduced after the second oxidation [Fig. 3.13(g) and (h)]. This is likely due to the removal of gold layer and dewetting and recrystallization during second oxidation. It is also evident that the shapes of the structures seen in Fig. 3.13(g) and (h) are not affected substantially by the last oxidative anneal. Conical structures tend to change in shape more compared to the cylindrical ones (pillars). This also aligns to the fact that sharp edged conical structures would potentially be more suitable for sensing applications. Overall, sequence II-B shown in Fig. 3.11 enabled most successful carbonization of 3D printed polymers within a CMOS-compatible temperature window.

### 3.2 Characterization

#### 3.2.1 Shrinkage of structures

Alongside the qualitative analysis of aforementioned processing sequences, the amount of volumetric shrinkage of polymer structures during their carbonization was quantified. This
Figure 3.13: SEM images of polymer cone (C1010 in Table 3.1) and pillar (P2020 in Table 3.1) structures processed using sequence II-B shown in Fig. 3.11. (a and b) as printed structures; structures after the following consecutive steps: (c and d) oxidation at 340 °C for 10 minutes on a heated stage, (e and f) anneal in Ar at 500 °C for 10 minutes in RTP, and (g and h) sputter etch for 30 seconds and final oxidation at 420 °C for 15 minutes on a heated stage [41].
would give an idea of the dimension of the final carbonized microelectrodes and quantify the processing sequence in terms of shrinkage. Table 3.2 shows a volumetric fraction of the 3D printed material remaining after each step of processing sequence II-A and II-B of Fig. 3.11. The volumetric percentage of residue material was calculated as follows,

\[
\% \text{ of residual material volume, after } x \text{ processing step} = \frac{V_0 - V_x}{V_0} \times 100\% \quad (3.7)
\]

where, \(V_0\) and \(V_x\) are volumes of as-printed polymer structure and the same structure after \(x\) processing step, respectively. Table 3.2 also shows that maximum shrinkage occurs during the first oxidative/stabilizing anneal.

### 3.2.2 Thickness of insulating layer

The titanium oxide (TiO\(_x\)) layer works as an insulator between the metal electrodes and the electrochemical environment. This needs to be thick enough to provide insulation between the electrochemical analyte and the transducer. Therefore, the thickness of thermally grown TiO\(_x\) is an important parameter that determines robustness of this insulation resulting from the oxidation process. Titanium oxides formed by using both micro-hot plate and RTP were considered to characterize the oxide growth. For this purpose, insulating oxide grown on titanium metal around the structures was characterized by optical reflectometry and ellipsometry. Reflectometry records the amount of reflected light from the sample surface at different wavelengths while the incident light is normal to the sample surface. For a sample in air, reflectance depends on the refractive index (\(\eta\)) and absorptivity (\(k\)) following the relation [81]

\[
R = \frac{(\eta - 1)^2 + k^2}{(\eta + 1)^2 + k^2} \quad (3.8)
\]

Therefore, light is incident and subsequent reflectance are recorded to obtain multiple equations at multiple wavelengths. From these equations, \(\eta\) and \(k\) are solved that correspond to a specific material. Also, thicker films produce greater number of oscillations for a given wavelength range. However, if the film is too thin, there may not be enough reflectance oscillation thereby providing too less information to solve model parameters. On the other hand, ellipsometry records reflectance at a non-normal angle and at two different
Table 3.2: Relative volume of pillar structures (P2020 in Table 3.1) after each step of two modified processing sequences II-A and II-B shown in Fig. 3.11 [41].

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Step after which volume of the structure was measured</th>
<th>Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-A</td>
<td>1: 3D printing</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2: Stabilizing anneal</td>
<td>2.71</td>
</tr>
<tr>
<td></td>
<td>4.a: Second oxidative anneal</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>5.a: End of processing</td>
<td>0.31</td>
</tr>
<tr>
<td>II-B</td>
<td>3D printing</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2: Stabilizing anneal</td>
<td>2.42</td>
</tr>
<tr>
<td></td>
<td>3.b: Ar anneal</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>5.b: End of processing</td>
<td>0.72</td>
</tr>
</tbody>
</table>
polarizations. It gives twice as much information for analysis, and therefore, more sensitive to thin layers. Moreover, variable-angle ellipsometry can run reflectance measurements at multiple angles thereby generating significantly more information for analysis and solving parametric equations.

Fig. 3.14 shows the thickness of TiO\textsubscript{x} grown on Ti coated chips as a function of oxidation time and other oxidation conditions. Other oxidation conditions include the chamber where oxidation is being performed, and oxidation temperature. The difference in the TiO\textsubscript{x} thicknesses grown during anneals on the hot plate and in RTP could be due to the difference in the actual temperature of the sample surface and the fact that oxidation in pure oxygen occurs at a faster rate compared to oxidation in air. This also potentially explains why overoxidation was observed initially when precursors were oxidized in RTP. Also, annealing in Ar can partially reduce some of TiO\textsubscript{x} already formed on the surface, thereby decreasing the effective thickness of the oxide layer. Therefore, presence of gold layer during carbonizing anneal is helpful in reducing catalytic effect. Hence, thinning of TiO\textsubscript{x} during Ar anneal (processing sequence II-A in Fig. 3.11) may have a negative effect when electrical insulation of the areas surrounding carbonized electrodes is important.

3.2.3 Electrochemical characterization

If a metal is immersed in a water-based electrolyte, ions are immediately adsorbed around the metal surface (and opposite ions are accumulated right outside the first adsorbed layer layer) to create a double layer capacitor within a couple of nanometer space. When a voltage is applied at the metal electrode, an electric field is created between this electrode and the electrolyte across this capacitor. Fig. 3.15 shows the equivalent circuit model of the electrode where \( C_{dl} \) represents the double layer capacitor. However, this capacitor itself does to represent any charge transfer across the electrode-electrolyte interface. However, electron transfer might occur between electrolyte and electrode as well as material deposition/removal on the electrode surface. These can cause charge transfer or current across the interface. The resistance associated with this charge transfer is represented by Faradaic impedance, \( R_F \) in Fig. 3.15.

Most of the electrochemical cells consist of at least two electrodes, Fig. 3.16 shows the
**Figure 3.14:** Measured thickness of TiO$_x$ grown on a metallized silica chip during oxidative anneal for 5, 15, and 30 minutes in 420 °C on a hot plate (dashed line in the plot is used to indicate a trend). The triangle corresponds to the TiO$_x$ thickness on a metallized silica chip at the end of oxidative anneal at 450 °C for 10 minutes. The circle corresponds to the TiO$_x$ thickness on a metallized silica chip at the end of the two-step annealing process (oxidative anneal at 450 °C for 10 minutes followed by anneal in Ar at 500 °C for 10 minutes [41].)

**Figure 3.15:** Equivalent circuit model of an electrode. $R_F$ and $C_{dl}$ correspond to the resistance and capacitance, respectively, of the double layer capacitor.
Figure 3.16: Equivalent circuit model of an electrochemical cell including two electrodes in an electrolyte. \( C_{dl-1} \) and \( C_{dl-2} \) are double layer capacitors, \( R_{F-1} \) and \( R_{F-2} \) are Faradaic impedances, and \( R_{sol} \) is the solution resistance.
equivalent circuit model of a two-electrode system where \( C_{dl-1} \) and \( C_{dl-2} \) are double layer capacitors, \( R_{F-1} \) and \( R_{F-2} \) are Faradaic impedances, and \( R_{sol} \) is the solution resistance in between these two electrodes.

Now, in order to measure the potential across an electrode and the electrolyte, it might sound reasonable to probe one end of the voltmeter to the electrode and another to the electrolyte solution. However, as soon as a probe is inserted into the electrolyte, a potential will be formed across it. Therefore, the measured potential will be the difference between the actual potential and this developed potential. Besides, in case of a change in applied voltage across these two electrodes, it is hard to anticipate in which ratio this change in voltage will be divided. Therefore, to overcome these issues, the idea of reference electrode is introduced. The potential across the interface between the solution and the reference electrode is constant. Therefore, any change in applied voltage can be attributed to the working electrode only since the voltage drop in the reference electrode remains constant. It is important to remember that the working electrode and the reference electrode are usually placed as close as possible to each other to minimize the solution resistance between them. Examples of reference electrode are standard calomel electrode and Ag/AgCl electrode. Alongside maintaining a constant potential, ideally a reference electrode should also have negligible impedance compared to the working electrode. Therefore, the simplified equivalent circuit model can be represented by Fig. 3.17 where impedance of reference electrode is negligible compared to that of the working electrode.

However, there is a problem in using reference electrode. If significant current passes through the reference electrode, it changes the potential of the reference electrode, thereby violating the constant potential property of the reference electrode. Hence, another electrode (auxiliary or counter electrode) is used in the setup to collect the current density coming from the working electrode. However, other than supplying or draining the current, counter electrode should cause minimal disturbance within the system.

Electrical impedance measurements were carried out using an electrochemical system (PARSTAT 2273, Princeton Applied Research) connected to a 3-electrode electrochemical cell (Fig. 3.18) in the presence of \( K_3[Fe(CN)_6] \), which is a model electrochemically active agent added to the background KCl electrolyte. The electrochemical cell was already available in
Figure 3.17: Equivalent circuit model of an electrochemical cell including working and reference electrodes in an electrolyte. The reference electrode ideally provides a constant potential with a negligible impedance.
Figure 3.18: (a) 3-electrode electrochemical cell used for electrical impedance measurement of the carbonized structures. (b) Electrochemical cells 3D printed and used in this work. Formlabs 3D printer was used to 3D print the cells. To create stl files for 3D printing, 3D CAD part of the COMSOL software was used to compile and export stl files. (c) electrochemical cell right before connecting to the working electrode. (d) electrochemical cell while connected to the counter electrode (Pt wire, top left), reference electrode (Flexref 178581, top right) and working electrode (the chip at the bottom) [41].
the cleanroom with reference and counter electrodes connected to it. An elastomer O-ring was used to seal the cell against the chip under test. In order to maintain the sealing, sufficient pressure was applied from the top, and solution was added from the top also through the cell. A platinum wire and a Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. The amplitude of the probing AC voltage was 10 mV with a DC bias of 0 V measured against the reference Ag/AgCl electrode. The concentrations of $\text{K}_3[\text{Fe(CN)}_6]$ and KCl were 10 mM and 1 M, respectively. Fig. 3.19 shows the impedance spectra [with the electrochemical system under test in inset (a)] measured for similarly processed metallized silica chips with and without an array of carbonized structures. A large array of structures was used to ensure significant signal to be collected by the electrodes. As can be seen, the capacitive nature of the interfacial impedance dominates in the range of approximately 1–100 Hz, and corresponds to sloped lines in this range. Also a very low impedance is observed beyond 100 Hz. The minimum impedance at frequencies above approximately 1000 Hz is determined by the bulk electrolyte resistance, while the change in the slope at the low frequency limit is due to active currents contributing significantly below 1 Hz. The origin of active currents can be twofold: (1) due to defects and dielectric leakage in the TiO$_x$ layer; (2) due to the presence of electrically conductive carbon structures. The leakage in the dielectric can be caused if the insulating layer is too thin. The presence of electrical conducting carbon can explain an approximately six times decrease in low-frequency impedance of the samples with carbonized structures.

The inset (b) in Fig. 3.19 shows a simplified equivalent circuit of the electrochemical system that includes interfacial capacitance $C_i$, interfacial resistance $R_i$, electrode effective resistance $R_{el}$ and bulk electrolyte resistance $R_{be}$. According to this equivalent circuit, the total impedance $Z$ can be expressed as,

$$Z = \frac{1}{2\pi f C_i} + \frac{1}{R_i} + \frac{1}{R_{el}}^{-1} + R_{be}$$

(3.9)

where, $f$ is the frequency. By matching experimental data to the impedance spectra (Fig. 3.19) calculated using this equivalent circuit, it was found that estimated values of $C_i$ changed from 4.5 µF to 8.0 µF due to the presence of carbonized structures.
Figure 3.19: Absolute values of impedance measured as a function of frequency for similarly processed metallized chips with (solid circles) and without (crosses) an array of carbonized structures. Inset shows (a) the experimental system and (b) its equivalent circuit. The simulated impedance spectra shown with dashed and solid lines for the system, respectively, with and without carbon electrodes were obtained by fitting to the experimental data [41].
Chronoamperometry is an example of potential step method. A potential step from $E_1$ to $E_2$ is provided as input and current response is recorded as a function of time. $E_1$ and $E_2$ are chosen in a way so that the redox potential is in between $E_1$ and $E_2$. An upward pulse causes oxidation in the system whereas a downward pulse generates reduction. Chronoamperometric measurements were carried out to study electrochemical responses caused by presence of carbonized structures in the presence of $K_3[Fe(CN)_6]$ which is used as a model electrochemically active agent added to the background electrolyte. The background electrolyte increases the conductivity thereby increasing the speed of the reaction in the cell.

In the preliminary tests, the chronoamperometric behavior of the chips with and without carbonized structures was compared (Fig. 3.20). In the chronoamperometric mode, the potential between the working electrode and the reference Ag/AgCl electrode was maintained at 0.8 V. During the impedance measurements the amplitude of the probing AC voltage was 10 mV. The concentrations of $K_3[Fe(CN)_6]$ and KCl were 10 mM and 1 M, respectively. As can be seen in Fig. 3.20, the steady state current measured in the chronoamperometric mode is approximately 100 nA when no carbonized structures are present. This current can be considered as a noisy background current. The current is almost 3 orders of magnitude higher when an array of carbonized structures is present on the chip. This current response is also dependent on the active surface area of the electrodes meaning a larger surface area will be able to collect more current thereby providing larger signal. This proves that the electrochemical reaction associated with the measured current occurs predominantly on the surface of the carbonized structures while the surrounding area is significantly less electrochemically active due to the presence of an electrically insulating TiO$_x$ layer. The exponential drop in current can be explained as follows: in the beginning the electrode can react freely with solution generating a high current. As time goes on, the chemical product starts to accumulate on the electrode surface causing lesser reduction on the clogged interface. This reduces the current response over time.

### 3.2.4 Raman spectroscopy

A comparative analysis is required to understand the degree of carbonization of this processing sequence compared to pyrolysis conducted at higher temperatures. Therefore,
Figure 3.20: Chronoamperometric response of a sample with carbonized nanostructure and a sample with no carbonized structure in 10 mM $K_3[Fe(CN)_6]$ and 3.5 M KCl. Potential step was $E_0=0.199 \, \text{V}$ to $E_1=0.8 \, \text{V}$ [43].
Raman spectra was collected and compared for the structures carbonized at different temperatures. The Raman spectra was obtained using a Raman microscope (InVia, Renishaw, Inc.). As can be seen in Fig. 3.21, two distinct peaks at ≈ 1350 cm\(^{-1}\) and ≈ 1590 cm\(^{-1}\) are attributable to D and G bands, respectively. D-band (defect band or disorder band) is produced by hybridized vibrational modes associated with the graphene edge. D-band comes from local defects or disorders present in carbon. G-band comes from sp\(^2\) bonded graphitic sheets [105]. It is a result of interactions between the stacked graphene layers. The ratio of intensities between D and G bands is frequently applied to determine the amount of defects in carbon materials [94]. Fig. 3.21 gives a ratio of almost unity (≈ 0.99) between the bands. It validates the presence of numerous defect sites. On the surface of crystal, defects levels throughout the band gap are due to the presence of dangling bonds [40]. Free radicals are those atoms which have very few bonding partners. Thus they cannot satisfy their valences and possess unpaired electrons. A free radical existing in an immobilized environment is called a dangling bond. These dangling bonds can recombine with other dangling bonds, work as reactive intermediate, contribute to intramolecular reactions, or help in charge transfer reactions. This is possible because acidic and basic groups are available since it has an unpaired electron in the atomic orbital [112, 122]. Therefore, these carbonized polymers are potentially active and sensitive in electrochemical sensing [44]. The peaks become narrower and more pronounced as the annealing temperature increases indicating that carbonization is not complete at 500 °C. This is expected since in order to maintain compatibility with CMOS electronics, the carbonization temperature was not raised above 500 °C. Raising the annealing temperature also reduces background fluorescence that is typically observed when products of incomplete pyrolysis are present. However, the exact amount of carbon can be quantified using other materials characterization tools, such as transmission electron microscopy, mass spectrometry, and X-ray diffraction. Although the exact quantification of the degree of carbonization achieved in the implemented CMOS-compatible processing sequence is beyond the scope of this work, a substantial fraction of carbon present in structures carbonized at 500 °C is evident from the spectra shown in Fig. 3.21.
Figure 3.21: Raman spectra of 20 µm × 20 µm polymer cones (C2020 in Table 3.1) pyrolyzed (1) in a single Ar anneal at 500 °C, (2) in a single Ar anneal at 600 °C and (3) in a sequence of Ar anneals at 600 °C and 950 °C for 10 minutes each. All anneals were done in RTP [41].
3.3 Summary

A fabrication sequence has been developed for creating carbon based electrodes on metallized substrates by pyrolyzing microscale structures 3D printed using two-photon polymerization. Two-photon polymerization was achieved using commercially available Nanoscribe tool. The novelty and uniqueness of the processing sequence consists in creating electrically insulating surrounding during multi-step carbonization sequence. The multi-step processing sequence included stabilizing anneal in air and carbonizing anneal in Ar. The demonstrated processing was optimized to minimize undesirable structural changes occurring in polymer precursors during their pyrolysis. It was observed that significant shrinkage occurs during the initial oxidation phase. It was also found that the presence of certain metals, in particular Ti, has a pronounced adverse effect on shape retention during the pyrolysis. However, Ti is required to provide insulation by forming titanium oxide during oxidation. To address this issue, a modified processing sequence was developed. The optimized processing sequence achieved carbonization with better shape retention and minimal artifacts. Nonetheless, significant shrinkage in structures was observed irrespective of the presence of metallization, with smaller structures being affected more substantially in this regard. Carbonization of polymer precursors was verified using Raman spectroscopy and impedance measurement.
Chapter 4

Carbonization of Polymer using Localized Joule Heating

Portions of this chapter have been published as:


Although a significant degree of carbonization was successfully demonstrated within CMOS compatible temperature window, complete carbonization is known to require temperatures significantly above CMOS compatible threshold of 700 °C. To address this issue, localized heating, induced by electric currents, was proposed. To explain this idea further, the plan was to drive current through the partially pyrolyzed polymer so that it heats up locally and self-pyrolyzes even more completely thereby transforming into a pure carbon material through this process. While these localized heating methods were shown to be very promising for variety of emerging applications [72, 137, 79], based on the literature search,
they have not been applied to carbonization of 3D printed polymer structures. Therefore, the objective was to identify a set of technological parameters, such as power density, local temperature, and processing speed, that lead to controllable transformations of 3D printed polymer micro and nano-structures into functional carbon-based materials under conditions of spatially confined heating. This approach will extend applicability of 3D printing based on two-photon polymerization to variety of emerging applications, such as low-cost implantable sensors integrated with flexible electronics for biomedical industry.

A similar approach was taken previously where the authors developed a steady-state one-dimensional drift-diffusion thermal-electric model of graphite rod under an externally applied bias voltage [82]. They observed a non-uniform Joule heating-initiated temperature distribution along the rod whereas maximum temperature was generated at the center. Also, maximum temperature increased by multiple times when applied voltage was doubled. Based on their analysis, they also predicted that such Joule heating mechanism can be further implemented for thermochemical conversion, such as pyrolysis and gasification. Joule heating of graphite fibers was also used to analyze thermal expansion properties in a graphite/epoxy composite [120].

Despite its clear potential, this approach involves several technological and design challenges. Also, previously demonstrated pillar and cone structures are not suitable for applying voltage across them. First of all, in order to conduct current, electrically insulating polymer structures need to be converted into a carbon-rich material with appreciable electric conductivity. This conductivity would further allow drive current through the structure and initiate Joule heating. This step needs to remain within the CMOS-compatible technological window. To address this challenge, new structures were designed that facilitate biasing across the device for the proposed localized Joule heating. The geometrical parameter in this design phase is also challenging since structures need to maintain their shapes during the partial pyrolysis process so that voltage can be applied across them for Joule heating. Also, it was observed that 3D printed polymer structures tend to shrink and deform significantly during the pyrolysis. Thus, it needs to be verified that the structures printed according to these new designs can withstand initial thermal processing physically and mechanically. As it was later observed, structures smaller than 10 µm struggle to survive initial processing
sequence and thus can not be reliably used for Joule heating. Moreover, the 3D printed and subsequently partially pyrolyzed structures need to form stable connections with metal electrodes to enable biasing.

4.1 Analytical Approximation and COMSOL simulation

Analytical approximations were explored to approximate electrical power delivery at different sections of the system, namely bridge, pillars and metal leads. The objective was to determine required experimental conditions to obtain complete pyrolysis of partially pyrolyzed polymer (PPP, produced from CMOS-compatible heating and annealing of non-conducting polymer precursor) structure through Joule heating approach. For this, a thin PPP wire bridge was considered in between two PPP pillars connected to two metal electrodes. Although the starting precursor material of both bridge and pillars will be same, the geometrical parameters will be different. The bridge will be of smaller diameter thereby having larger resistance and producing higher joule heating. On the other hand, pillars will be of larger diameter. Metal electrodes will be used to facilitate voltage biasing. Using experiment-based realistic geometrical parameters, a passive component (resistor) based model of the experimental structure was developed. Within a safe voltage limit of 30 V, and for a wide range of resistivity values, this stationary model was used to estimate current flow and electrical power at metal, pillars, and bridge sections of the system. This power will vary as a function of reduced resistivity of pyrolyzed precursor during localized annealing. This will also determine the feasibility of the designed approach within a safe and reasonable voltage limit. For analytical approximation, the following assumptions were considered,

- This is a steady-state system.
- Unidirectional heat flow is considered.
- No internal heat generation within the pillars.

For analytical approximation, total current through the structure, \( I \), was calculated using,
\[ I = \frac{V}{R} \] \hspace{1cm} (4.1)

where, \( V \) is the applied voltage bias, and \( R \) is the total resistance calculated using,

\[ R = R_{\text{metal}} + R_{\text{pillars}} + R_{\text{bridge}} \] \hspace{1cm} (4.2)

where, \( R_{\text{metal}}, R_{\text{pillars}}, \) and \( R_{\text{bridge}} \) are the resistances of metal, pillars, and bridge, respectively. \( R_{\text{metal}}, R_{\text{pillars}}, \) and \( R_{\text{bridge}} \) have been determined using the following equations,

\[ R_{\text{metal}} = \frac{\rho_{\text{metal}} L_{\text{metal}}}{H_{\text{metal}} W_{\text{metal}}} \] \hspace{1cm} (4.3)

\[ R_{\text{pillars}} = 2 \times \frac{\rho_{\text{pillar}} L_{\text{pillar}}}{\pi r_{\text{pillar}}^2} \] \hspace{1cm} (4.4)

\[ R_{\text{bridge}} = \frac{\rho_{\text{bridge}} L_{\text{bridge}}}{\pi r_{\text{bridge}}^2} \] \hspace{1cm} (4.5)

where, \( \rho_{\text{metal}}, \rho_{\text{pillar}}, \) and \( \rho_{\text{bridge}} \) are the resistivities of metal, pillar, and bridge, respectively, \( L_{\text{metal}}, L_{\text{pillar}}, \) and \( L_{\text{bridge}} \) are the length of metal, pillar, and bridge, respectively, \( H_{\text{metal}} \) and \( W_{\text{metal}} \) are the thickness and width, respectively, of metal, \( r_{\text{pillar}} \) and \( r_{\text{bridge}} \) are the radii of pillar and bridge, respectively. Electrical powers of metal \( (P_{\text{metal}}) \), pillars \( (P_{\text{pillar}}) \) and bridge \( (P_{\text{bridge}}) \) were calculated by

\[ P_{\text{metal}} = I^2 R_{\text{metal}} \] \hspace{1cm} (4.6)

\[ P_{\text{pillar}} = I^2 R_{\text{pillars}} \] \hspace{1cm} (4.7)

\[ P_{\text{bridge}} = I^2 R_{\text{bridge}} \] \hspace{1cm} (4.8)

As seen before, pyrolyzed precursor experiences significant shrinkage of about 50\% in diameter, 90\% in height, and 99\% in volume. Table 4.1 shows the list of geometrical
Table 4.1: Dimensions of bridge-on-pillars structures used for analytical approximation and COMSOL simulation.

<table>
<thead>
<tr>
<th></th>
<th>Metal(Platinum)</th>
<th>P-2510252</th>
<th>A-2530183</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pillar</td>
<td>Bridge</td>
<td>Pillar</td>
</tr>
<tr>
<td>Length (m)</td>
<td>9.5×10^{-3}</td>
<td>–</td>
<td>25×10^{-6}</td>
</tr>
<tr>
<td>Width (m)</td>
<td>5×10^{-6}</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Height/thickness (m)</td>
<td>5×10^{-8}</td>
<td>25×10^{-6}</td>
<td>–</td>
</tr>
<tr>
<td>Diameter (m)</td>
<td>–</td>
<td>10×10^{-6}</td>
<td>2×10^{-6}</td>
</tr>
</tbody>
</table>
parameters used for analytical approximations and COMSOL simulations. Based on estimated shrinkage of the P-2510252 structure, the geometrical parameters of A-2530183 were used for analytical approximation and COMSOL simulations.

Fig. 4.1(a) shows the power generated in metal, pillar and bridge sections of the bridge-on-pillars structure as a function of decreasing bridge and pillar resistivity for an applied voltage of 30 V (close to the safe range of voltage source). It shows that, due to the designed thinner bridge compared to the pillar section, bridge generates higher power compared to any other section, even to metal, for as low as bridge and pillar resistivity of $10^{-4}$ Ohm-m. Fig. 4.1(b) shows shows power generation at bridge as a function of anticipated decrease in resistivity for a starting bridge and pillar resistivity. The observed peaks in the plots correspond to the maximum power when the resistances of bridge and pillar match. It also shows that power of $\mu$W or more can be generated when starting bridge and pillar resistivity is 1 Ohm-m or less.

Finite-element based COMSOL simulation was conducted to determine temperature gradient within the structure in an environment approximating experimental condition. For this a gaseous environment was considered surrounding the structure to replicate experimentally present flowing forming gas (2% H$_2$ + 98% Argon). To simulate heat loss from the structure surface through the surrounding gas, radiation and convection (gas velocity 0 ms$^{-1}$) was considered while surface emissivity of the bridge section was considered to be 0.8 Wm$^{-2}$. To take into account the change in thermal conductivity as a function of increasing bridge-on-pillars structure due to applied bias, temperature dependent thermal conductivity of the surrounding gas was considered. Heat capacity at constant pressure, relative permittivity, density, and thermal conductivity of the bridge-on-pillars structure were 1420 J/(kg.K), 1, 1190 kg/m$^3$, and 2 W/mK.

Fig. 4.2(a) shows the a 3D CAD model used for 3D printing of bridge-on-pillars structure with the geometrical dimensions of P-2510252. It shows that the pillars were noticeably longer and wider compared to the bridge to make sure that the pillar does not shrink all the way to substrate from high temperature treatment. Fig. 4.2(b) shows the structure meshing of 3D COMSOL model in a gaseous environment used for temperature estimation as a function of applied bias and electrical conductivity. The geometrical dimensions of
Figure 4.1: (a) Comparison of estimated electrical power on metal leads, pillars, and bridge section as a function of bridge and pillar resistivity of the electrically conducting 3D bridge-on-pillars structure for assumed geometrical dimensions (A-2530183). (b) Estimated electrical power at the bridge section of the bridge-on-pillars structure as a function of decreasing bridge resistivity from the same starting bridge and pillar resistivity for assumed geometrical dimensions (A-2530183).
**Figure 4.2:** (a) Bridge-on-pillars structure having dimensions of A-2530183 designed by CAD for 3D printing using two-photon polymerization. (b) Structure meshing for COMSOL simulation having dimensions of A-2530183.
the 3D COMSOL model are analogous to A-2530183, to take into account the estimated shrinkage of structure P-2510252 from high temperature processing.

When the structure is surrounded by a gaseous environment, heat dissipation from the bridge is dominated by dissipation through the gas rather than sinking through the pillars. Fig. 4.3(a) shows the normal heat flux emanating from the surface of the bridge section when surrounded by a gas with thermal conductivity of 0.05 W/mK. Each curve corresponds to an initial electrical conductivity of the partially pyrolyzed pillar and bridge. As the electrical conductivity increases, the heat flux emanating from the surface increases due to the expected increase in the bridge temperature. However, for each value of electrical conductivity, the heat flux remains fairly constant even if the thermal conductivity of the partially pyrolyzed structure changes. Fig. 4.3(b) shows the change in average temperature at the bridge as a function of thermal conductivity of surrounding gas. Each curve corresponds to the applied electrical power to the structure while applied voltage bias was 30 V. Electrical power was varied when electrical conductivities varied from 1 S/m to $10^4$ S/m. It shows that, for each delivered power level, as thermal conductivity of the structure increases, heat dissipates faster through the gas thereby reducing the average temperature of the bridge. Based on the literature and considering the potential temperature window of 400-600 °C, the thermal conductivity of the gaseous environment was considered to be 0.05 W/mK during COMSOL simulation [118].

In the COMSOL, the rate of heat transfer through the surrounding is determined by the following equation [21]

$$ - \mathbf{n} \cdot \mathbf{q} = \epsilon \sigma (T_{\text{amb}}^4 - T_{\text{body}}^4) $$

(4.9)

where, $\mathbf{q}$ is the radiative heat transfer, $\epsilon$ is the emissivity of the body, $\sigma$ is the Stefan-Boltzmann constant ($=5.67 \times 10^{-8}$ J/s.m$^2$.K$^4$), $T_{\text{amb}}$ is the ambient temperature in kelvin, and $T_{\text{body}}$ is the surface temperature of the bridge in kelvin.

Fig. 4.4(a) shows the temperature distribution throughout the simulation model when the ambient temperature was 400 °C, electrical conductivity was 10 S/m, and an electrical bias of 30 V was applied. It shows that the maximum temperature is generated within
Figure 4.3: (a) Heat flux emanating from and normal to the bridge surface as a function of thermal conductivity of bridge when the structure is surrounded by a gas of thermal conductivity of 0.05 W/mK. Each curve corresponds to the starting electrical conductivity of the partially pyrolyzed polymer. (b) Average temperature of the bridge section of bridge-on-pillars structure as a function of thermal conductivity of surrounding gas. Each curve corresponds to the electrical power applied to the structure. Electrical power was varied by varying electrical conductivity of the structure from 1 to $10^4$ S/m. In both (a) and (b) applied bias was 30 V, thermal emissivity and thermal conductivity of bridge were 0.8 W/m$^2$ and 2 W/mK, respectively.
Figure 4.4: (a) Heat map of the COMSOL model of bridge-on-pillars structure having the dimensions of A-2530183 and electrical conductivity of 100 S/m. (b) Simulated average difference between temperatures within the bridge section of the bridge-on-pillars structure and ambient 400 °C as a function of applied bias voltage across the pillars. Each curve corresponds to a starting electrical conductivity of both bridge and pillar. (c) Simulated difference between the local temperature of the bridge and ambient 400 °C along the bridge section of the bridge-on-pillars structure for an applied bias voltage of 30 V. Each curve corresponds to a starting electrical conductivity of both bridge and pillar. In all the cases of (a), (b), and (c), thermal conductivity of bridge and surrounding gas were 2 and 0.05 W/mK, respectively and thermal emissivity of bridge was 0.8 W/m².
the active bridge region compared to the pillars. Fig. 4.4(b) shows the average temperature difference between the bridge section of the bridge-on-pillars structure and ambience (400°C) as a function of applied bias voltage across the pillars. Each curve corresponds to a starting electrical conductivity of both bridge and pillar while the ambient temperature is 400 °C. It shows that the average temperature can be within 400 °C to 3000 °C when conductivity changes from $10^3$ to $10^4$ S/m applying a safe voltage of 30 V. Fig. 4.4(c) shows temperature difference between the local temperature of the bridge and ambient 400 °C along the bridge length for an applied voltage of 30 V and a conductivity range of 1 to $10^4$ S/m. An important observation here is that the temperature difference difference drops near the ends of the bridge. This says that heat dissipation through the pillars is not strong and heat dissipation through the gaseous environment is the dominant heat dissipation mechanism. Also, this output is observed considering uniform bridge thickness profile, and therefore, any experimental change in thickness will affect the temperature distribution.

4.2 Complete carbonization of partially pyrolyzed polymers

4.2.1 Chip layout and pyrolysis of polymers

The experimental steps of the this approach stem from the aforementioned study on CMOS-compatible carbonization of polymers. However, addressing distinct technological challenges as mentioned above requires modification of several processing steps. The bridge-on-pillars structures needed to be connected to an external environment to facilitate biasing. As such, a platinum-on-titanium metal stack was used as the electrode on silica substrate. The reason for using titanium and platinum are as follows: titanium provides adhesion and platinum provides better thermal stability. Thus, titanium would make sure than that metal electrodes are attached to the substrate and platinum would ensure minimum reaction with 3D printed structures during anneals. Specifically, 10 nm titanium (Ti) and 50 nm platinum (Pt) metal stacks were used as electrodes. The electrode layouts were designed using Layout Editor tool. The electrode layouts were generated in the industry standard GDSII format.
for photolithographic mask fabrication. Multiple replica of the layout was printed on a single wafer to have multiple samples for testing from a single wafer. The electrodes were patterned on a 100 mm silica wafer using a sequence of contact photolithography and metal lift off. The wafer was then diced into 15 mm × 15 mm chips using an Accretech dicing saw (Accretech-SS10). During dicing, it was required to make sure that proper blade was being used, otherwise it would damage the wafer. The layout of the patterned single chip is shown in Fig. 4.5, where Fig. 4.5(a) shows the layout of a single chip, and Fig. 4.5(b) shows the zoomed-in view of the center where the bridge-on-pillars structures were to be printed. On a single chip, six designs could be printed, processed, and characterized. The distances between the electrodes were selected to match the bridge lengths of 5, 10 and 20 µm in the bridge-on-pillar structures that are subsequently printed using the 2-photon polymerization (2PP) technique.

Bridge-on-pillars structures were 3D printed using the commercially available 2PP tool. Two sets of geometrical parameters were used for printing 3D bridge-on-pillars structures as shown in Table 4.2. Similar to the aforementioned processing sequence, bridge-on-pillars structures were carbonized using a two-step carbonization process (Fig. 4.6), where the first step included heating the chip and holding it at 340 °C for 10 minutes in the presence of air to initialize oxidation. The next step involved a carbonizing anneal in argon (Ar) or Hydrogen (H₂) and Ar at 500-950 °C for 30 to 27 hours in a rapid thermal processing tool (First Nano EasyTube® 3000). It was seen that structure P-2510252 can overlap well and thus can maintain better connection with metal electrodes after high temperature processing. Before and after various processing steps, a scanning electron microscope (SEM, Zeiss Merlin) was used to image the structures, and Raman spectroscopy (Renishaw InVia) was used to determine the degree of carbonization.

Conductivity of the bridge section of the bridge-on-pillars structure, σ was calculated using the following formula,

\[ \sigma = \frac{1}{\rho} \]  (4.10)
Figure 4.5: Layout of a chip with 6 pairs of photolithographically patterned metal electrodes. (a) Layout of the entire chip. (b) Zoomed-in center section where 6 bridge-on-pillars structures were 3D-printed using 2PP.

Table 4.2: Dimensions of designed polymer bridge-on-pillars structures 3D-printed using 2PP.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Pillar</th>
<th>Bridge</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-2010202</td>
<td>20 μm</td>
<td>20 μm</td>
</tr>
<tr>
<td>P-2510252</td>
<td>25 μm</td>
<td>25 μm</td>
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</table>

<table>
<thead>
<tr>
<th>Height (μm)</th>
<th>Diameter (μm)</th>
<th>Length (μm)</th>
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<td>20</td>
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</tr>
<tr>
<td>25</td>
<td>10</td>
<td>25</td>
<td>2</td>
</tr>
</tbody>
</table>
Figure 4.6: Process sequence to obtain partially pyrolyzed electrically conducting bridge-on-pillar structures on silica substrates. 10 nm titanium (Ti)/50 nm platinum (Pt) stack was used as metal leads to facilitate electrical biasing. Structures were initially 3D printed using two-photon polymerization method and then developed. A CMOS-compatible, two-step annealing process was followed to obtain partially carbonized bridge-on-pillars structures.
\[ \rho = \frac{RA}{L} \]  

(4.11)

where, \( \rho \) is the resistivity, \( R \) is the resistance, \( A \) is the cross-sectional area, and \( L \) is the length of the bridge. The cross-sectional area, \( A \) was calculated using the following formula,

\[ A = \pi r^2 \]  

(4.12)

where \( \pi = 3.14159 \) and \( r \) is the radius of the bridge. While measuring current from an applied voltage sweep, resistance was calculated from the slope of the current-voltage graph. In chronoamperometric measurements, resistance was calculated from measured current and an applied voltage of 9.945 V. When a fixed bias was applied using a voltage source, resistance was determined from measured current and calculated voltage drop across the bridge structure.

### 4.2.2 Obtaining high electrical conductivity through pyrolysis

Analytical approximation and COMSOL simulation indicate that conductivity in the order of 10 S/m is required to generate temperature of 900 °C within the bridge section. Since 3D printed bridge-on-pillars structure is insulating in nature, the structures need to be pyrolyzed first to achieve such electrical conductivity for driving current. For this, the similar two-step carbonization process as discussed before was used. However, to achieve conductivity of 10 S/m or more, following the oxidative anneal, longer annealing in 500 °C and 600 °C were used in RTP. Table 4.3 shows a list of samples processed at 600-900 °C for 10 minutes to 27 hours. While processing, it is important to confirm the structural stability and proper connectivity throughout the structure. Fig. 4.7 shows optical microscopy and SEM images after various stages of processing of sample 600-20h-A and 600-20h-B. Fig. 4.7(a) shows optical microscopy images of sample 600-20h-A and 600-20h-B after 3D printing. It shows the optical transparency of the polymer structures after 3D printing. Some structural defects formed between polymer and metal leads can also be observed which can be mostly attributed to cavitation during 3D printing. Fig. 4.7(b) shows SEM images of the 3D printed structures.
Table 4.3: Experimental samples with labels and corresponding processing steps to achieve high enough electrical conductivity to drive current.

<table>
<thead>
<tr>
<th>Label</th>
<th>Processing steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>600-20h-A</td>
<td>Oxidative anneal at 340 °C on hot plate and holding for 10 mins</td>
</tr>
<tr>
<td>600-20h-B</td>
<td>Anneal in Ar at 600 °C for 20 hours in RTP</td>
</tr>
<tr>
<td>600-16h</td>
<td>Anneal in Ar at 600 °C for 16 hours in RTP</td>
</tr>
<tr>
<td>950-10m-A</td>
<td>Anneal in Ar at 950 °C for 10 minutes in RTP</td>
</tr>
<tr>
<td>950-10m-B</td>
<td>Anneal in Ar at 950 °C for 10 minutes in RTP</td>
</tr>
<tr>
<td>500-600-27h-A</td>
<td>Anneal in Ar at 500 °C for 1 hour in RTP</td>
</tr>
<tr>
<td>500-600-27h-B</td>
<td>Anneal in Ar at 600 °C for 30 minutes in RTP</td>
</tr>
<tr>
<td></td>
<td>Anneal in Ar+H₂ at 600 °C for 5 hours in RTP</td>
</tr>
<tr>
<td></td>
<td>Anneal in Ar at 600 °C for 20.5 hours in RTP</td>
</tr>
</tbody>
</table>

Figure 4.7: Optical microscopy and SEM images of structures 600-20h-A and 600-20h-B at different steps of processing. (a) Optical microscopy and (b) SEM image of as printed bridge-on-pillars structures standing on metal leads over a silica substrate. (c) Optical microscopy images of structures on silica substrate with metal electrodes after oxidative anneal at 340 °C on hot plate for 10 minutes in presence of air. (d) SEM image of structures on silica substrate with metal electrodes at the end of annealing at 600 °C in RTP.
which clearly presents the distinct bridge-on-pillar shape of the as-printed structure. Some structural defects caused by cavitation is also visible in SEM images that were not observable from optical microscopy images. Fig. 4.7(c) shows optical microscopy images of the structures after oxidative anneal at 340 °C. It shows that the structures lose their transparency as a result of oxidation of polymers. Also, significant shrinkage is observed compared to their 3D printed footprint. Fig. 4.7(d) shows the SEM image of the bridge-on-pillars structures at the end of their annealing at 600 °C in RTP. One important observation here is that after melting and shrinking during annealing, pillars can overlap with metals maintaining uniform contacts and bridge can hang in between the pillars without collapsing. Also, height of the annealed pillars is dependent on the height of the 3D printed pillars.

Fig. 4.8(a) shows the conductivity of samples 600-20h-A, 600-20h-B, 600-16h, 950-10m-A, and 950-10m-A as a function of annealing time. The samples show conductivity of less than 1 S/m if the annealing time is less than 5 hours at 600 °C for samples 600-20h-A, 600-20h-B, and 600-16h. However, the conductivity keeps on increasing as the processing time at 600 °C rises for these samples. It shows that a conductivity of 16.9 S/m was achieved after 20 hours of anneal in Ar 600 °C at samples 600-20h-A and 600-20h-B whereas a conductivity of 15 S/m was achieved after 16 hours of anneal in Ar 600 °C at sample 600-16h. Fig. 4.8(a) also presents conductivity of samples 950-10m-A and 950-10m-B annealed at 950 °C for 10 minutes in Argon in RTP. It is clear that the maximum conductivity achieved in the long annealing process at 600 °C is still almost 2 orders of magnitude lower than that of a sample annealed at 950 °C for 10 minutes.

Fig. 4.8(b) shows measured conductivity of samples 600-20h-A, 500-600-27h-A, and 500-600-27h-B as a function of elapsed days after their processing at 600 °C. This tells that this conductivity achieved by longer anneal at 600 °C is not stable, rather it decays over time and it can decay by an order of magnitude in about 40 days. The proposed hypothesis is that by longer annealing the polymer can reach a metastable state of higher electrical conductivity, but as the material stabilizes over time, it can reduce to a lower electrically conductive state.

Fig. 4.9 shows Raman spectroscopy of the sample 500-600-27h-A after multiple annealing steps at 500 °C and 600 °C for 1-27 hours, and of sample 950-10m-A after 950 °C anneal for 10 minutes. It was observed that annealing at Only 500 °C for up to 1 hour exhibits
Figure 4.8: (a) Measured conductivity of the bridge section of bridge-on-pillars structures of samples 600-20h-A, 600-20h-B, 600-16h, 950-10m-A, and 950-10m-B as a function of increasing annealing time at 600 °C and 950 °C in RTP. (b) Drop in measured bridge conductivity over time of samples 600-20h-A, 500-600-27h-A, and 500-600-27h-A.
Figure 4.9: Comparison among Raman spectra at the end of various processing steps in 500 °C and 600 °C of sample 500-600-27h-A (500-600-27h-A¹, 500-600-27h-A², and 500-600-27h-A⁴) and at the end of annealing in 950 °C of sample 950-10m-A.
high background fluorescence. This background fluorescence drops with increasing annealing temperature and time, and after an additional anneal of 2.5 hours at 600 °C, the spectrum is quite similar for both 500-600-27h-A and 950-10m-A. In the spectra, D-band, also known as defect band and G band are visible at 1345 cm$^{-1}$ and 1595 cm$^{-1}$, respectively. Both D-band and G-band are associated with in-plane vibration of hexagonal graphitic layers. D-band is also caused by structural imperfections. The width and relative intensities of these two bands are functions of processing temperatures. A broad G’-band (first overtone of D-band) occurs at $\approx 2750$ cm$^{-1}$ in 950-10m-A which is absent in sample 500-600-27h-A (annealed for a relatively shorter time and lower temperature) and weak in longer annealed 500-600-27h-A.

4.2.3 Experimental observation of current-induced localized Joule heating

Fig. 4.10(a) shows temperature dependency of conductivity of sample 950-10m-A up to 250 °C. It shows a fairly linear trend. Fig. 4.10(b) shows the change in conductivity as a function of bias voltage in an ambient room temperature. The starting conductivity of the sample at 0.05 V bias was 687 S/m. After 6 V bias, the conductivity starts to increase non-linearly up to the bias voltage of 8.7 V. Beyond 8.7 V, the conductivity drops sharply indicating a damage within the bridge. Based on the linear regression and calculated temperature coefficient from Fig. 4.10(a), the right y-axis in Fig. 4.10(b) shows an estimated temperature within the bridge. It shows that temperature as high as $\approx 1450$ °C can be generated within the bridge. This gives a strong indication that high starting conductivity of 10 S/m can potentially generate high temperature in a sample annealed at 600 °C also.

Fig. 4.11(a) shows normalized electrical conductivity of sample 500-600-27h-A as a function of increasing ambient temperature. This electrical conductivity was determined from current-voltage relationship of not greater than 1 V to make sure that significant Joule heating was not introduced in the system causing non-linear current-voltage characteristics. The dotted line shows a fairly linear trend with increasing temperature having a slope of 0.0656. This relationship was used in the next experiment to estimate local temperature
Figure 4.10: (a) Change in normalized conductivity as a function of ambient temperature (25.2 to 250 °C) of sample 950-10m-A. (b) Conductivity (primary y axis) and estimated average temperature (secondary y axis) of the bridge section of sample 950-10m-A as a function of applied bias voltage.
Figure 4.11: (a) Change in normalized conductivity as a function of ambient temperature (23 to 400 °C) of sample 500-600-27h-A. (b) Measured electrical conductivity and corresponding estimated temperature of sample 500-600-27h-A as a function of applied power.
within the bridge when a higher electrical bias was applied to the sample to drive it in non-linear current-voltage region.

Fig. 4.11(b) shows the conductivity and corresponding temperature as a function of applied power when bias voltage of 28 V and higher were applied across the bridge-on-pillar structure in series with a current limiting resistor. The ambient temperature during the entire experiment was 400 °C to increase the conductivity of the bridge. The right y-axis shows the estimated temperature corresponding to this conductivity based on the conductivity-temperature relationship obtained from Fig. 4.11(a). It shows that a temperature of ≈727 °C can be generated within the bridge. However, it needs to be mentioned that this estimated temperature is an estimate of average temperature, and higher temperature can potentially be generated at the thinner cross-sections of the bridge. Also, this process is hard to control due to thermal runaway conditions when the bridge goes into nonlinear conductivity region. Therefore, it is advised to use a constant current source to precisely control the current flow. Instead of starting with a higher conductivity bridge-on-pillars structure, irreversible conductivity can also be achieved by using higher voltage supply. However, that approach may be limited due to not being compatible with CMOS technology.

Fig. 4.12 shows an optical microscopy image of the sample 500-600-27h-A when bias voltage was 31.6 V, series resistance was 50 kOhm, and measured current current was 300 µA. The image was taken in a dark ambience. A bright light spot was observed within the bridge which shows a significant temperature increase compared to the dark 400 °C ambience. This also shows that wire is not uniform in thickness thereby generating the most temperature in the narrowest region. However, this bright spot was gone after 20 minutes and current dropped to zero indicating damage/discontinuity in the structure. Fig. 4.12(b) shows the SEM of the sample 500-600-27h-A after the current dropped to zero. It shows a breakage within the bridge section. This can be explained by evaporation at high temperature of the narrow bridge and subsequent thinning of the bridge. This experiment is a clear observation of the hypothesis that partially pyrolyzed polymer having a starting conductivity of ≈10 S/m at room temperature can be locally pyrolyzed at ≈727 °C through electrical current-driven Joule heating when applied bias voltage is high enough and the conductivity is increased by increasing the ambient temperature.
Figure 4.12: (a) Optical image of sample 500-600-27h-A (connected in series with a 50 kOhm resistor, not shown in the image) under a bias voltage of 31.6 V, while the ambient temperature was 400 °C. (b) SEM image of sample 500-600-27h-A after bridge section broke as a result of generating high temperature within the bridge from driving high current of ≈300 µA while the ambient temperature was 400 °C.
4.2.4 Processing for electrochemical characterization and relevant issues

Partially pyrolyzed samples need to be completely carbonized and then implemented for electrochemical characterization. In order to do so, entire chip needs to be insulated from the electrochemical solution except the completely carbonized bridges. As such, this work explored the feasibility of achieving complete carbonization using Joule heating while also maintaining an polymerized insulation outside the bridge. Therefore, the entire chip was coated with 530 nm parylene using a parylene coater to create insulation. The idea was to apply voltage bias across the pillars to drive current through the structure and generate enough Joule heating within the bridge so that it would completely carbonize both the partially pyrolyzed bridge and the parylene coating. Parylene over metal electrodes was conveniently scratched off the metal surface using tweezers to facilitate voltage biasing. Fig. 4.13(a) and (b) show SEM images of two bridge-on-pillars structures after coating with parylene. Since the samples are coated with parylene, there was some charging affecting the image quality. The images show that the parylene coating can cause the bridges to come in contact with the substrate. Fig. 4.13(c) and (d) show SEM images of bridge on pillars structures after applying a voltage of ≈112 V. The images show that the structures can get damaged after applying a high voltage bias. Also, use of parylene coating can potentially react with the partially pyrolyzed polymer at high temperature causing damages at multiple places throughout the bridge. However, at an applied bias voltage of ≈112 V, a sharp increase in current was observed causing an irreversible change in conductivity before the bridge collapsed (Fig. 4.14). This is also consistent with the previous conclusion that irreversible conductivity can be achieved by using high enough applied voltage. SEM images of outcomes of similarly processed structures are also shown in appendix. These structures did not show any current conduction when voltage was applied across them. This also points to the fact that parylene coating might have negatively affected the stability of the structure. It can be seen that the structures tend to overlap with the substrate after parylene coating. Therefore, increasing pillar height can increase the robustness of the bridge. However, based on Equation 4.11, increasing pillar height increases pillar resistance thereby reducing current
Figure 4.13: (a)-(b) SEM images of bridge-on-pillars structures annealed at 950 °C followed by a parylene coating of 530 nm over the entire sample. (c)-(d) SEM image of annealed (at 600 °C) and parylene coated (530 nm) bridge-on-pillars structures followed by applying a bias voltage of \( \approx 112 \text{ V} \).
Figure 4.14: I-V characteristics of a bridge-on-pillars structure oxidized at 340 °C on hot plate, annealed in argon at 600 °C for 10 hours, and then coated with parylene.
and delivered power to the bridge. On the other hand, one potential advantage in using parylene is that it can be oxidized on the CMOS chips. An alternative method would be to deposit a titanium layer on the wafer that can be oxidized after 3D printing of the structure. This oxidation will provide an insulating layer thereby reducing the necessity of additional polymer coating at the end of carbonization.

Finally, a comparison with state-of-the-art literature is shown in Table 4.4. A wide range of positive and negative photoresists have been used to fabricate conducting pyrolyzed precursor. One important observation from the table is that the starting conductivity of this work was lower compared to some works which is due to lower carbonization temperature used in this work to maintain CMOS compatibility. However, use of current driven Joule heating increased the conductivity of the sample in this work.

4.3 Summary

In this chapter, a processing sequence to obtain complete carbonization of partially pyrolyzed polymer using localized Joule heating has been developed. Analytical approximation and finite element based modeling was used to estimate required operating conditions to initiate sufficient Joule heating for carbonization. Longer annealing in inert atmosphere and increasing ambient temperature were used to increase conductivity of partially pyrolyzed polymer. By applying a cleanroom-safe voltage, irreversible increase in conductivity was observed. Estimated average temperatures of 1450 °C and 727 °C were obtained for samples primarily annealed at 950 °C and 600 °C, respectively. For the sample annealed at 600 °C, although this estimated temperature of 727 °C is not the ideal temperature for complete carbonization, this approach experimentally verifies that Joule heating can substantially increase the localized temperature within the bridge section. Another important point here is that for partial pyrolysis, rapid thermal annealing was conducted at 600 °C which is slightly higher than the CMOS-compatible temperature window. However, it has been previously observed that annealing at 500 °C reduces background fluorescence [42]. Therefore, substantial long annealing at 500 °C can potentially increase conductivity of partially pyrolyzed polymer suitable for driving current and initiate Joule heating. Thus,
Table 4.4: Comparison of this work with state-of-the-art pyrolyzed carbon.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Substrate</th>
<th>Photoresist</th>
<th>Deposition method</th>
<th>Maximum carbonization temperature (°C)</th>
<th>Conductivity range (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[58]</td>
<td>Silicon</td>
<td>AZ-4330, OIR-897, XPSU</td>
<td>Spin-coating</td>
<td>600–1000</td>
<td>10⁻⁵ to 10⁻¹</td>
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<td>[92]</td>
<td>SiO₂/Si</td>
<td>SU-8 and AZ P4620</td>
<td>Spin-coating and baking</td>
<td>700 to 1000</td>
<td>4.72×10¹ to 1.6×10⁴ and 1.02×10² to 2.075×10⁴</td>
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<td>[32]</td>
<td>Silicon</td>
<td>SU-8</td>
<td>near-field electromechanical spinning</td>
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<td>477 to 18100</td>
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<td>[8]</td>
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</table>
the experimental observation in this work demonstrates a progressive step towards CMOS-compatible carbonization by incorporating localized Joule heating of partially pyrolyzed polymer.
Chapter 5

Conclusion

5.1 Original Contribution

Custom-designed lab-on-CMOS chips offer the advantage of individually addressing transducers or sensing elements. It can also potentially minimize interference from ambience since the transducer is tightly packed with the readout electronics. Therefore, lab-on-CMOS electrochemical sensor is potentially a viable solution for commercialized sensing products due to its low cost in fabrication and high sensitivity.

In this work, an optimized processing sequence has been developed for fabricating carbon based microelectrodes on metallized substrates by pyrolyzing 3D printed polymer microstructures. The novelty and exclusivity of the developed processing sequence are,

- Forming electrical insulation around the carbonized microelectrodes during the multi-step carbonization process.
- Proving feasibility of achieving complete carbonization of partially pyrolyzed polymer using electrical current-driven localized Joule heating.

This processing sequence produces carbonized microstructures that can be integrated with CMOS-based readout electronics for lab-on-CMOS electrochemical sensing. The developed processing sequence was optimized to reduce unwanted structural changes in 3D printed polymers during their carbonization. It was observed that catalytic effect of specific
metal oxides, particularly titanium oxide, can adversely affect the shape of precursors during their carbonization. As such, the processing sequence was modified to reduce this catalytic effect. However, independent of the presence of metal, substantial shrinkage in the precursors was observed. Verification of pyrolytic conversion of polymers was obtained using Raman spectroscopy and impedance measurement.

To address the incomplete carbonization as the outcome of our initial processing sequence, electrical current-based localized Joule heating was proposed. To determine the optimum processing conditions, analytical approximation and FEM-based COMSOL simulation were performed. Simulation shows a conductivity of 10 S/m can potentially generate more than 700 °C when an electrical bias of 30 V is applied and ambient temperature is 400 °C. It was determined that temperature treatment at 600 °C for 2 hours can only provide partially pyrolyzed polymer with conductivity of 0.015 S/m. However, using a longer anneal time at 600 °C, this conductivity can temporarily increase by multiple orders of magnitude. Finally, it was experimentally observed that under an applied bias of 31.6 V and ambient temperature of 400 °C, partially pyrolyzed polymer with conductivity of 10 S/m can generate an estimated temperature of 727 °C. However, this approach showed that localized Joule heating can be initiated within this bridge-on-pillars structure by driving current, thus showing feasibility of carbonization without raising the temperature of the entire chip above 500 °C. Starting with a precursor of higher conductivity will drive more current (thereby increasing the temperature). Also, applying a higher bias will increase the temperature also. Therefore, the proposed method is feasible for localized complete carbonization of partially pyrolyzed polymer. However, it needs to be noted that maximum voltage bias that can be applied to the structure is limited by the CMOS technology being used for signal processing circuitry. Also, nonlinear increase of electrical conductivity of the bridge material under high bias is hard to control since current increases rapidly and can potentially damage the structure. Use of a current source can help in avoiding this runaway condition. In summary, the scientific contribution of this work is successfully demonstrating a processing sequence that reduces annealing temperature of carbonizing electrodes within CMOS tolerable temperature.
5.2 Potential Future Research

The research conducted in this dissertation can be expanded in the following directions,

- Localized heating approach can also be implemented by applying laser. This can be implemented by either using laser integrated to Raman spectroscopy or the laser used in two photon polymerization.

- Further research can be conducted in determining specific parameter control, such as heat generation based on geometrical parameters, surrounding gas properties, and electrical and thermal conductivities of partially pyrolyzed precursors. That will lead to developing industry-standard CMOS compatible microelectrodes.

- The developed processing sequence can be implemented on structures with larger sizes than what is discussed in this work. It is expected that that will increase the reactive surface area thereby increasing electrochemical sensitivity of the carbonized precursors.

- This processing sequence can be implemented on 3D printed structures on a CMOS chip and characterize using on-chip CMOS electronics. This will ultimately show the effect of processing temperature on both electrodes and readout electronics on the lab-on-CMOS sensing system.
Bibliography


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Appendices
A Processing defects

During the overall span of this work multiple processing artifacts were observed from time to time. They can be caused by design flaws, material non-uniformities, and tool imperfections. However, this needs to be pointed out that these defects did not necessarily cause any degradation of performances of the developed process during this work. Fig. 1 shows issues with disconnecting pillars and metal electrodes post-annealing when bridge length is 5 µm. This was due to the stress by the bridge on the pillars during high temperature anneal. Such issue was further avoided by using bridge length length of 10 µm or longer.

Fig. 2 shows SEM images of post-anneal bridge-on-pillars structures. During 3D printing (before anneal), the pillars did not overlap perfectly with the metals thereby causing disconnection after anneal. This issue was later avoided by using larger pillar footprint.

Fig. 3 shows SEM images of 3D printed pillars where the pillars did not cross-link properly during photopolymerization process. This can be addressed by adjusting laser power and scanning rate in the CAD tool. On the other hand, high laser power can potentially cause cavitation. Therefore, during 3D printing, laser power needs to be adjusted. For printing bridge on pillar structures, this work used 30% laser power of the tool.

Fig. 4 shows SEM images of metal electrodes with defects on them. It can be reduced by refining the combination of metal evaporation and photolithographic patterning steps. Specifically, during metal evaporation, evaporation rate and thickness of metal layers can be modified. Also, during photolithography, photoresist type, thickness, baking time, and temperature, and exposure doze can be modified to improve the defects.

Fig. 5 shows SEM images of bridge-on-pillars structures that were annealed at 950 °C and then parylene coated. No current were measured in these structures.
Figure 1: (a) and (b) show bridge on pillars structures with bridge length of 5 \( \mu \)m after oxidation at 340 °C and annealing at 600 °C.
Figure 2:  (a) and (b) show annealed Bridge-on-pillars structures where the 3D printed pillars were not perfectly aligned with the metal electrodes.
Figure 3: (a) and (b) show 3D printed pillars with defected cross-linking.
Figure 4: (a) and (b) show defects on metal electrodes after metal evaporation and photolithography.
Figure 5: (a) and (b) show SEM images of annealed (at 950 °C), and parylene coated (530 nm) bride-on-pillars structures.
Vita

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