CONJUGATED CARBON MONOLAYER MEMBRANES – SYNTHESIS AND INTEGRATION TECHNIQUES

BY

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DISSERTATION

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ABSTRACT

The existence of graphene, a single sheet of graphite and the simplest class of conjugated carbon monolayer, discovered in 2004, has attracted immensely interests from scientific community. The research in this area has grown exponentially attributed to its exceptionally high electron mobility, high elastic moduli, and observations of unconventional phenomena in physics. Unfortunately, the original technique for producing graphene sheet on insulating substrates, i.e. by mechanical exfoliation from a piece of graphite, is not scalable. Hence, it is utmost important to find approaches for producing large area graphene or improving film transfer quality. It is also interesting to explore other types of related two-dimensional materials. The first part of this dissertation describes a strategy for the synthesis of a class of conjugated carbon monolayer membranes. The process starts with the formation of self-assembled monolayer of alkyne-containing monomers on flat or structured solid support such as SiO$_2$ and Si$_3$N$_4$ followed by chemical crosslinking within monolayer. Once linked, the membranes are robust enough to be released from the support and transferred to other surfaces. Likewise, three-dimensional objects, such as balloons and cylinders, with monolayer thickness can be generated with similar method. The second part focuses on graphene layer which is epitaxially grown on SiC wafer. This growth technique has been known for producing large-area graphene films, but the graphene film is required to be exploited on the growth substrate due to unavailability of transfer procedure. I adopted and improved the techniques, used for transferring carbon nanotube, to transfer graphene films from SiC substrates to arbitrary substrates. The technique utilized a bilayer film of either gold/polyimide or palladium/polyimide as a transfer element. The properties of transferred film were characterized by different techniques including Raman spectroscopy, SEM, AFM and STM. I finally fabricated simple devices on this transferred graphene sheet to measure electrical properties of the film.
To my parents.
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CHAPTER 1

INTRODUCTION

Graphene has recently been anticipated as a front-runner for future electronic material, likely to surpass carbon nanotube due to its compatibility to current fabrication technology. It is actually a 2D allotrope of carbon element where all carbon atoms ($sp^2$ hybridization) are arranged into a hexagonal lattice. Also, it can be considered as a member of conjugated carbon monolayers. Except from its electrical properties, it is one of the strongest materials ever measured which finds itself promising for application in nanoelectromechanical systems (NEMS). Still, many problems need to be solved. First of all, the highest quality graphene is still produced by the micromechanical exfoliation, also known as peeling method. It was the original technique where first flakes of graphene were discovered. A drawback of this method is that the size of monolayer graphene flakes is very tiny while most of the deposited flakes are multilayer. Besides, the locations where graphene flakes are deposited are uncertain. In summary, this method of graphene production is not scalable. Some other approaches for mass producing graphene have been vastly studied. The details on each method will be discussed later on. A growth technique mainly used in my research is thermal annealing of silicon carbide (SiC) substrate. Another major problem of graphene is that it is a semimetal which means that it is impossible to switch off a graphene device. Many strategies, such as cutting a graphene sheet into nanoribbons, have also been proposed for turning it into a semiconductor; however, these are out of my dissertation scope. Except from graphene, other conjugated carbon monolayers might also possess different but fascinating electrical properties. A goal of my research is to explore other strategies to synthesize conjugated carbon monolayers via organic synthesis as well as to study their properties. The other goal emphasizes on developing techniques towards transferring large and uniform films of high quality graphene sheets from growth substrates to other target substrates such as oxide surface and plastic. The quality of films has been determined by a variety of characterizations.
Construction of thesis

Chapter 2 reviews the current synthetic approaches of conjugated carbon monolayer membranes although the focus is mainly on graphene synthesis.

Chapter 3 presents a strategy on organic synthesis of a conjugated carbon monolayer from Aryl alkyne-containing monomers on the surface of oxide or nitride via sequential steps of self-assembly and chemical cross-linkage. A method for transfer this membrane is also provided. In spite the film is not electrically conductive, ones find the synthetic strategy motivating.

Chapter 4 describes the transfer technique of graphene films epitaxially grown on SiC wafers to other substrates. The size of transferred film covers square millimeters area of receiving substrate. The electrical property of transferred film is determined from device fabrication.

Chapter 5 reports a modified and improved transfer technique of graphene films grown on SiC substrates. Not only is the size of film equal to the size of growth substrate, but multiple generations of graphene films can also be produced from a single substrate by peeling off graphene layer-by-layer. Each transferred film contains lower defect density compared to that transferred by the technique in last chapter. Further characterizations, including STM, are presented.
CHAPTER 2

BACKGROUND ON SYNTHETIC APPROACHES OF CONJUGATED CARBON MONOLAYERS

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Conjugated Carbon Monolayer Membranes: Methods for Synthesis and Integration

Monolayer membranes of conjugated carbon represent a class of nanomaterials with demonstrated uses in various areas of electronics, ranging from transparent, flexible and stretchable thin film conductors, to semiconducting materials in moderate and high performance field effect transistors. Although graphene represents the most prominent example, many other more structurally and chemically diverse systems are also of interest. This chapter provides a review of demonstrated synthetic and integration strategies, and speculates on future directions for the field.

2.1 Introduction

Assemblies of organic molecules in monolayer films are of longstanding interest due to their ability to control transport and release across interfaces, and to define surface chemistry, wetting behavior, as well as friction, lubrication, wear and other aspects of tribology. Such materials, often in the form of bilayers, are also critically important to the function and structure of nearly all biological systems. Historically, work on synthetic films has focused on chemically bound monolayers created by processes of self-assembly [1-3] and van der Waals collections of molecules in films formed with Langmuir-Blodgett techniques [4-6]. Renewed and expanded excitement in this broader field arises from recent reports of organic monolayers formed using these and related approaches as semiconductors [7] and gate dielectrics [8,13] in field effect transistors, thereby demonstrating useful electronic properties in de-
vices and even simple circuits. Most significantly, research on graphene, viewed as a class of conjugated carbon monolayer material, indicates that superlative electronic transport and mechanical properties can be achieved. Examples include elastic moduli in the range of 1 TPa [14], electron field effect mobilities up to 200,000 cm²V⁻¹s⁻¹ [15–17], with ballistic transport characteristics over distances approaching a micron at room temperature [15–18], and realization of exotic phenomena such as the half-integer Hall effect [19, 20], previously observed only in the highest purity and most sophisticated inorganic semiconductor structures [21].

Some of the earliest graphene devices used small pieces of films exfoliated from bulk samples of highly ordered pyrolytic graphite (HOPG) using Scotch tape [22], in a largely uncontrolled process that is nevertheless extremely useful for research purposes. Although certain classes of transfer printing techniques [23, 24] might allow exfoliation to be used in realistic applications, direct synthetic methods can provide not only more scalable integration strategies but also improved control over the chemical, morphological and dimensional properties of the materials. This chapter provides a brief review of progress in this rapidly evolving field of conjugated carbon monolayer membranes, with an emphasis on synthesis and techniques for manipulating these materials. The topics include not only routes to graphene but also to more chemically diverse systems, in layouts ranging from flat films and membranes to ribbons, suspended ‘drumheads’, pleated sheets, balloons and tubes.

2.2 Synthetic Approaches

Most envisioned applications of these classes of membranes demand synthetic methods that are capable of creating large area, uniform monolayer sheets or ultrathin films of small flakes or ribbons. Means for transferring these materials from the substrates on which they are synthesized or assembled to other surfaces for device integration are also typically required. This section focuses on the first challenge; the next describes progress on the second. The synthesis approaches include those that are designed specifically for graphene or graphene-like materials and others that are more broadly useful, as discussed in that order in the following.

2.2.1 Reduced Graphene Oxide from Graphite

Exposing graphite, in powder form, to mixtures of sodium nitrate (NaNO₃) and sulfuric acid (H₂SO₄) and oxidizing agents such as potassium permanganate (KMnO₄)
can produce a form of graphite that is highly functionalized with hydroxyl, epoxide, and carboxyl groups [25]. Sonication of this material, referred to as graphite oxide (GO) [26], in water leads to suspensions of exfoliated monolayer flakes of GO that can
be formed into ultrathin films by spray coating [27, 28], vacuum filtration [28, 31], drop casting [28, 31] and related techniques. Figure 2.1a provides a schematic illustration and Figure 2.2a provides an image. The vacuum filtration method is notable because self-limiting flow fields tend to produce films with thicknesses in the monolayer range. Thick deposits of flakes stacked in lamellar geometries are also possible, by increasing the suspension volumes and deposition times [30]. Chemical reduction achieved, for example, by exposure to hydrazine vapor (N₂H₄) followed by thermal annealing (200°C) in inert environments can remove the functional groups to yield films of reduced GO [29]. Such films are electrically conducting, with semi-metallic character in field effect transistor devices that is qualitatively similar to those built with pristine graphene, but with far inferior characteristics owing to incomplete reduction and defects [27, 29]. The electron mobility of individual reduced GO flakes is between ≈2 and ≈200 cm²V⁻¹s⁻¹ [29]. Near monolayer films composed of large collections of flakes exhibit values of ≈0.2 cm²V⁻¹s⁻¹ [29], likely limited by junction resistances between flakes. The elastic moduli of individual pieces of reduced GO are ≈0.25 TPa [32], also somewhat lower than pristine graphene. Other methods can accomplish exfoliation and solution suspension without chemical functionalization. For example, organic solvents such as N-methylpyrrolidone with surface energies similar to graphite have been used effectively [28]. Even in such cases, however, the electrical properties are not significantly improved over those made from reduced GO. In spite of these non-ideal aspects, films of the type described in this section have characteristics that might make them attractive as flexible and/or transparent conducting coatings in displays, touch screens or related devices.

### 2.2.2 Graphene Nanoribbons from Carbon Nanotubes

A different approach to graphene uses carbon nanotubes as an alternative to HOPG and graphite powder for the carbon source material. Figure 2.1b and Figure 2.2b provide illustrations and micrographs, respectively. Here, chemically reacting [33] or physically etching [34] a narrow strip along a nanotube yields a graphene nanoribbon (GNR). In the first case, GNRs form from oxidation of carbon bonds with potassium permanganate (KMnO₄) in concentrated sulfuric acid (H₂SO₄). This reaction produces oxidized GNRs that require further reduction using hydrazine to remove oxygen species at the edges [33]. The other approach uses Ar plasma etching of nanotubes, partially embedded in a film of poly(methylmethacrylate) (PMMA) [34]. Removing the PMMA releases GNRs. Multiwalled nanotubes (MWNTs) seem to be the preferred starting material for both processes; further advances may en-
Figure 2.2: Images of various types of conjugated carbon monolayer membranes. a) Atomic force microscope (AFM) image of reduced graphene oxide flakes drop-casted onto a Si wafer [31]. b) AFM image of a graphene nanoribbon (GNR) and an unreacted multiwalled carbon nanotube (MWNT) after a chemical unzipping process [34]. c) Scanning electron microscope (SEM) images of graphene films grown by chemical vapor deposition (CVD) on a film of Ni (300 nm thick) and on a foil of Ni (1 mm thick) (inset) [40]. d) AFM image of graphene layers grown over terraces of 4H-SiC. [48] e) Optical image of a chemically crosslinked, conjugated carbon monolayer membrane transferred to an oxidized Si wafer. The chemical structure shows the active functional group of the monomer used to form this film [61]. f) AFM image of this type of monolayer membrane, grown on a substrate with a periodic relief structure (depth ≈35 nm) and then transferred to a flat oxidized Si wafer. The inset schematically illustrates the structure of this film [61]. g) TEM image of monolayer balloons formed by growth on SiO$_2$ spheres followed by removal of the SiO$_2$ by etching in HF vapor. The insets show magnified views (upper left) and schematic illustrations (lower right) [61]. h) Optical image of a tubular monolayer membrane formed by growth on a silica optical fiber followed by removal of the fiber by HF vapor. The monolayer tube is filled with liquid that remains from the etching process. The inset shows a schematic illustration [61].
able use of single walled nanotubes (SWNTs) [33]. For many applications, the long, narrow geometries of GNRs offer advantages over small flakes that typically result from exfoliation from HOPG. In particular, such layouts, for widths narrower than ca. 10 nm, lead to bandgaps sufficiently large for use in transistors with good switching behavior [34, 35], but typically with much lower mobilities due to edge effects. Although carbon nanotube based routes are very recent, one could imagine, for example, implementing them with horizontally aligned arrays of SWNTs grown on quartz [36, 37] to yield similarly configured arrays of narrow GNRs, for natural integration into planar electronic devices, such as field effect transistors.

### 2.2.3 Graphene by Chemical Vapor Deposition

As illustrated schematically in Figure 2.1c, large area films of single and few layer graphene can be formed on metal surfaces by direct chemical vapor deposition from hydrocarbon gases, such as methane, at temperatures of ca. 1,000 °C [38–40]. Certain aspects of these approaches have origins in work done on related systems in the 1970’s. [41–43] Recent progress demonstrates that thin Ni films and optimized cooling conditions can yield films that are mostly one monolayer thick, with some disorder determined, at least in part, by the polycrystalline structure of the Ni [38–40]. Increasing the grain size in the Ni, or using single crystal metals such as Ru(0001) [44], can improve the uniformity and increase the size of the grains of graphene to areas of a few hundred square microns. The properties of the individual grains can approach those of mechanically exfoliated graphene from HOPG, as evidenced, for example, by electron mobilities as high as 4,000 cm²V⁻¹s⁻¹ and by observation of half-integer Quantum Hall behavior in films transferred from the growth substrate using methods described in a following section [40]. Figure 2.2a shows representative graphene materials formed in this way. Very recent work with Cu foils demonstrates uniform, single layer (ca. 95%, by area) graphene over square centimeters, also with mobilities up to 4,000 cm²V⁻¹s⁻¹ [45]. A notable feature of these CVD approaches is the possibility for substitutional doping by introducing other gases, such as NH₃, during the growth [46].

### 2.2.4 Graphene from SiC

Epitaxial growth of graphene by thermal sublimation of Si from the surface of a single crystalline SiC wafer at 1,200 – 1,500 °C represents one of the first scalable methods to produce large area films of graphene [47, 49]. Here, removal of Si leaves
surface carbon atoms that reconstruct into graphene layers and grow continuously on the flat surfaces of suitably prepared (i.e. H\textsubscript{2} anneal at 1,600 \degree C followed by controlled cooling) hexagonal SiC wafers (4H or 6H), including over atomic steps (see Figure 2.11 and Figure 2.24). The thicknesses of the graphene deposits depend on annealing time and temperature \[49\]. Graphene can form on wafers that present either polar face (i.e. Si-face (0001) or C-face (000\overline{1})). In both cases, the properties of the first layer of graphene are not understood clearly \[49\]. The overlayers, on the other hand, are known to have good properties despite submicron domain sizes \[50\], where top-gated transistors show electron mobilities as high as 5,000 cm\textsuperscript{2}V\textsuperscript{−1}s\textsuperscript{−1}. SiC derived graphene is currently unique in its ability to enable large collections (i.e. hundreds) of devices (e.g. transistors) on a single substrate \[51\]. Further improvements in grain sizes and defect densities can be achieved by growth under an Ar atmosphere of \(\approx 1\) bar, rather than in ultrahigh vacuum (UHV) conditions. The Hall mobilities reported in these studies increased from 710 cm\textsuperscript{2}V\textsuperscript{−1}s\textsuperscript{−1} (UHV) to 2,000 cm\textsuperscript{2}V\textsuperscript{−1}s\textsuperscript{−1} (Ar) \[52\].

2.2.5 Graphene and Related Materials by Chemical Synthesis

Theoretical calculations suggest that properties equally remarkable to but different from those of graphene might be possible in other two dimensional (2D) conjugated carbon networks, such as graphyne and graphdiyne \[53, 54\]. In such cases, materials synthesis will likely require the techniques of organic chemistry \[55\] to provide a level of molecular control over the structure that would be impossible to accomplish with other routes. Past work demonstrates that two dimensional fragments of graphene and related materials can be achieved in large quantities, but with ultra-small lateral dimensions (<5 nm), using Scholl coupling reactions on oligophenylene precursors \[56\]. Due to rapidly decreasing solubility with increasing size, larger formats might demand two-step approaches that begin with the assembly of two dimensional, monolayer films followed by chemical crosslinking, as shown in Figure 2.1b. Exposure to radiation provides one means to accomplish this crosslinking, to yield mechanically robust monolayer films using conjugated carbon molecular species formed either in self-assembled monolayers (SAMs) \[57\] covalently linked to solid supports or Langmuir-Blodgett films at liquid interfaces \[58\]. For example, self-assembled monolayers (SAMs) of biphenylthiols on gold form crosslinks upon irradiation with electrons \[57\]. SAMs processed in this manner are sufficiently robust to form freestanding membranes capable of transfer to other substrates, after removing the gold \[58\]. Pyrolysis of these materials, which are initially electri-
cally insulating, under UHV conditions can convert them into a conductive form \cite{59}. In another example, Langmuir monolayers of amphiphilic derivatives of polydiacetylenes can be crosslinked by exposure to UV light to yield monolayer films with some indication of semiconducting behavior \cite{60}, although vastly inferior to graphene.

More advanced approaches rely on chemical crosslinking of SAMs to enable formation of planar membranes as well as structured films and those with fully 3D layouts ranging from spherical coatings, balloons, capsules, tubes and other complex topologies \cite{61}. The original work on this system exploited aryl alkynes as monomers due to their highly conjugated, carbon functionality, and to their ability to be chemically crosslinked by alkyne metathesis \cite{62}, oxidative copper coupling \cite{63}, or palladium-catalyzed cross coupling \cite{63}. To assemble SAMs of these molecules on oxide bearing substrates, pendant hydroxyl groups on an aryl ring can be reacted with 3-(triethoxysilyl)propyl isocyanate to yield a carbamate group linked to a siloxane tether \cite{61}. Di-functional and hexa-functional monomers form SAMs readily on oxide and nitride substrates from heated solutions. Mo(IV)-catalyzed vacuum driven alkyne metathesis \cite{62} and Hay-type coupling conditions \cite{63} can achieve the crosslinking, thereby forming mechanically robust conjugated carbon monolayers with thicknesses in the range of 1-2 nm. Spectroscopic studies and examination by atomic force microscopy, scanning tunneling microscopy and transmission electron microscopy indicate near complete crosslinking into dense membranes that are largely free of holes or porosity \cite{61}. Conducting the chemistry on flat substrates yields flat films. Structured supports lead to films with corresponding geometries. For example, silica fibers or colloidal spheres can be used to form tubes and balloons, after etching away the silica \cite{61}. Figure 2.2e-h shows some examples of motifs this method accesses. The main disadvantage with these synthetic schemes is that the degree of order in the films is very low, thereby leading to poor electronic properties. Strategies that use crystalline substrates or other means to achieve large, ordered regions in the SAMs and crosslinking reactions that do not substantially degrade this order have the potential to lead to significant improvements. In their current form, these amorphous materials might be most useful in applications that rely on mechanical, wetting, chemical or related properties.
Figure 2.3: Schematic illustration of the transfer printing process and micrographs of representative examples. a) Applying an elastomeric stamp to a donor substrate (blue) and then quickly peeling it away lifts the film (gold). b) Van der Waals interactions adhere the film to the surface of the stamp, prior to transfer to a target substrate (red). c) Slowly peeling the stamp away transfers the film to the target, thereby completing the process. d) Atomic force microscope (AFM) image of graphene flakes (3-12 nm thick) transferred from a piece of highly ordered pyrolytic graphite (HOPG) to an oxidized Si substrate [23]. e) Optical image of a graphene sheet transferred from a SiC substrate to an oxidized Si wafer using a gold/polyimide carrier film [66]. f) Scanning electron microscope (SEM) image of a collection of graphene flakes (0.9-5 nm thick) transferred from HOPG to an oxidized Si wafer using a rigid stamp [24]. g) Optical image of graphene grown by chemical vapor deposition on a Ni film transferred to an oxidized Si substrate with an elastomeric stamp [40].
2.3 Transfer printing

The synthesis approaches described in the previous sections yield films on substrates that are often not desirable for their application in devices. As an example, the metal films needed for CVD growth provide low resistance transport pathways in parallel with the overlying graphene coating, thereby electrically shorting devices that are constructed on top. In other cases, such as graphene formed by sublimation on SiC, the areas are limited by the available sizes of the wafers. In these and many other situations, an ability to transfer the films from the growth substrate to a different surface, either selectively or in uniform sheets, is needed. Methods that use soft, elastomeric stamps have been exploited with considerable success for printing inorganic semiconductor nanoribbons/membranes [23, 64] and aligned arrays of SWNTs [65]. More recently, adapted versions have been applied to graphene in various forms (i.e. derived from SiC [66], CVD grown on Ni [40], exfoliated from HOPG [23, 24], deposited from GO flakes [29], and crosslinked carbon monolayers formed by chemical synthesis [61].) Figure 2.3 schematically illustrates the process and shows some examples of transferred films. Thin polymer or metal films often serve as ‘carriers’ for the monolayer to facilitate transfer. Removing the carrier by selective etching completes the process. Lifting these films onto the stamps is most commonly achieved through non-specific van der Waals interactions with the surface of the stamp. These adhesive forces can be relatively strong at high peel rates, due to viscoelastic behavior of the elastomers that are typically used for the stamps [67]. By contrast, adhesion is comparatively weak at slow peel rates, thereby providing a kinetic control strategy for printing [23]. With these and other related methods [24, 29, 34], transfer yields can approach 100%, even with the most challenging graphene [24, 40] and monolayer systems [61].

2.4 Prospects

The first reports of single layer graphene and its electronic properties in 2004 [22, 47] led immediately to broad, worldwide research activities on this material. Many of the basic properties are now understood, mainly from studies of individual flakes mechanically exfoliated from HOPG [14, 20, 22]. Parallel efforts on growth [38, 40, 44, 48, 50, 52], particularly in the last several years, have yielded methods that appear extremely promising for large scale sheets and films. Techniques of transfer printing [23, 24, 65] have been successfully adapted for use with these materials, thereby enabling their integration with diverse types of substrates. This collective
body of work suggests that realistic, scalable routes to graphene and its implementation in important devices and systems are, or will soon be, available. Still, there remains much work to be done and opportunities to address. Immediate next steps might include, for example, a search for methods to form large area, aligned arrays of GNRs for applications in certain areas of electronics. A longer term future for work on synthesis and integration might lie in the development of strategies capable of forming much broader and more chemically diverse classes of conjugated carbon monolayer membranes. Chemical synthetic approaches, like those described in Section 2.2.5, have promise, but present considerable complications that still require solutions to the significant challenges of control of morphology, degree of crystallinity and other characteristics that influence important physical properties. Substrate templated growth, as demonstrated recently over small areas, provides an example of a potentially powerful scheme [68, 69]. Development of these or completely different techniques represents an appealing direction for future research.

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2.5 References


CHAPTER 3

SYNTHESIS OF LINKED CARBON MONOLAYER:
FILMS, BALLOON, TUBES, AND PLEATED SHEETS


Synthesis of Linked Carbon Monolayers: Films, Balloons, Tubes, and Pleated Sheets

Because of their potential for use in advanced electronic, nanomechanical, and other applications, large two-dimensional, carbon-rich networks have become an important target to the scientific community. Current methods for the synthesis of these materials have many limitations including lack of molecular-level control and poor diversity. Here, we present a method for the synthesis of two-dimensional carbon nanomaterials synthesized by Mo- and Cu-catalyzed cross-linking of alkyne-containing self-assembled monolayers on SiO$_2$ and Si$_3$N$_4$. When deposited and cross-linked on flat surfaces, spheres, cylinders, or textured substrates, monolayers take the form of these templates and retain their structure on template removal. These nanomaterials can also be transferred from surface to surface and suspended over cavities without tearing. This approach to the synthesis of monolayer carbon networks greatly expands the chemistry, morphology, and size of carbon films accessible for analysis and device applications.

3.1 Introduction

In contrast to carbon nanotubes, fullerenes and various derivatives, the synthesis of large 2D sheets such as graphene, graphyne, and graphdiyne extending over micrometers in lateral dimensions is either in its infancy or has significant limitations. In fact, the synthesis of 2D carbon networks has been recognized as an
Graphene, the simplest of the 2D conjugated carbon nanomaterials, is produced by micromechanical cleavage of bulk graphite (HOPG) or by thermal decomposition of silicon carbide \[8, 9\]. However, these approaches lack the molecular-level control necessary to define the chemical makeup of these systems. Scholl coupling reactions on oligophenylene precursors \[10\] produce small (<15 nm) 2D graphene fragments with improved molecular diversity, and radiation induced modifications of self-assembled \[11, 12\] or Langmuir–Blodgett \[13\] monolayers create larger sheets, but with reduced control of the chemistry. Polyelectrolytes \[14\] represent a different class of chemistry that can form 2D \[15\] and 3D \[16\] nanomaterials. These films are formed through deposition of separately synthesized polymers, often in layer-by-layer assemblies, in the form of relatively thick (typically >5 nm) films governed by electrostatic interactions. These limitations, together with those associated with the planar, radiation-cross-linked monolayers, motivate the need for alternative approaches to these classes of materials. A potential solution to the formation of large 2D conjugated carbon nanomaterials would employ a two-step procedure involving the formation of self-assembled monolayers (SAMs) with highly functionalized monomers followed by chemical cross-linkage of the SAMs to form linked monolayers. Figure 3.1 shows the overall process beginning with the formation of SAMs of suitably designed carbon precursors on solid supports, followed by chemical cross-linking to yield covalently bonded networks with monolayer thicknesses. Not only could these materials adopt the geometry of the support, but they could also be transferred by using printing-like techniques to other substrates or lithographically patterned into desired geometries. This chapter introduces the use of synthetic organic methods to create linked carbon monolayers and monolayer membranes in forms ranging from planar or structured films and membranes, to spherical coatings, balloons, tubes, and other complex topologies.

### 3.2 Experimental Procedures

In order to prevent this chapter from being lengthy, the synthesis procedures for all monomer molecules are separated to APPENDIX.
Figure 3.1: Schematic illustration of linked monolayer formation. (A) Self-assembled monolayers (SAMs) are synthesized on a substrate, then cross-linked to form linked monolayers. This approach is applied to the formation of 3D topologies (i), structured sheets (ii), and membranes (iii). The box above iii provides an idealized view of the chemical structure for a linked monomer network formed from monomer 3. (B) Chemical structures of monomers 1-3.
General

Silicon nitride was deposited via plasma enhanced chemical vapor deposition (PE-CVD) onto a silicon wafer with a 300 nm thermal oxide (Process Specialties Inc.). TEM was performed on a JEOL 2010 LaB6 TEM. SEM was performed on a Hitachi S-4700 high resolution SEM. AFM was performed on a Digital Instruments Dimension 3100 AFM.

3.2.1 Cleaning Procedures for Flat Substrates

Silicon oxide, silicon nitride, and quartz (75 mm × 25 mm × 1 mm purchased from Chemglass) substrates were cleaned prior to use by heating to 90°C in a 3:1 H_2SO_4/H_2O_2 solution for two hours (caution: piranha solution is explosive and care should be taken while using this mixture). The substrates were rinsed thoroughly with deionized water then blown dry with a stream of nitrogen.

3.2.2 Representative Synthesis of SAMs on Flat Substrates

A freshly cleaned and dried substrate was placed in a reaction vial containing a 0.015 M solution of 2,5-di(prop-1-ynyl)benzyl 3-(triethoxysilyl)propylcarbamate in toluene and TEA (10 mM) under a nitrogen atmosphere. The vial was sealed and heated to 95 – 100°C for 24 h. The substrate was removed and rinsed once with toluene, twice with dichloromethane, and sonicated for 5 min in toluene. The rinse was repeated and the substrate was sonicated for 5 min in methanol. The rinse was repeated and the substrate blown dry under a stream of nitrogen.

3.2.3 Preparation of SiO_2 and Spheres and Glass Fibers

Non-porous 330-nm SiO_2 spheres purchased from Bangs Laboratories and 125-µm optical fibers (stripped of acrylate coating) purchased from Thorlabs were cleaned by heating to 90°C for 2 h in a 6 M solution of HCl. The objects were rinsed with water, methanol, and dichloromethane followed by drying under vacuum at 100°C overnight.

3.2.4 Representative Synthesis of SAMs on Objects

Freshly cleaned and dried objects were placed in a reaction vial containing a 0.015 M solution of 2,5-di(prop-1-ynyl)benzyl 3-(triethoxysilyl)propylcarbamate in ethanol.
and TEA (10 mM) under a nitrogen atmosphere. The vial was sealed, heated to 95 – 100 °C, and stirred by a rotatory plate for 24 hr. The substrates were removed and rinsed twice with methanol, twice with dichloromethane, and sonicated for 5 min in methanol.

3.2.5 Synthesis of Linked Monolayers on Flat Surfaces via Mo(IV) Alkyne Metathesis

In a glovebox, 5.0 mg of trisamidomolybdenum(IV) propylidyne and 3.3 mg of p-nitrophenol were dissolved in 3 mL of trichlorobenzene in a reaction vial. The substrate was added, the flask was sealed, and then place under a vacuum of ca. 20 in of Hg for 22 h. The substrate was removed from the vial and rinsed once with DMF, once with a 0.1 M solution of sodium diethylcarbamodithioate in DMF, once with toluene, twice with dichloromethane then sonicated in toluene for 5 min. The rinse was repeated and the substrate was sonicated for 5 min in methanol. The rinse was repeated a third time and the substrate was blown dry with a stream of nitrogen.

3.2.6 Synthesis of Linked Monolayers on Objects via Mo(IV) Alkyne Metathesis

The same procedure used for flat surfaces was followed except objects were cleaned by transferring to microcentrifuge tubes exposed to repeated washing/centrifuge cycles with same solvents as above.

3.2.7 Synthesis of Linked Monolayers via Cu-coupling

In a reaction vial was dissolved 20 mg of CuCl in 3 mL of dry, degassed acetone. To this suspension was added 61 µL TMEDA and the solution was allowed to stir under a nitrogen atmosphere at room temperature for 30 minutes. At this time, the substrates were added and the reaction vial purged with oxygen from a balloon. The mixture was stirred under an oxygen atmosphere for 15 h. The substrate was removed from the vial and rinsed once with DMF, once with a 0.1 M solution of sodium diethylcarbamodithioate in DMF, once with toluene, twice with dichloromethane then sonicated in toluene for 5 min. The rinse was repeated and the substrate was sonicated for 5 min in methanol. The rinse was repeated a third time and the substrate was blown dry with a stream of nitrogen.
3.2.8 Film Transfer

A photoresist (AZ 5214, Clariant) layer was uniformly spin coated onto a silicon nitride coated wafer with a monolayer at 3000 rpm for 30 s and baked at 110 °C for 2 min. The wafer was then exposed to a 49% HF solution for 2 min. The sample was then submerged in water to release the photoresist/monolayer film from the wafer. The photoresist/monolayer film was transferred to another solid surface (i.e., Si wafer with 300 nm thermal SiO₂) by carefully dipping a solid substrate into the water and removing with photoresist/monolayer film on top. The photoresist was finally removed by sonicating in acetone for 5 min, rinsing with IPA, DI water, and drying with a stream of nitrogen, to leave only monolayer film on the new solid support.

3.2.9 Line and Space Patterning for Height Measurement

First, the substrate, which has a linked monolayer film grown on Si wafer with 300 nm SiO₂, was spin coated with a photoresist (AZ 5214, Clariant) at 3000 rpm for 30 s, followed by prebaking at 110 °C for 2 min. Second, the substrate was aligned with a 5 µm line/space chrome mask on the MJB3 mask aligner (SUSS MicroTec) and exposed to a UV Hg lamp (365 nm) for 9 s with an intensity of 12 mW/cm². The substrate was then developed in a developer (AZ 327 MIF developer, Clariant) for 40 s resulting in 5 µm line/space photoresist stripes on the substrate. Next, the substrate was exposed to oxygen plasma (20 sccm O₂, 150 mTorr, 150 W) by reactive ion etching system (Unaxis, Plasma Therm) for 30 s. The photoresist was finally removed by sonicating in acetone for 5 min, rinsing with IPA, DI water, and drying with a stream of nitrogen.

3.2.10 Contact Angle Measurements

The advancing contact angles were measured with a Rame-Hart 100 goniometer. Contact angles were measured on 6 different spots of the polished side of the silicon wafer for each sample.

3.2.11 UV-Visible Spectroscopy

The UV-Vis absorption spectra were recorded on a Shimadzu (UV-160A) spectrophotometer. The monolayers grown on a quartz slide (Chem Glass, UV-grade, 92% transmission at 270 nm) were placed in a 1 cm cuvette and the absorbance was measured using a clean quartz slide as a background.
3.2.12 Fluorescence Spectroscopy

Fluorescence spectra were recorded on a Photon Technology International (QM-1) fluorometer by suspending the non-porous silicon oxide sphere with SAMs or linked SAMs in methanol (≈ 1 mg/mL) in a 1 cm quartz cuvette.

![Fluorescence spectrum](image)

Figure 3.2: A representative secondary ion mass spectrum of linked SAM from 2 on its growth substrate (Si wafer with 300-nm thermal SiO₂).

3.2.13 Secondary Ion Mass Spectrometric measurements

Secondary ion mass spectrometric measurements were carried out in a TOF-SIMS instrument ( Cameca ) equipped with a cesium ion gun. We measured SIMS of both SAMs and linked SAMs on their growth substrates and observed SIMS fingerprint spectra (Fig. 3.2) with complex correlations to the molecular weight fragments. Moreover, only small fragments (mass-to-charge ratio <400) from polymers were emitted because of chemical degradation by the high fluence of ions.

3.2.14 Raman Spectroscopy

The light scattered by the samples was analyzed with a Spex triplemate triple-grating monochromator (SPEX Industries, Edison, New Jersey) with the entrance slit set at 200 µm, a liquid-N₂-cooled CCD detector (Roper Scientific, Trenton, NJ), and a data acquisition system (Photometrics, Tucson, AZ). A video camera was also attached to the front port of the monochromator to facilitate laser alignment and positioning of the samples. Laser excitation (514.5 nm) was provided by an Ar ion laser (Coherent, Palo Alto, California). All the measurements were performed in ambient conditions.
The modulus measurements involved several steps. First ribbons were fabricated and transferred to a prestrained slab of PDMS. Specifically, this process started with the sputter deposition of a uniform layer of Au (thickness, ≈100 nm) on a linked SAMs on its SiO$_2$/Si growth substrate. This Au layer played the role of structural support during the transfer. Next, a layer of photoresist (diluted AZ5214, 1:1 with AZ thinner, 3000 rpm, 1 min) was spin cast on this substrate. Conformal contact of a PDMS phase mask consisting of 5 μm/5 μm line-and-space patterns, followed by flood exposure to ultraviolet light (Karl SUSS, contact aligner) for 7 s patterned the exposure of the resist, via a near field phase shift photolithography technique [18, 19]. After removing the PDMS phase mask, the substrate was developed for 20 s in developer (AZ 327 MIF), thereby yielding ≈500-nm wide lines of photoresist, spaced by ≈5 μm. These features of resist acted as an etch mask in an ion-milling process that removed the exposed Au/Linked SAMs. Oxygen plasma (PlasmaTherm) then removed the remaining photoresist. Dipping the substrate in HF undercut etched the SiO$_2$ and released ribbons of Au/Linked SAMs from the substrate. A flat slab of PDMS (10:1 weight ratio of base to curing agent; Dow Corning Sylgard 184) was used to pick up the released ribbons (still on substrate). At this stage, the ribbons were inverted, i.e., the linked SAMs was exposed to air while the Au layer was in contact with the PDMS. Another piece of PDMS, cured (20:1 weight ratio of base to curing agent; Dow-Corning Sylgard 184) and prestrained to 20–30%, was gently contacted and slowly peeled off of the PDMS with the ribbons of Au/Linked SAMs, thereby transferring these ribbons to the PDMS (20:1) slab. While maintaining the prestrain, the exposed Au was removed with an Au etchant (Transcene, Inc.) and thoroughly rinsed with deionized water. Finally, the prestrain was released to induce buckling in the linked SAMs. The samples, before and after release of the prestrain, were characterized by atomic force microscopy, AFM (Asylum, MFD).

For the calculation of the modulus of the linked SAMs (film), the following formula [20] was used:

$$E_{film} = \left( \frac{\lambda}{2\pi h} \right)^3 \left[ \frac{3(1 - \nu_{film}^2)}{1 - \nu_{PDMS}^2} E_{PDMS} \right]$$

where $E_{PDMS}$ and $E_{film}$ are the moduli of the PDMS and linked SAMs, respectively, $\nu_{PDMS}$ and $\nu_{film}$ are the Poisson ratios, $h$ is the thickness of the linked SAMs and $\lambda$ is the buckling wavelength.
3.2.16 Chemical Amplification

The chemical amplification process for evaluating the defect densities and barrier properties of SAMs and linked SAMs on their growth substrates consisted of: (i) formation of SAMs and linked SAMs on Si(100) wafers with native oxide; (ii) anisotropic etching of Si (KOH (52 g)/H\textsubscript{2}O (226 mL)/IPA (74 mL), 70°C, 25 min) to convert and amplify defects in the SAMs and linked SAMs into easily imaged, micron-scale pits in the Si, and (iii) imaging the pits by optical microscopy.

The process for evaluating transferred linked SAMs consisted of: (i) transfer of a linked SAM onto a substrate of Au(200 nm)/Cr(5 nm)/SiO\textsubscript{2}(300 nm)/Si with Au and Cr deposited by electron beam evaporation, and SiO\textsubscript{2} grown thermally; (ii) exposure of the linked SAMs/Au/Cr/SiO\textsubscript{2}/Si substrate to an etchant for Au (Transene, Inc); (iii) immersion in aqueous HF to remove exposed SiO\textsubscript{2} in the regions where the gold was removed; (iv) anisotropic etching of the Si (KOH (52 g)/H\textsubscript{2}O (226 mL)/IPA (74 mL), 70°C, 25 min) to convert and amplify defects in the exposed regions into easily imaged, micron-scale pits in the Si; (v) removal of the remaining gold by aqua regia; and (vi) imaging the pits in the etched silicon substrate by optical microscopy.

Figure 3.3: Source drain current-gate voltage characteristics of a representative back-gate-linked SAM from 2 device (A) and polymer electrolyte gate-linked SAM from 2 device (B). Insets show schematic illustrations of cross section and optical image of device.

3.2.17 Electrical Measurements

Field effect transistor devices were used to probe the charge transport characteristics of the linked SAMs. Two types of devices were fabricated. The first used a
conventional back gate geometry with a doped Si wafer as the gate and a layer of thermally grown SiO$_2$ as the gate dielectric. In the first step of the fabrication of this type of device, a thin layer of isopropanol (IPA) was placed on a linked SAMs grown a SiO$_2$(300 nm)/Si substrate. A shadow mask, based on a TEM grid (Gilder Grids, 150 Mesh, Ted Pella, Inc.), was then placed on the IPA surface. Evaporation of IPA led to good physical contact of the shadow mask with the linked SAM due to the action of capillary forces. Blanket electron beam evaporation ($10^{-6}$ Torr; Temescal BJD 1800) of Ti (5nm) and Au (50nm) formed square-shaped contact pad arrays to define source and drain electrodes and channels with widths and lengths of 230 $\mu$m and 14 $\mu$m, respectively. Electrical measurements on linked SAMs were carried out in air using a semiconductor parameter analyzer (Agilent 4155C), using an Agilent Metrics I/CV Lite program and a GBIP communication interface to a computer. Triaxial and coaxial shielding were used with a Signatone probe station to yield high signal/noise ratio measurements of small current levels. The bias between the source and drain electrodes was 0.1 V. Measurements on these devices at room temperature reveal the resistivities on the order of $10^5$-$10^6$ $\Omega$-cm, independent of gate bias as shown in Fig. 3.3A.

The second type of transistor device used polymer electrolyte gating. In this case, source and drain electrodes were patterned in the same geometries and with the same techniques as those used for the conventional devices described above. A solution 30% 1:3 (w:w) LiClO$_4$:polyethyleneimine in methanol was used as the polymer electrolyte. The electrolyte was placed in a poly-(dimethylsiloxane) fluidic channel formed with a piece of molded PDMS on top of a linked SAM. A silver wire immersed in the electrolyte was used to apply gate voltages between -0.5 V and 0.5 V. The bias between the source and drain electrodes was 0.1 V. The measured source-drain currents were smaller than $\approx 10$ nA (Fig. 3.3B), comparable to the gate leakage in these devices. The conclusions from these measurements are consistent with those from devices with the more conventional back-gate device geometry.

### 3.2.18 Preparation of Substrate with Patterned Holes

A substrate with patterned holes was prepared by using Solvent Assisted Micro-Molding (SAMIM) [21]. First, a film of epoxy with the thickness of $\approx 10$ $\mu$m (NanoSU-8, MicroChem, formulation 10) was deposited onto a glass slide by spin coating at 3000 rpm for 30 seconds, followed by soft-baking at 65°C and 95°C for 1 minute and 5 minutes, respectively. Second, the quasi 3D type of mold made of acryloxy perfluoropolyether (a-PFPE) was wetted with ethanol and gently placed
into conformal contact on soft-baked substrate from the first step for 30 minutes. The mold was then peeled off from the substrate followed by exposure of the substrate to a UV Hg lamp (365 nm) from an MJB3 mask aligner (SUSS MicroTec) for 30 seconds with an intensity of 12 mW/cm² and re-baked at 65 °C and 95 °C for 1 minute and 5 minutes, respectively. Finally, the substrate was hard baked at 180 °C for 5 minutes and coated with thin films of Ti/Au (2 nm/ 50 nm) by electron beam evaporation system (Temescal).

![Figure 3.4: Atomic force microscope (AFM) characterization of structured growth substrate. (A) Tapping mode AFM image of patterned substrate. (B) An averaged line cut from (A), revealing a relief depth of 35 nm.](image)

3.2.19 Preparation of Smoothed Patterned Substrate

The above procedure was followed except the SU-8 was spin coated on a silicon wafer. The steps were smoothed by exposure to thermal flow at 60 °C for 6 min after peeling off the mold and prior to UV exposure. This smoothing resulted in a decrease of the steps from 350 nm to 35 nm and the sharp edges became sloped (Fig. 3.4). Finally, a 50-nm silicon oxide film was deposited onto the plasmonic crystal using PECVD instead of coating with Ti/Au films.

3.2.20 XPS Spectroscopy for Characterization of Metal Content

XPS spectroscopy was used to determine whether metal remains on the surface after the Mo(IV) catalyzed linkage of a SAM of 1. We found the doublet for Mo(3d₅/₂) and Mo(3d₃/₂) at 226 and 239 eV, corresponding well to the literature data for Mo [22]. A strong C(1s) peak appeared at 283 eV. Integration of the XPS peaks for Mo and C generated a molybdenum-to-carbon ratio of 1.45% at the surface. Quantitative analysis of trace amount of Cu catalysts in linked SAMs from 2 and 3 was
difficult because of the low kinetic energy the photoelectrons.

3.3 Results and Discussion

Aryl alkynes are attractive monomers for this chemistry because they are a chemically diverse class of molecules that are already highly conjugated, contain primarily carbon by mass, and can be chemically linked through a variety of methods including alkyne metathesis \[23\], oxidative Cu coupling \[24\], and Pd-catalyzed cross-coupling \[24\]. Di-functional monomers (1 and 2) and a hexa-functional monomer (3) were synthesized with triethoxysilyl groups attached by a carbamate group to the aryl core (Fig. 3.1B). Details on chemical syntheses are provided at APPENDIX. SiO\(_2\)-or Si\(_3\)N\(_4\)-coated substrates or quartz/glass slides were immersed in monomer solutions (\(\approx 15\) mM monomer, \(\approx 10\) mM triethylamine, 90 – 100\(^\circ\)C, 24 h, toluene) creating SAMs that exhibited similar advancing contact angles (74 – 80\(^\circ\)) for all three monomers (Table 3.1). Two different cross-linking chemistries were used to form linked monolayers from these SAMs. Mo(IV)-catalyzed, vacuum-driven alkyne metathesis \[23\] linked the dipropyne SAMs derived from 1. Cu-catalyzed Hay-type coupling conditions \[24\] created linked monolayers from SAMs of monomers 2 and 3. The advancing contact angles consistently decreased by 6, 11, and 20\(^\circ\) for the dipropyne (1), diacetylene (2), and terphenyl (3) chemistries, respectively. After exposing the SAMs to the linkage conditions, it was found that very little residual metal remained on the substrate.

<table>
<thead>
<tr>
<th>Support</th>
<th>SAM 1</th>
<th>Linked SAM 1</th>
<th>SAM 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon oxide</td>
<td>74(^\circ) (1)</td>
<td>69(^\circ) (2)</td>
<td>75(^\circ) (1)</td>
</tr>
<tr>
<td>Silicon nitride</td>
<td>74(^\circ) (2)</td>
<td>70(^\circ) (2)</td>
<td>77(^\circ) (1)</td>
</tr>
<tr>
<td>Quartz</td>
<td>74(^\circ) (2)</td>
<td>69(^\circ) (1)</td>
<td>76(^\circ) (2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Support</th>
<th>Linked SAM 2</th>
<th>SAM 3</th>
<th>Linked SAM 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon oxide</td>
<td>64(^\circ) (2)</td>
<td>80(^\circ) (1)</td>
<td>59(^\circ) (1)</td>
</tr>
<tr>
<td>Silicon nitride</td>
<td>64(^\circ) (2)</td>
<td>80(^\circ) (1)</td>
<td>62(^\circ) (1)</td>
</tr>
<tr>
<td>Quartz</td>
<td>65(^\circ) (3)</td>
<td>86(^\circ) (2)</td>
<td>56(^\circ) (3)</td>
</tr>
</tbody>
</table>

Table 3.1: Contact angle measurements for SAMs and linked SAMs from 1, 2, and 3 on SiO\(_2\), silicon nitride, and quartz wafers.

UV-visible (UV-vis) absorption spectra of the SAMs on UV-grade fused quartz closely matched spectral features of the monomers in solution (Fig. 3.5). The
linked monolayer of 1 on quartz possesses a new shoulder at 330 nm (Fig. 3.6A). Because this new shoulder is small it suggests incomplete polymerization or the formation of oligomers [25, 26]. Similarly, the linked monolayer from 2 on quartz possesses a broad new peak at 370 nm (Fig. 3.6D) that matches the absorbance of poly(1,4-phenylene-1,3-butadiynylene) derivatives [26, 27]. This has been described as a delocalized $\pi \rightarrow \pi^*$ transition in molecules comprised of multiple 1,4-diphenylbutadiyne chromophores [26]. The appearance of these lower-energy peaks suggests an increased delocalization of electrons on oligomerization/polymerization resulting from increased conjugation [27]. The spectrum of the linked monolayer of 3 is significantly broadened compared with that of the original SAM (Fig. 3.7). No polymers have been synthesized previously from monomers structurally similar to 3, but the broadening of the absorbance spectra is likely a result of the extensive cross-linking that is possible with this monomer (for an idealized network, see Fig. 3.1).

Figure 3.5: UV-Vis spectra of monomers in dichloromethane. (A) Dipropyne monomer 1. (B) Diacetylene monomer 2. (C) Terphenyl monomer 3.

Methanol suspensions of SAMs of diacetylene (2) coated on 330-nm nonporous SiO2 spheres exhibit dramatic changes in fluorescence emission on conversion to linked monolayers. A SAM from 2 primarily has a large emission at 315 nm ($\lambda_{ex} = 275$ nm; Fig. 3.6E, blue curves) similar to that of the monomer in solution (Figs. 3.8). On cross-linking, the emission at 315 nm ($\lambda_{ex} = 275$ nm) weakened significantly and a new emission appeared at 405 nm when excited at 370 nm (Fig. 3.6E, red curves).

Raman spectroscopy provided a convenient means to determine the conversion of
Figure 3.6: Spectroscopic data and AFMs of SAMs, linked monolayers, and transferred monolayer membranes. (A) Absorption spectra of a SAM (blue), a linked monolayer (red), from 1 on quartz. (B and C) Tapping-mode AFM of a SAM and a linked monolayer, respectively, from 1 patterned into stripes by photolithography and oxygen-reactive ion etching. The averaged line cuts show a step height of 1.1 nm for the SAM and 1.4 nm for the linked monolayer. (D) Absorption spectra of a SAM (blue), a linked monolayer (red), and a transferred monolayer membrane (green) from 2 on quartz. (E) Fluorescence spectra (λ_{ex} = 275 nm, Left; λ_{ex} = 370 nm, Right) of a SAM (blue curves), a linked monolayer (red curves), and an etched monolayer membrane from 2 (green curve) on 330-nm-diameter SiO$_2$ spheres. Peak heights were normalized to the 315-nm emission of the SAM from 2. (F) Raman spectra of a SAM (blue), linked monolayer (red), and transferred monolayer membranes on a Si wafer with 300 nm thermal SiO$_2$ (green) from 2.
Figure 3.7: UV-Vis spectra of a SAM of 3 (blue) and linked monolayer of 3 (red) on quartz.

SAM 2 to a linked monolayer. Raman spectra of SAM 2 on SiO$_2$(300 nm)/Si showed a peak at 2,101 cm$^{-1}$, corresponding to the C≡C stretching mode in terminal phenyl acetylenes (Fig. 3.6F) [28, 29]. On exposure of the SAM to cross-linking conditions, the peak at 2,101 cm$^{-1}$ shifts to 2,204 cm$^{-1}$ corresponding to the C≡C stretching mode in phenyl diacetylene [30, 31]. The disappearance of the peak from the terminal phenyl acetylene indicates nearly complete conversion of the monomers in the SAM to the corresponding linked monolayer. A variety of conjugated polymers have been previously synthesized that resemble these linked monolayers [26, 27, 32, 33]. The spectroscopic changes observed in the monolayer-supported systems are similar to those seen in the literature examples. However, direct comparisons are difficult because the electronics of these polymers are significantly different and very few examples of poly(1,4-phenylene-1,3-butadiynylene) exist (similar to linked SAMs of 2 and 3). Collectively, the changes in the UV-vis, fluorescence, and Raman spectra provide strong evidence that the SAMs undergo the desired reaction to form linked carbon monolayers.

In addition to spectroscopic measurements, SAMs and linked monolayers were patterned into 5-µm lines/5-µm space by simple oxygen-reactive ion etching through a layer of photoresist patterned by photolithography. By atomic force micrographs (AFMs), the linked monolayers formed from 1 exhibited only a slight increase in film thickness compared with their SAM precursors (e.g., 1.1-1.4 nm; Fig. 3.6B and C). MM2 molecular geometry optimization of 1 gives a monomer height of ≈1.5 nm, depending on the torsion angle of the aryl rings. The SAM and linked monolayer thicknesses are also similar to those measured for other related system of similar
Figure 3.8: (A) Fluorescence spectra of Diacetylene monomer 2 excited at 275 nm in methanol. (B) Fluorescence spectra of Terphenyl monomer 3 excited at 350 nm in methanol. (C) Combined fluorescence spectra for SAMs and linked SAMs from 2 on SiO$_2$ spheres suspended in methanol from excitation at 275 nm. Bare SiO$_2$ spheres (blue), SAMs from 2 (green) linked SAM from 2 (red). (D) Fluorescence from excitation at 370 nm. Bare SiO$_2$ spheres (blue), SAM from 2 (green), linked SAM from 2 (red). Peak heights were normalized to the 315 nm emission of the SAM from 2. (E) Fluorescence spectra of SAMs from 3 on SiO$_2$ spheres at 350 nm excitation. (F) Fluorescence spectrum of linked SAMs from 3 on SiO$_2$ spheres at 350 nm excitation.

molecular sizes [13, 34]. These data indicate that the unlinked and linked SAMs consist of single layers of monomers aligned approximately perpendicular to the surface. The small increase in thickness on cross-linking may be caused by either a change in the orientation of the benzene rings or by the increased average roughness (0.18-0.27 nm). AFM measurements on patterned linked monolayers from 2 and 3 indicate similarly small increases in thickness of 0.5 and 0.3 nm, respectively, rela-
tive to their SAMs. Unlike the films associated with 1, for which only monolayers form, SAMs from 2 and 3 form multilayers (2.8 and 4.7 nm, respectively) presumably by thermal polymerization during deposition of these reactive multifunctional monomers.

To illustrate the versatility of this approach, we describe methods to release the linked monolayers from their growth substrate and transfer the resulting monolayer membrane to other substrates. These film manipulations made it possible to examine the structural integrity of the monolayer membranes and compare their behavior with the corresponding SAMs. To accomplish this, photoresist is uniformly spin cast onto the SAMs or linked monolayers followed by patterning if desired, and liftoff by selective etching of the support (i.e., bulk SiO$_2$ or thin films of SiO$_2$ or Si$_3$N$_4$ on other materials) with concentrated HF. The photoresist/SAM or photoresist/monolayer membrane hybrid films are transferred to other substrates and sonicated in acetone to remove the photoresist.

Spectroscopic measurements were performed to examine the possibility of chemical changes in the transferred film induced by exposure to HF, liftoff, and transfer. The UV/vis spectrum of the monolayer membrane from 2 transferred to a UV grade quartz slide reveals a small shift of the absorbance peak at 275 nm, but the absorption of poly(1,4-phenylene-1,3-butadiynylene) chromophores at 365 nm remains unchanged (Fig. 3.6D, green curve). When the monolayer membrane from 2 grown on silicon oxide beads were etched with aqueous HF, the fluorescence spectra (Fig. 3.6E, green curve) showed a slight increase in intensity, but no change in the overall peak signature ($\lambda_{ex} = 370$ nm). Finally, when a sample of monolayer membrane from 2 was transferred to a Si wafer with 300 nm thermal SiO$_2$, no change in the Raman peak at 2,204 cm$^{-1}$, corresponding to the C≡C stretching mode in diphenyl diacetylene, was observed (Fig. 3.6F, green curve). Together, these results suggest that the chemical nature of the monolayer membrane remains unchanged after HF etching and transfer.
Figure 3.9: Characterization of transferred monolayer membranes. (A) AFM images of a ribbon of a monolayer membrane from 2 (width = 500 nm) on a prestrained PDMS substrate before (Upper) and after (Lower) releasing the prestrain. (B) Image of a sample of monolayer membrane from 2 transferred to a substrate of Au(200 nm)/Cr(5 nm)/SiO$_2$(300 nm)/Si after wet etching the Au with a ferricyanide solution in a circular region (dashed line) surrounding the membrane. The etched areas appear as dark blue; the unetched gold region in the center corresponds to the transferred monolayer membranes. (Inset) An optical micrograph of a silicon substrate that supports a linked monolayer, collected after exposure to KOH etchant. The arrow indicates an etched pit corresponding to a pinhole defect in the monolayer. (C) Reflection mode optical micrograph of a monolayer membrane from 2 transferred to a Si wafer with a 300-nm thermal SiO$_2$ layer. (Inset) High-magnification micrograph of folds in the film. (D) Reflectance optical micrograph superimposed on tapping-mode AFM image of a monolayer membrane from 1 transferred to a Si wafer with a 300-nm thermal SiO$_2$ layer. (E) Tapping-mode AFM image and line-cut height profile showing a monolayer membrane from 1 with regions of 1.8- and 3.3-nm height, consistent with folding on transfer to a Si wafer with a 300-nm thermal SiO$_2$ layer. (F) Low-magnification TEM image of a monolayer membrane from 1 transferred to a holey carbon-coated grid. The arrow points toward a small defect in the film created by the transfer process. (Inset) An electron diffraction pattern with rings at 1.1 Å and 2 Å, but otherwise no significant in-plane ordering. (G) High-magnification TEM image of a monolayer membrane from 1 transferred to holey carbon-coated grid showing a film largely free of pinhole defects.
We explored the modulus and structural integrity in two different types of experiments. First, the transfer of narrow ribbons of monolayer membranes to prestrained elastomeric substrates of poly(dimethylsiloxane) (PDMS) was studied. Releasing the prestrain leads to a nonlinear buckling instability that produces a one-dimensional, sinusoidal pattern of relief. Fig. 3.9A shows AFM images of a ribbon of a monolayer membrane from 2 before and after releasing the prestrain. This type of buckling response will only occur in ribbons of material with high levels of structural integrity and moduli that are much higher than the PDMS \[20\]. Quantitative analysis of the buckling wavelength, with the known modulus of the PDMS \[35\] and the measured thickness of the monolayer membrane, yielded moduli between 1 and 10 GPa. These values are typical of polymers of similar materials. They are lower than single crystals of dicarbazolyl polydiacetylene (45 GPa) \[36\] and of graphene (\(\approx 1\) TPa) \[37\].

Second, to examine the structural integrity and barrier properties of SAMs, linked monolayers, and transferred monolayer membranes, we used wet etching based chemical amplification \[38\] to evaluate the area density of defects in the films. The defect densities in linked monolayers on their growth substrates [Si(100) with a native oxide layer] are 1.6 \(\times\) 10^3, 1.4 \(\times\) 10^3, and 9.1 \(\times\) 10^2 defects per mm^2 for 1, 2, and 3, respectively (Fig. 3.9B Inset). Several factors could contribute to the density of defects in the linked monolayers, such as defects on growth surfaces, defects in SAMs formation, and defects as a result of polymer shrinkage. Although polymer shrinkage may be an issue, especially for molecule 3, it is challenging to assess its influence without information on packing density during the SAM formation. In particular, if the initial SAMs are packed very tightly, cross-linkage may actually result in expansion instead of shrinkage. The densities in linked monolayers are \(\approx 10\) times lower than those of the corresponding SAMs, suggesting a linking mechanism that tends to eliminate defects. The defect densities in the linked monolayers are, in fact, only slightly higher than well developed alkanethiolate SAMs on gold \[38\], which are known to have much better order and quality than SAMs of silanes. Similar studies performed on a monolayer membrane from 2 transferred to a substrate of Au(200 nm)/Cr(5 nm)/SiO_2(300 nm)/Si indicated a \(\approx 10\)-fold increase in defect density compared with the same linked monolayer on its growth substrate (Fig. 3.9A). This increase is due, at least in part, to slight mechanical damage during transfer. Release of stresses associated with polymerization shrinkage could also contribute.

Although monolayer films are invisible on most substrates, we found that these transferred monolayer membranes could be visualized directly under an optical mi-
croscope when supported by oxidized Si substrates with an oxide layer of 300 nm, similar to observations in single-layer graphene [8]. The Si wafer with 300 nm thermal SiO$_2$ was selected because the phase contrast between the monolayer membrane and the wafer results in a shift from violet-blue to blue [39]. For all transferred films, we observed flat, continuous films largely free of defects over areas of several square millimeters (Fig. 3.9C). Near their edges, these monolayer membranes exhibited folds, holes, and tears, which we attribute to the transfer process.

The transferred monolayer membranes were also analyzed by AFM and transmission electron microscopy (TEM). A folded region of a transferred film from 1 showed clear correlations between thickness determined by tapping-mode AFM and intensity of the optical micrograph (Fig. 3.9D). The transferred monolayer membrane from 1 has a slightly increased thickness (1.8 nm) that likely results from a layer of water between the film and SiO$_2$ surface [8]. Additionally, a folded area has a thickness (3.3 nm) that is approximately twice the nominal thickness for the rest of the film (Fig. 3.9E). The folding ability of these nanometer-thick films is a testament of their mechanical strength. TEM images of a monolayer membrane from 1 transferred to a holey carbon grid revealed a tightly packed monolayer with uniform thickness and very few pinhole defects that may have been invisible using AFM (Fig. 3.9F and G).

The STM image (Fig. 3.10A) was obtained by transferring linked SAM of 1 onto a freshly cleaved highly oriented pyrolytic graphite surface. The crosssectional height is $\approx$1.4 nm. (B) An AFM image of linked SAM of 1 on the growth substrate (Si wafer with 300 nm thermal oxide). The AFM tip radius = 2 nm. The RMS of linked SAM of 1 is 0.17 nm, nearly identical to that of bare SiO$_2$ surface. (C) A TEM image of transferred linked SAM of 1 on a holey carbon TEM grid under a low dose condition, showing what appear to be strands of polymers separated by a distance of $\approx$3.35 Å.
freshly cleaved highly oriented pyrolytic graphite surface. Although certain insights can be obtained from such images, molecular scale detail was difficult to obtain. We believe that residue associated with manipulation and synthesis of the linked SAM of represent the main challenge to achieving molecular resolution[40]. As an alternative, we conducted ultra-high resolution AFM measurements with AFM tips that have radii of curvature as small as 2 nm. Figure 3.10B shows a typical result. The rms roughness of linked SAM of 1 is 0.17 nm, nearly identical to that of the bare SiO$_2$ growth surface. No filamentary structures were visible. As a final set of data, we performed high resolution TEM on transferred linked SAM of 1 under a low dose conditions. Images (Fig. 3.10C) show what appear to be strands of polymers separated by a distance of ca. 3.35 Å, which might provide direct information on the possibility of woven network structures. These features may, however, be caused by even slight damage induced by exposure to the electron beam.

The low density of defects and the high structural integrity of the linked monolayers allowed the creation of more exotic film geometries. Transfer of a monolayer membrane from 1 onto a substrate with an array of cylindrical holes (≈440 nm diameter, ≈400 nm depth) produces suspended monolayer “drumheads” that were nondestructively imaged by AFM and scanning electronic microscopy (SEM; Fig. 3.11A and B). Again, the absence of torn regions illustrates the remarkable mechanical robustness of these systems.

The ability to form linked monolayers on a wide range of planar, nonplanar, or three-dimensional substrates creates further opportunities for fabrication of unusual structures. For example, a linked monolayer from 1 was formed directly on a substrate with an array of shallow voids (≈35 nm), also see Fig. 3.4 to produce a continuous linked monolayer in the form of a 2D “pleated sheet” (Fig. 3.11C and D). On transfer of the membrane, the AFM power spectrum shows an in-plane periodicity of the “pleats” that matches that of the growth substrate. However, the relief is only ≈1.2 nm, as might be expected from partial or complete folding of the monolayer membrane in the regions corresponding to the edges of relief in the substrate.

This strategy also allowed the formation of linked monolayers on 3D objects as well. SAMs of 1 were deposited on 226 ± 16 nm nonporous SiO$_2$ spheres with a procedure similar to that used for flat substrates. After linking, the SiO$_2$ substrate was removed by HF vapor etching to yield empty monolayer membrane “balloons.” Fig. 3.11 shows TEM images of monolayer-coated spheres (Fig. 3.11E) and balloons (Fig. 3.11F). Histograms created from observation of many such objects show a
Figure 3.11: Images of “unusual” monolayer membrane structures. (A and B) SEM and AFM images, respectively, of a membrane from 1 transferred onto a substrate with a square array of cylindrical holes (diameters ≈440 nm and depths ≈400 nm) to form “drumhead” structures. Red arrows point to the same region of the film that is suspended over the edge of a hole. (C and D) AFM and high-resolution AFM images, respectively, of a monolayer membrane from 1 grown on a substrate similar to that in A, but with relief depths of ≈35 nm, and then transferred to a flat Si wafer with a 300-nm thermal SiO$_2$ layer. (C Inset Upper Left) Power spectrum of the AFM image, indicating a well defined periodicity consistent with that of the growth substrate. (C Inset Lower Right) Illustration of a “pleated sheet.” (E and F) TEM images and diameter distributions of a monolayer membrane from 1 deposited on SiO$_2$ spheres imaged on a holey carbon-coated grid before (E) and after (F) HF vapor etching of the SiO$_2$. Insets are illustrations of the imaged structures. (G-I) Time-resolved reflection mode optical micrographs of a tubular membrane from 3 filled with HF/water immediately after HF vapor etching of optical fiber, after 20 min open to the air, and after complete drying, respectively. Insets are illustrations of the imaged structures. (J) AFM image of this collapsed tube. The line scan corresponds to an average over the area indicated by the rectangle.

Close correspondence between sphere and balloon diameters, but the balloons have a slightly wider distribution and smaller size (diameters, 168 ± 32 nm) because of partial collapse on removal of the silica support. A similar process was carried out with ≈125-µm-diameter optical fibers by using SAMs of 3. Immediately after the HF vapor etch, water droplets were observed within the hollow fibers. Fig. 3.11G, H, and I show time-sequential optical micrographs illustrating evaporation of this encapsulated water. The AFM image in Fig. 3.11J shows that the monolayer membrane that remains after drying is consistent with the nominal layer thickness (≈4.5
nm center thickness), although capillary forces induced by the contracting HF/water droplet may be responsible for large nonuniformities near the edges. In a saturated environment, the water-filled monolayer membrane tubes maintain their shape for hours without tearing, providing additional evidence of their robustness.

A remaining topic of interest involves how the monolayer membranes are being held together. Although it could be envisioned that these membranes are being held together by polysiloxane formation during SAM deposition, transfer of unlinked SAMs of 1 and 2 yielded neither films nor film fragments. For the SAM of 3, film fragments were observed but they were smaller and contained many more defects than the corresponding monolayer membrane. The small fragments in this case likely result from inadvertent cross-linking by air oxidation or by thermal polymerization under the SAM deposition conditions. Additionally, if these membranes were being held together through polysiloxanes it is highly unlikely that they would stand up to treatment with HF. Exposure of SAMs from 1 and 2 to the linkage conditions, yields linear oligomeric/polymer chains. Conceivably, these chains can be held together in a woven network, although this type of geometry is not necessary to explain the structural integrity of the films; previous studies of related systems indicate that purely noncovalent interactions can yield similar properties [13, 41]. However, monolayer membranes from 3 are most likely held together because of multiple cross-linking. Both of these proposed mechanisms would explain the mechanical strength of the monolayer membranes on removal of the support and their flexibility to adopt the geometry of the given support.

### 3.4 Summary

In conclusion, we have shown that linked carbon monolayers can be formed on a variety of solid surfaces. These linked monolayers are synthesized by linking three different alkyne-containing monomers with two different carbon-carbon bond-forming reactions [Mo(IV)-catalyzed alkyne metathesis and Cu-catalyzed Hay coupling]. The linked monolayers synthesized on flat surfaces have extremely large aspect ratios and are easily transferred from the native surface by protecting with photoresist and etching the inorganic substrate. These monolayer membranes are sufficiently robust to be suspended over 440-nm-diameter holes without tearing. The linked monolayers were also prepared on structured surfaces and 3D supports, and the freestanding monolayer membranes maintained the shape of the original support.
after etching. This approach to the synthesis of monolayer carbon networks provides a powerful method to explore the properties and device applications of a wide variety of carbon films. Other linking chemistries and monomers are currently being explored for the synthesis of conducting, 2D monolayer films.

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3.5 References


CHAPTER 4

TRANSFER TECHNIQUE OF GRAPHENE LAYERS GROWN ON SILICON CARBIDE WAFERS

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Transfer of Graphene Layers Grown on SiC Wafers to Other Substrates and Their Integration into Field Effect Transistors

This chapter presents a simple method for transferring epitaxial sheets of graphene on silicon carbide to other substrates. The graphene was grown on (0001) face of 6H-SiC by thermal annealing at 1,550°C in a hydrogen atmosphere. Transfer was accomplished using a peeling process with a bilayer film of gold/polyimide, to yield graphene with square millimeters of coverage on the target substrate. Raman spectroscopy provided evidence that the transferred material is single layer. Back gated field-effect transistors fabricated on oxidized silicon substrates with Cr/Au as source-drain electrodes exhibited ambipolar characteristics with hole mobilities of ≈100 cm²V⁻¹s⁻¹, and negligible influence of resistance at the contacts.

4.1 Introduction

Graphene [1] is a promising material for high speed electronics due to its exceptionally high carrier mobilities [2], and ballistic transport characteristics [3]. Some of the earliest work involved graphene derived by mechanical exfoliation from bulk pieces of highly ordered pyrolytic graphite (HOPG) [1 2]. Although pristine quality films can be achieved this way, the samples are small, typically below 100 µm², the yields are low and the ability to control the positions, shapes and orientations are limited. Other approaches for mass production of graphene are under active investigation; these include epitaxial growth on SiC substrates [4 5], chemical vapor deposition growth on metal surfaces [6 7], and chemical reduction of graphene oxide (GO)
The first method relies on Si sublimation and graphization of C atoms on the SiC by annealing at high temperature under ultra high vacuum (UHV). This approach is promising, but its current implementation requires the use of SiC as the device substrate. This feature frustrates integration with silicon technologies, and requires the use of top gate transistor device geometries. Here, we report procedures for transferring graphene films epitaxially grown on SiC to other substrates. Fabrication of field effect transistors using graphene transferred onto Si wafers with layers of SiO$_2$ on their surfaces reveals the properties of the materials and suggests the possibility for integration with silicon electronics. Transfer of graphene from the SiC growth wafer to another substrate followed procedures similar to those recently reported for carbon nanotubes [10] as illustrated in Fig. 4.1.

Figure 4.1: Schematic illustration of the steps for transferring graphene grown on a SiC wafer to another substrate (SiO$_2$/Si in this case).

4.2 Experimental Procedures

4.2.1 Epitaxial Growth of Graphene on SiC Substrates

We used 5×25 mm$^2$ rectangular pieces of (0001) face 6H-SiC cut from a wafer (II-VI, Inc.) and coated with 200 nm Ta on their back sides (electron beam evaporation; Temescal BJD1800). Such samples were installed in an ultrahigh vacuum chamber with a base pressure 10$^{-10}$ Torr and heated to 1,550°C by passing current through the Ta layer for 6 hours in a hydrogen atmosphere of 2×10$^{-7}$ Torr while the temperature was monitored by a radiation thermometer (CHINO IR-CAQ). The as-
grown samples were then characterized by low energy electron diffraction (LEED), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy.

4.2.2 Transfer Procedures of Graphene Layers from SiC Substrates

In the first step (Fig. 4.1), the graphene/SiC sample was coated with a layer of Au (≈100 nm; electron beam evaporation; Temescal BJD1800) and then with a layer of polyimide (≈1.4 µm; poly(pyromellitic dianhydride-co-4,4′-oxydianiline) amic acid solution (Sigma-Aldrich, Inc.), 3000 rpm for 30s, baked at 110 °C for 2 minutes to remove the solvent and partially cure the polymer. Peeling this bilayer film away from the SiC wafers lifted some of the graphene from the SiC wafer. Delivering the film to a target substrate (silicon wafer with thermal oxide, for the work reported here) and then removing the PI and the Au with oxygen plasma reactive ion etching (PlasmaTherm, 100 mTorr, O₂ 20 sccm, 100 W, 30 minutes) and wet chemical etching (Transene, Inc.), respectively, completed the process.

4.2.3 Device Fabrication on Transferred Graphene Films

Back gated field effect transistor devices were fabricated on graphene transferred to a 300 nm thick, thermally grown layer of SiO₂ on a Si substrate with source and drain electrodes (Cr/Au, 5 nm/50 nm) patterned by electron beam lithography, electron beam evaporation and lift-off.

4.3 Results and Discussions

4.3.1 Characterizations of Epitaxial Graphene on SiC Substrate

Inspection of the resulting samples by LEED revealed a characteristic pattern of multilayer graphene. XPS and Raman spectroscopy confirmed this result. These observations are consistent with previous reports using related growth techniques. The details are shown below.

After two hours of heating on SiC substrate using conditions provided in the main text, in-situ LEED revealed a (6√3 × 6√3) pattern typical for a one-two layers thick graphene1 as shown in Fig. 4.2a while after the final treatment the LEED pattern
Figure 4.2: Characterization of the as-deposited graphene on SiC(0001) substrate. (a) in-situ LEED pattern with $E_p = 187$ eV after 2 hours of annealing at 1,550°C in hydrogen atmosphere at $2 \times 10^{-7}$ Torr. (b) in-situ LEED pattern with $E_p = 106$ eV after the final 6 hours annealing at the same conditions. (c) A typical $3 \mu m \times 3 \mu m$ tapping-mode AFM image of as-grown graphene/SiC sample showing terraces of $400 \pm 100$ nm with single and double Si-C bilayers step heights. (d) XPS spectrum of the C$_{1s}$ region of the as-grown sample exhibiting a SiC peak at 283.4 eV, graphene peak at 284.5 eV and a small adventitious carbon peak at 285 eV. (e) Raman spectrum showing D, G and 2D peaks, which corresponds to epitaxial multilayer graphene.

was characteristic for multilayer graphene in Fig. 4.2). A typical $3 \times 3 \mu m^2$ tapping-mode AFM image (Asylum Research MFP-3D) of as-grown graphene/SiC sample, shown in Fig. 4.2c, exhibits terraces of average width $350 \pm 120$ nm and with single and double Si-C bilayers step heights. Ex-situ XPS spectra were collected using a Kratos Axis Ultra photoelectron spectrometer with monochromatic Al K$_\alpha$ radiation, at an electron emission angle of 0° and a pass energy of 20 eV. Fig. 4.2d shows the C$_{1s}$ region exhibiting a SiC peak at 283.4 eV, graphene peak at 284.5 eV and a small adventitious carbon peak at 285 eV. The binding energy scale was referenced to the Si$_{2p}$ line of SiC at 101.4 eV. An estimate of the thickness of the graphene layer was made using a two-layer model assuming a thin continuous sheet of graphene on a semi-infinite thick SiC substrate with the equation of Biedermann [11]. Inelastic mean-free paths for graphene (3.08 nm) and for SiC (2.6 nm) were calculated using the method of Tanuma, Powell and Penn (TPP-2M) [12] at the kinetic energy of the C$_{1s}$ photoelectron excited by Al K$_\alpha$ X-rays. The quantities of graphene and
SiC were determined by fitting the C$_{1s}$ region collected at an electron emission angle of 0° using a Shirley background [13], a Gaussian-Lorentzian line-shape for SiC, and a Doniach-Sunjic [14] line-shape for graphene based upon fitting the C$_{1s}$ of highly-ordered pyrolytic graphite. The small peak due to adventitious carbon contamination was neglected in the thickness calculation. The estimate for a 0.2 mm diameter area of the surface using the methods described above yielded a value of 1.5 nm for the average graphene thickness. Finally, Raman spectrum (488 nm excitation), as shown in Fig. 4.2e, adjusted by SiC background subtraction [15], showed D, G and 2D peaks at 1365 cm$^{-1}$, 1589 cm$^{-1}$ and 2716 cm$^{-1}$, respectively. These peak positions, incorporated with the broad shape of 2D peak, correspond to those of epitaxial multilayer graphene, which are typically blue-shifted compared to those of exfoliated graphene.

4.3.2 Physical Characterizations of Transferred Graphene on SiO$_2$/Si Substrate

We examined the transferred graphene layers by optical microscopy, Raman spectroscopy and atomic force microscopy (AFM). Fig. 4.3a shows a low magnification optical image of a transferred layer of graphene on a SiO$_2$ (300 nm)/Si substrate. Here, well known contrast mechanisms enable direct visualization of the graphene [16], to reveal large areas (i.e. square millimeters) of transferred material, with good uniformity. These areas exceed significantly those of previous reports, either of transferred material from a bulk piece of HOPG [1-3] or from SiC [17]. Raman spectroscopy (488 nm excitation) revealed expected peaks at the D, G and 2D bands, 1355, 1586 and 2689 cm$^{-1}$, respectively (Fig. 4.3b). The positions of G and 2D peaks are red-shifted, compared with those observed on the SiC substrate immediately after growth, to values closer to those of exfoliated graphene. This result is consistent with relaxation of compressive strains that can exist in graphene on SiC. The shape of the 2D peak is symmetric, narrow and well described by a single Lorentzian curve, suggesting that the film is single layer graphene [15, 17]. The relatively large D peak, implies a substantial content of defects and disorder, associated at least in part with edges in the transferred material [18]. The AFM image in Fig. 4.3c indicates that the film contains holes with sizes, densities and shapes that vary with position. In many cases, the shapes and orientations correlate well with steps observed on the SiC substrate. Fig. 4.3d shows a section line scan from the AFM image (Fig. 4.3c). These data indicate that the film thickness is uniform, although
Figure 4.3: Properties of graphene transferred from SiC to SiO$_2$(300 nm)/Si. (a) Optical image of a piece of graphene covering square millimeters. (b) Raman spectrum showing the expected D, G and 2D peaks. Inset shows 2D peak data, and a fit to a single Lorentzian form. (c) AFM image of a representative region, corresponding to the red dotted square area of (a). This image reveals tears, holes, and wrinkles in the film, many of which are at least partly associated with the transfer process. (d) AFM section line scan across the film, indicating a uniform thickness of $\approx 1.4$ nm, for the region in proximity to the blue circled area.

The value exceeds that expected for single layer graphene, possibly due to residue from the transfer process. Because we did not observe a substantial density of holes in the graphene on SiC before transfer, we speculate that these and related imperfections are, at least partly, introduced in the transfer process. In addition to holes, the AFM scan of Fig. 4.3c shows wrinkles in certain regions, likely also generated during the transfer process but also known to be present in graphene grown on SiC [19].
4.3.3 Electrical Characterizations of Transferred Graphene Film on SiO₂/Si Substrate

The optical micrograph of fabricated devices is depicted in Fig. 4.4a. The source/drain electrodes are labeled as L1, L2, L3 and R1, R2, R3, R4, R5, which correspond to structures visible on the left and right sides of the image, respectively. The channel widths (W) and lengths (L) vary from 10 to 250 μm and from 10 to 200 μm, respectively, although in several cases the coverage of the graphene itself defines the effective width. Transfer curves and Iₔ-Vₕ characteristics were measured at room temperature using a semiconductor parameter analyzer (Agilent Technologies). Fig. 4.4b shows plots of the drain current (Iₔ) as a function of the applied gate voltage (Vₕ) for various devices. (We note that not all of these devices were electrically isolated from one another by patterned etching of the graphene, but many were
effectively isolated due to the geometry of coverage in the transferred material). These transfer curves indicate ambipolar modulation characteristics consistent with the expected semi-metallic character of graphene. The Dirac points occur at positive gate voltages, likely due to atmospheric doping [20]. Some mild level of hysteresis was typically observed, as shown in Fig. 4.4b. Qualitatively, we found that the magnitudes of $I_D$ generally scale in the expected manner with $W/L$, with discrepancies that can be accounted for by different densities of holes in the graphene.

To analyze these results quantitatively, neglecting fringing fields, possible anisotropies in the transport and effects of neighboring electrodes, we extracted the field effect mobility from a selected device that incorporated a region of graphene with a relatively low level of holes (3% of total area, i.e. device with electrodes R3 and R4). The $I_D$-$V_D$ characteristics and the dependence of $R$, the total resistance of the device (i.e. $V_D/I_D$ at $V_D = -0.04$ V) on $V_G$ appear in Fig. 4.4c and Fig. 4.4d, respectively. The Dirac point is $\approx 80$ V. The slope of the transfer curve near this point, $dI_D/dV_G$, is $\approx -5 \times 10^{-8}$ A/V, corresponding to a hole mobility of $\approx 100$ cm$^2$V$^{-1}$s$^{-1}$ calculated using a standard MOSFET model with a parallel plate gate dielectric capacitance of $1.15 \times 10^{-8}$ F/cm$^2$. This mobility is certainly influenced by the presence of holes and related defects, none of which is accounted for in this simple analysis. Other reports of transistors based on graphene derived from SiC involve top gate geometries, all built on the SiC wafer. The mobilities in those cases range from $\approx 500$ to $\approx 5000$ cm$^2$V$^{-1}$s$^{-1}$ with Dirac points near zero [21–23]. Additionally, the on/off ratios for each device can be directly derived from each transfer curve shown in Fig. 4.4b. In particular, the device with electrodes R3 and R4 has a value of $\approx 8$.

To examine the role of contacts in devices such as the one of Fig. 4.4, we performed a scaling analysis, shown in Fig. 4.5a. This analysis used all measured devices, with a simple procedure to account for the different densities of holes. In particular, we used a scaled resistance defined by

$$R = R_S \left( \frac{1}{\frac{\%gW}{L}} \right) + 2R_C$$

where $R$ is total resistance of device, $R_S$ is sheet resistance of the conducting layer, $R_C$ is the contact resistance and $\%g$, the percentage of graphene coverage, as determined from the SEM image analysis. The contact resistance, extracted from the y intercept of the plot in Fig. 4.5a, is below 1 kΩ indicating a negligible role of contacts in the device operation for the range of channel lengths examined here. The inverse of the slope defines the sheet conductance ($1/R_S$) at different gate voltages.
Figure 4.5: Scaling analysis of the behavior of graphene field effect transistors. (a) Plot of device resistance as a function of scaled channel geometry. The small y-intercept is consistent with a contact resistance that is small (< 1 kΩ) and, to within uncertainties, independent of $V_G$. (b) Plot of sheet conductance, evaluated from the slopes of linear fits to the data of (a), as a function of $V_G$. Linear fits determine the Dirac voltage (x intercept) and the apparent mobility (slope).

Fig. 4.5b shows the scaling of this quantity with the L, revealing a hole mobility of $\approx 90 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, roughly consistent with the device of Fig. 4.4. Although the large positive value of the Dirac point prevents accurate determination of the electron mobility, its magnitude appears comparable to that for holes.

4.4 Summary

In conclusion, graphene films epitaxially grown on SiC substrate were transferred to oxidized Si wafers for the fabrication of bottom gate field effect transistors. AFM, Raman, LEED and electrical measurements revealed the essential features of the materials. Key attractive aspects of these procedures are the scalability to large areas and possibly area selective transfer, the apparent ability to remove single layers of graphene from multilayer deposits, and the applicability to wide ranging classes of substrates, due to room temperature operation. Directions for further study include reducing the level of defects in the films, achieving improved transport properties and developing procedures for SiC substrate re-use.
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4.5 References


CHAPTER 5

TOWARDS MULTIPLE TRANSFER OF GRAPHENE LAYERS GROWN ON SINGLE SILICON CARBIDE WAFER


Layer-by-Layer Transfer of Multiple, Large Area Sheets of Graphene Grown in a Multilayer Deposit on a Single SiC Wafer

Here we report a technique for transferring graphene layers, one by one, from a multilayer deposit formed by epitaxial growth on the Si-terminated face of a 6H-SiC substrate. The procedure uses a bilayer film of palladium/polyimide deposited onto the SiC substrate and then mechanically peeled away and placed on a target substrate. Orthogonal etching of the palladium and polyimide leaves atomically pristine sheets of graphene with sizes of square centimeters. Repeating these steps transfers additional layers from the same SiC substrate. Raman spectroscopy, low energy electron diffraction, X-ray photoelectron spectroscopy, scanning tunneling, atomic force, optical and scanning electron microscopy reveal key properties of the materials. The sheet resistances determined from measurements of four probe device structures were found to be $\approx 2$ kΩ/square, close to expectation. Graphene crossbar structures fabricated in stacked configurations demonstrates the versatility of the procedures.

5.1 Introduction

Graphene currently lies at the center of one of the most active fields of research in science and engineering, due to its exotic physics, to interesting challenges in its growth and, most importantly, to its promise for use in electronic systems of the future [1–3]. The most widely explored form of graphene is obtained in small pieces, in a poorly controlled process of mechanical or chemical exfoliation from bulk pieces of graphite. Promising approaches to large area graphene include epitaxial growth on
silicon carbide substrates (SiC) [4, 5], and chemical vapor deposition (CVD) on metal surfaces [6, 7]. Most envisioned applications require a process for transferring the graphene from these growth substrates to target substrates for device integration. In the case of CVD, etching of the metal releases the graphene and prepares it for transfer, using stamps or related processes [6–8]. Two recent reports describe methods for transfer of graphene from SiC [9, 10]; both use on mechanical peeling rather than etching. In the first, thin films of Au deposited onto graphene grown on the Si-face of a SiC wafer provide the adhesion necessary for transfer. A thin, polymeric backing layer serves as a mechanical support for the peeling process, in an overall scheme conceptually similar those designed for the transfer of random networks and aligned arrays of single walled carbon nanotubes [11]. Removal of the polymer and the Au using orthogonal etching methods after transfer completes the process. This scheme separates the adhesive layer (i.e. Au) from the structural component (i.e. polymer), to allow separate optimization of each. Careful analysis of data, including Raman spectroscopy, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), suggests the possibility for selective transfer of only the uppermost graphene layer on the SiC [9]. Total areas are limited, however, by the moderate adhesion of Au to graphene. In another report, thermal adhesive tape is shown to enable large area transfers, but in a mode that removes almost all of the graphene layers (typically several) from the surface of the SiC [10].

In the following, we demonstrate a process for transfer of single layers of graphene from multilayer deposits on SiC, over large areas with high yields. Interestingly, this process can be repeated to enable a layer-by-layer transfer of multiple, large area sheets of graphene from a single SiC substrate. Subsequently, we describe the process in detail, and present various measurements on the films before and after transfer from SiC, ranging from low energy electron diffraction (LEED), to X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and scanning tunneling microscopy (STM). Four point probing of the transferred layers reveals sheet resistances comparable to those of single layer graphene CVD grown on Cu surface [8]. In a final example, we show a complex graphene structure fabricated by our transfer technique.
Figure 5.1: Schematic illustration of procedures for layer-by-layer transfer of graphene layers grown on a SiC wafer to other substrates. (a) Multilayer graphene grown on the Si face of 6H-SiC. (b) Bilayer of Pd and PI deposited on the SiC as an adhesive layer and mechanical support, respectively, for peeling and gently transferring graphene to a target substrate. Only the top graphene layer is removed and transferred. (c) The same SiC substrate coated again with Pd/PI, followed by transfer to produce another graphene film. (d) Same process repeated a third time.

5.2 Experimental Procedures

5.2.1 Improved Strategy for Layer-by-Layer Transfer of Graphene Layers from SiC Substrates

Figure 5.1 illustrates the method for multiple transfers of single-layer graphene from epitaxial material on a SiC(0001) wafer. The first step involves growth on SiC at
1,550°C (Fig. 5.1a), using conditions described in a following section. Depositing a thin layer of Pd (100 nm; electron beam evaporation; Temescal BJD1800) and then coating with polyimide (PI; \(\approx 1.4 \mu m\); Poly(pyromellitic dianhydride-co-4,4′-oxydianiline), amic acid solution; spun at 3000 rpm for 30s, partially cured at 110°C for 2 minutes) prepares the substrate for transfer, in which the Pd/PI/graphene film is peeled away manually (Fig. 5.1b) and then gently placed onto an SiO\(_2\)/Si substrate (300 nm SiO\(_2\), Process Specialties, Inc.). Removing the PI film by reactive ion etching (March RIE; 20 sccm O\(_2\), 150 mTorr, 150 W, 30 mins) followed by the Pd film by wet etching using a commercially available HCl/FeCl\(_3\)-based Pd etchant (Pd Etchant TFP, Transene, Inc.) leaves only the transferred graphene. Repeating this sequence of steps (except for the graphene growth) with the same SiC substrates allows additional layers of graphene to be transferred (Fig. 5.1c,d.)

5.2.2 Epitaxial Growth of Graphene on SiC Substrates

The growth used rectangular (5 mm \(\times\) 25 mm) pieces of SiC(0001) wafer (II-VI, Inc.) coated with layers of Ta (200 nm; electron beam evaporation; Temescal BJD1800) on their back sides (C-face) to serve as heating elements. Each substrate was loaded into a UHV chamber \((2 \times 10^{-9} \text{Torr})\) and heated, via current passed through the Ta, and degassed overnight at 600°C, monitored by an infrared thermometer (CHINO IR-CAQ; \(\epsilon = 0.90\)). Increasing the temperature to 1,400°C under a flux of Si (Si\(_2\)H\(_6\); \(2 \times 10^{-6} \text{Torr}\)) served to improved the surface morphology for the growth step [12]. Finally, annealing under atomic hydrogen \((4.2 \times 10^{-6} \text{Torr})\) at 1,550°C for 2 hours formed graphene films.

5.2.3 Sample Preparation for STM Measurement

To prepare suitable samples, a layer of graphene was transferred onto a Si substrate with 300 nm thermal oxide, and then cut to a size of 2 mm \(\times\) 8 mm. Electrodes of Au (60 nm) evaporated onto both ends provided electrical connections. The sample was then installed into a UHV-STM system for STM measurement.

5.2.4 Device Fabrication for Sheet Resistance Measurement

Four-point probing devices were fabricated on graphene transferred to a 300 nm thick, thermally grown layer of SiO\(_2\) on a Si substrate. The electrodes were de-
fined by photolithography followed by Cr/Au deposition (5 nm/50 nm) using an electron beam evaporator and lift-off in acetone. Then, oxygen plasma (Plasma Cleaner PDC-32G, Harrick Plasma, Inc.; 200 mTorr, medium RF level, 3 min) etched graphene film outside the device channel, protected with a layer of photore sist, in order to electrically isolate each device. Finally, the photoresist film was removed by using n-methyl-2-pyrrolidone based solvent stripper (Remover PG, MicroChem Corp.) The sample was rinsed with isopropyl alcohol and dried with N2 gas flow.

5.3 Results and Discussions

5.3.1 Characterizations of Epitaxial Graphene on SiC Substrate

The LEED pattern in Fig. 5.2a, corresponding to the Si(3×3) of SiC(0001), and an ex situ AFM image (Asylum Research MFP-3D) in Fig. 5.2b show the state of the substrate before growth but after heating overnight. After the growth process was completed, thick, multilayer graphene deposits were formed, as evidenced in situ by the expected change in the LEED pattern from that of Si(3×3), corresponding to the SiC(0001) substrate, to C(1×1), corresponding to graphene (Fig. 5.2c) [13, 14]. Figure 5.2d shows an AFM image of a representative 4 µm×4 µm area. The wrinkles, formed during relaxation of compressive strains during cooling, are consistent with previous reports. XPS and Raman spectroscopy data in Fig. 5.2e and 5.2f, respectively, provide additional data. The three peaks in the C1s XPS spectrum (Kratos Axis Ultra photoelectron spectrometer) at 283.7 eV (red curve), 284.5 eV (green curve) and 285.2 eV (blue curve) can be assigned to SiC, graphene and an interface layer respectively [13, 15]. Thickness calculations that use relative intensities of the SiC and graphene peaks and calculated inelastic mean-free paths of both SiC and graphene at the kinetic energy of the C1s photoelectron yield a thickness of ≈2.50 nm. Details on data fitting and calculation are described at previous chapter. The background-subtracted Raman spectrum (JY Horiba LabRam HR800) collected with 532 nm excitation through a 100× air objective (laser spot diameter ≈1 µm) shows the expected G and 2D peaks at 1591.1 cm−1 and 2735.3 cm−1, respectively (Fig. 5.2f) [16]. These positions are blue-shifted compared to those of graphene layers derived from HOPG, consistent with compressive strains mentioned above [16]. The width of the 2D peak (FWHM) is 72.6 cm−1, typical for epitaxial graphene whose thickness is larger than bilayer [17]. The absence of the D peak, which is expected to lie between 1300-1400 cm−1, suggests that the deposits
Figure 5.2: Characterization of a SiC(0001) substrate and epitaxially grown graphene. (a) LEED pattern recorded *in situ* with $E_p = 174.3$ eV of SiC substrate after degassing overnight at 600°C. The data reveal the expected $(3 \times 3)$ SiC(1000) pattern. (b) A typical 4 $\mu$m $\times$ 4 $\mu$m tapping-mode AFM image of the SiC substrate. (c) LEED pattern with $E_p = 174.7$ eV, collected after growth, showing a $(1 \times 1)$ pattern from graphene. (d) AFM image of graphene on SiC, showing extended terraces with some graphene wrinkles. (e) XPS spectrum of the C$_{1s}$ region of the as-grown sample exhibiting a SiC peak at 283.7 eV, graphene peak at 284.5 eV and an interface layer peak at 285.2 eV. (f) Background subtracted Raman spectrum showing G and 2D peaks, suggesting multilayer graphene. D peak was not observed in this sample.

have a low density of defects.
Figure 5.3: Properties of graphene transferred from SiC to SiO$_2$(300 nm)/Si. (a) Digital camera image showing two transferred graphene films derived from a single SiC growth substrate. The films are uniform over square centimeter areas. (b) Optical image of a graphene sheet in (a) collected near the edge of the film. (c) AFM image of a representative region indicating a uniform thickness of $\approx 0.5$ nm. Some wrinkles and a tear were observed. (d) Raman spectrum showing the expected D, G and 2D peaks. The 2D peak is well-fitted to a single Lorentzian form. (e) C$_1$s core-level XPS spectra of a SiC substrate collected immediately after growth of graphene (black line), after 1$^{st}$ transfer step (red line), and after 2$^{nd}$ transfer step (green line). The peak associated with graphene weakens while one from SiC becomes stronger after each transfer step.

5.3.2 Physical Characterizations of Transferred Graphene Films on SiO$_2$/Si Substrates

We successfully transferred up to 6 layers with area yields of almost 100% for the 2-3 layers and 30% for the 3-4 layers. In the following, we focus on a representative
case of two transfers.

The transfer processes occurred immediately after measurements in previous section, for each cycle. Figure 5.3a provides a picture of two large (≈1 cm²) sheets of graphene derived from a single deposit on SiC, on substrates of SiO₂ /Si. The sizes are limited only by those of the SiC pieces and the sample mount in the growth chamber. The low magnification optical micrograph in Fig. 5.3b reveals good film uniformity, with a small fold near the edge on the lower right. Imaging by AFM near the edge indicates a thickness of ≈0.5 nm, as shown in Fig. 5.3c. Raman spectroscopy (Fig. 5.3d) reveals D, G and 2D peaks at 1347.9 cm⁻¹, 1597.0 cm⁻¹ (FWHM = 15 cm⁻¹) and 2690.0 cm⁻¹ (FWHM = 35.3 cm⁻¹), respectively. The appearance of the D peak implies a certain amount of defects, possibly introduced by the processing, although still much lower than previous results. The shape of the 2D band matches a single Lorentzian with narrow width (FWHM = 35.3 cm⁻¹); both features are consistent with single layer graphene [18] [19]. Red-shifting of this band relative to that on SiC can be attributed to relaxation of compressive strain upon release. The ratio of the G and 2D bands (I₂D/I_G) [7] and the blue-shifting of the G band relative to material on SiC (Fig. 5.3d) are likely influenced by residual doping associated with residues from Pd and/or its etching solution, consistent with observations in other contexts [20] [21]. C₁s XPS spectra (Fig. 5.3e) collected from the SiC substrate before the first transfer (black), after the first transfer (red) and after the second transfer (green), provide additional evidence for single layer nature of the transferred material. The carbon signals from graphene and SiC decrease and increase, respectively, in a sequential manner. The calculated thicknesses show a decrease in the graphene thickness on SiC from 2.1 nm to 1.53 nm and 0.68 nm corresponding to the spectra before transfer, after 1st transfer and 2nd transfer, respectively. The consistent change in thickness for each transfer suggests a layer-by-layer mode. Although the exact thickness does not match exactly the expectation for single layer graphene, the discrepancy can be attributed to the selection of parameters for the fitting (i.e. the inelastic mean-free path for graphene and SiC). Such outcomes are insensitive to the conditions for peeling, over the range examined, including various speeds and directions, using tweezers as well as stamps of poly(dimethylsiloxane), both along the length of the substrate and perpendicular to the terrace steps.
Figure 5.4: (a) Spatial derivative STM image of the transferred graphene film on SiO\(_2\)/Si. \(V_{\text{tip-sample}} = -0.12\) V and \(I_{\text{tunnel}} = 100\) pA. (b)-(d) The magnified areas of STM image (a). The trigonal structure was observed in (c) while honeycomb lattice were observed in (b) and (d). (e) The plot of density of states derived from (dI/dV)/(I/V) versus voltage (V) from STS of a graphene film derived from HOPG on Si and a transferred graphene film on SiO\(_2\)/Si.

5.3.3 Electrical characterizations of Transferred Graphene Films on SiO\(_2\)/Si Substrates

To gain unambiguous insights into the nature of the transferred layers, we performed atomic resolution STM, and scanning tunneling spectroscopy (STS). Measurements using a UHV-STM system appear in Fig. 5.4a-d. The results indicate both honey-
comb and trigonal lattices, the former of which is expected for single layer graphene \[22\]. The trigonal symmetry observed in the region is likely not due to the presence of multiple layers, since the surrounding area shows hexagonal symmetry and there are no steps in the surface. Rather, the symmetry is likely due to the curvature and local doping of the graphene in that region. Data from STS yields information on the local density of states, through the quantity \((dI/dV)/(I/V)\), as shown in Fig. 5.4e. The blue curve corresponds to an average of \(\approx 700\) spectra recorded on different areas of the surface. The red curve represents similar data collected from a sample of graphene exfoliated from HOPG and deposited on the Si(100) - 2x1:H surface. Clearly, the graphene synthesized on SiC and transferred to SiO\(_2\) has a higher density of states at low energies. This may result from the expected stronger interaction between graphene and SiO\(_2\), as compared to a fully H-passivated silicon surface. The green curve shows spectra recorded over contamination observed with the STM. The density of states clearly shows that this contamination is metallic and that it might be due to residual Pd. The curve minimum of transferred graphene film, slightly at positive bias, implies that the film was p doped.

To provide preliminary electrical evaluation and to demonstrate the ability to build devices with transferred material, we fabricated arrays of test structures for two and
four point measurements of sheet resistance. Figure 5.5a-c show arrays of devices and a magnified view of a representative case. Electrodes 1 and 2 provide a constant current of 0.1 A; electrodes 3 and 4 probe resistive drops in voltage in a region between electrodes 1 and 2. The results from five different devices on the same film indicate an average sheet resistance of $\approx 2.2 \, \text{k}\Omega/\text{square}$ with a variation, from maximum to minimum value, of 0.9 kΩ/square. These resistances are comparable to those of single layer graphene grown on Cu [8] and are much lower than those from chemically derived graphene film from graphene oxide (GO) [23]. More complete studies of the electronic properties represent topics of current work.

![Figure 5.5: (a) A graphene crossbar structure fabricated by transferring patterned graphene twice with perpendicular alignment. (b) Low magnification SEM image of graphene crossbar structure. (c) Height mode and (d) Phase mode AFM images of the same structure.](image)

5.3.4 Graphene Crossbar Structure

To demonstrate additional capabilities of the processes, we built crossbar structures (Fig. 5.6a) by double transfer of pre-patterned graphene films. Here, we first transferred graphene films from one SiC wafer to two different SiO\(_2\)/Si substrates. The
films were then separately patterned into 100 mm ribbons by photolithography and etching with an O\textsubscript{2} plasma. Finally, the resulting graphene ribbons were transferred from one of the SiO\textsubscript{2}/Si substrates to the other in a manner that aligned the ribbons in an orthogonal fashion. The SEM image (Hitachi S-4800 FE-SEM) in Fig. 5.6 reveals only a few tears associated with this double transfer procedure. Figure 5.6c and 5.6d present height and phase mode AFM images from the same 20 \( \mu \text{m} \times 20 \mu \text{m} \) AFM scan. The thickness of the vertical ribbon was \( \approx 0.5-0.6 \) nm.

5.4 Summary

In conclusion, the transfer techniques reported here offer an ability to produce multiple large area, single-layer graphene films from multilayer deposits on a SiC substrate. These outcomes might be useful for the creation of single-layer graphene from SiC and for its heterogeneous integration, for example, into a silicon-based electronics platform. Multilayer configurations, possibility for use in flexible electronics and other unconventional areas could also be valuable. Exploring these possibilities, and further characterization of the electrical and mechanical properties of the materials are topics of current work.

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5.5 References


SYNTHESIS OF MONOMERS FOR MAKING LINKED MONOLAYERS

General

All reagents were purchased and used as received without further purification unless otherwise noted. THF was dried by distilling from a sodium benzophenone ketyl. Triethylamine was dried by distilling from CaH₂. Toluene, methanol, and dichloromethane were dried by passing through a column of activated alumina prior to use. Ethanol was dried by distilling from magnesium ethoxide.

Synthesis of Monomers

2-(2,5-dibromobenzyloxy)-tetrahydro-2H-pyran

\[
\begin{align*}
\text{Br} & \quad \text{OH} \\
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

To a 250 mL flame dried round bottom flask equipped with a stir bar was placed 2.13 g of 2,5-dibromobenzyl alcohol (8.00 mmol, 1.00 equiv.) and 0.041 g of TsOH-H₂O (0.24 mmol, 0.03 equiv) in 40 mL of dichloromethane. To the suspension was added 2.0 mL of dihydropyran (24.0 mmol, 3.0 equiv.) via syringe. The reaction mixture was allowed to stir under a N₂ atmosphere at room temperature for 12 h. The reaction mixture was transferred to a separatory funnel, diluted with 50 mL of dichloromethane and washed twice with 20 mL of water and once with 20 mL of brine. The organic layer was dried over MgSO₄, filtered, and the solvent was removed in vacuo. The crude material was purified by column chromatography eluting with 10% dichloromethane/hexanes to 20% dichloromethane/hexanes to yield 2.26 g of a clear oil (90% yield).

2-(2,5-dibromobenzyloxy)-tetrahydro-2H-pyran, Rᵢ = 0.55, 1:4 EtOAc/Hexanes;
IR: 3054, 2987, 2948, 1266, 734; $^1$H-NMR (500 MHz CDCl$_3$): $\delta$ 1.53-1.69 (m, 3H), 1.70-1.84 (m, 2H), 1.85-1.96 (m, 1H), 3.55-3.61 (m, 1H), 3.87-3.93 (m, 1H), 4.51 (d, $J = 13.7$, 1H), 4.77 (d, $J = 13.7$, 1H), 4.78 (d, $J = 3.3$, 1H), 7.27 (dd, $J = 8.5$, $J = 2.5$, 1H), 7.39 (d, $J = 8.5$, 1H), 7.66 (d, 2.5, 1H); $^{13}$C-NMR (75 MHz CDCl$_3$): $\delta$ 19.2, 25.3, 30.4, 62.1, 67.8, 98.4, 120.7, 121.4, 131.4, 131.5, 133.6, 140.0; HRMS (E.I.) m/z (M)$^+$ calculated for C$_{12}$H$_{14}$Br$_2$O$_2$: 347.9361. Found: 347.9363.

2-(2,5-diethynylbenzyloxy)-tetrahydro-2H-pyran

![Chemical structure](image)

To a 50 mL sealed flask equipped with a stir bar under an argon atmosphere was dissolved 0.71 g of 2-(2,5-dibromobenzyloxy)-tetrahydro-2H-pyran (2.00 mmol, 1.00 equiv.), 0.60 g of trimethylsilyl acetylene (6.00 mmol, 3.00 equiv), 0.057 g Pd(PPh$_3$)$_2$Cl$_2$ (0.081 mmol, 0.040 equiv.), 0.080 g PPh$_3$ (0.031 mmol, 0.15 equiv.), and 0.039 g CuI (0.20 mmol, 0.10 equiv.) in 12 mL of triethylamine and 8 mL of THF. The flask was sealed and heated to 80$^\circ$C for 12 h. The mixture was allowed to cool to room temperature, filtered, and the solvent was removed in vacuo. The crude material was purified through a plug of silica eluting with 1:1 DCM/Hexanes and the crude product was taken on to the next step without further purification. The bis(TMS acetylene) was dissolved in 12 mL of a 1:1 mixture of MeOH and DCM in a 50 mL round bottom flask equipped with a stir bar. To the mixture was added 0.66 g of K$_2$CO$_3$ (4.80 mmol, 2.40 equiv). After stirring for 12 h under a nitrogen atmosphere at ambient temperature, the mixture was transferred to a separatory funnel and diluted with 30 mL of a saturated solution of NH$_4$Cl. The aqueous layer was extracted three times with 10 mL of ethyl acetate. The organic extracts were combined and washed once with 10 mL of brine. The organic layer was dried over MgSO$_4$, filtered, and the solvent was removed in vacuo. The crude material was purified by column chromatography eluting with 10% DCM/hexanes to 40% DCM/hexanes to yield 0.42 g of a light orange oil (87% yield over 2 steps). 2-(2,5-diethynylbenzyloxy)-tetrahydro-2H-pyran, $R_f = 0.25$, 3:7 DCM/Hexanes; IR:
$^{3289}, 2944, 2871, 1201, 1129, 1034$; $^1$H-NMR (400 MHz CDCl$_3$): $\delta$ 1.51-1.67 (bm, 3H), 1.68-1.83 (bm, 2H), 1.84-1.96 (bm, 1H), 3.17 (s, 1H), 3.38 (s, 1H), 3.53-3.61 (m, 1H), 3.88-3.96 (m, 1H), 4.66 (d, J = 13.8, 1H), 4.78 (t, J = 3.4, 1H), 4.90 (d, J = 13.8 1H), 7.66 (dd, J = 8.0, J = 1.5, 1H), 7.43 (d, J = 8.0, 1H), 7.65 (d, J = 1.5, 1H); $^{13}$C-NMR (75 MHz CDCl$_3$): $\delta$ 19.5, 25.7, 30.7, 62.3, 66.9, 79.1, 80.9, 83.5, 83.8, 98.7, 121.0, 122.9, 130.9, 131.0, 132.7, 141.5; HRMS (E.I.) m/z (M)$^+$ calculated for $C_{16}H_{16}O_2$: 240.1150. Found: 240.1154.

**(2,5-diethynylphenyl)methanol**

$\equiv$ $\equiv$ $\equiv$

\[ \text{THPO} \rightarrow \text{HO} \]

To a solution of 0.10 g of 2-(2,5-diethynylbenzyloxy)-tetrahydro-2H-pyran dissolved in 2.5 mL of MeOH in a 10 mL round bottom flask was added 0.016 g of TsOH-H$_2$O (0.084 mmol, 0.20 equiv.). The flask was sealed under a nitrogen atmosphere and allowed to stir for 12 h at ambient temperature. The reaction mixture was transferred to a separatory funnel and diluted with 15 mL of H$_2$O and extracted three times with 5 mL of DCM. The organic extracts were combined, washed one time with 10 mL brine, dried over MgSO$_4$, filtered, and the solvent was removed in vacuo. The crude material was purified by column chromatography eluting with 50% DCM/Hexanes to DCM to yield 46 mg of a tan solid (71% yield). (2,5-diethynylphenyl)methanol, $R_f = 0.18$, 2:5 DCM/Hexanes; mp: 70.5 – 71.5°C ; IR: 3275, 2925, 2867, 1048, 1026, 890, 828, 690, 623; $^1$H-NMR (500 MHz CDCl$_3$): $\delta$ 1.16 (t, J = 6.1, 1H), 3.17 (s, 1H), 3.42 (s, 1H), 4.81 (d, J = 6.1, 2H), 7.37 (dd, J = 8.0, J = 1.5, 1H), 7.44 (d, J = 8.0, 1H), 7.59 (dd, J = 1.5, 1H); $^{13}$C-NMR (75 MHz CDCl$_3$): $\delta$ 63.3, 79.1, 80.6, 83.0, 83.7, 120.5, 122.9, 130.7, 130.9, 132.7, 143.3; HRMS (E.I.) m/z (M)$^+$ calculated for $C_{11}H_8O$: 156.0575. Found: 156.0573.

**2,5-diethynylbenzyl 3-(triethoxysilyl)propylcarbamate**

To an oven dried 10 mL Schlenk flask equipped with a stir bar, was dissolved 0.080 g of (2,5-diethynylphenyl)methanol (0.51 mmol, 1.0 equiv) in 3 mL of THF under a N$_2$
atmosphere. To this solution was added 0.16 mL of triethoxy(3-isocyanatopropyl)silane (0.67 mmol, 1.3 equiv.) and 3.0 µL of dibutyltin dilaurate (0.005 mmol, 0.01 equiv.) via syringe. The flask was sealed and heated to 60°C. After 18 h, the reaction mixture was cooled to ambient temperature and the solvent was removed in vacuo. The crude material was purified by column chromatography eluting with 7-20% EtOAc/hexanes to yield 0.17 g of a light orange liquid (81% yield).

2,5-diethynylbenzyl 3-(triethoxysilyl)propylcarbamate, R$_f$ = 0.19, 1:4 EtOAc/Hexanes; IR: 3295, 2975, 2927, 2886, 1717, 1700, 1540, 1246, 1077, 957; $^1$H-NMR (500 MHz CDCl$_3$): $\delta$ 0.59-0.66 (m, 2H), 1.2 (t, J = 7.0, 9H), 1.57-1.68 (m, 2H), 3.16 (s, 1H), 3.17-3.24 (m, 2H), 3.41 (s, 1H), 3.81 (q, J = 7.0, 6H), 5.12 (bs, 1H), 5.23 (s, 2H), 7.36 (dd, J = 8.0, J = 1.3, 1H), 7.43 (d, J = 8.0, 1H), 7.52 (d, J = 1.3, 1H); $^{13}$C-NMR (75 MHz CDCl$_3$): $\delta$ 7.6, 18.2, 23.2, 43.5, 58.4, 63.9, 79.1, 80.2, 82.9, 83.9, 121.3, 122.7, 131.2, 132.6, 156.1; HRMS (E.I.) m/z (M)$^+$ calculated for C$_{21}$H$_{29}$NO$_5$Si: 403.1815. Found: 408.1813.

2-(2,5-di(prop-1-ynyl)benzyloxy)-tetrahydro-2H-pyran

In a glove box, 0.11 g of prop-1-ynyllithium (2.40 mmol, 3.00 equiv.) and 0.50 g of zinc bromide (2.20 mmol, 2.80 equiv.) were dissolved in 3 mL of THF. This solution was then added to a solution of 0.28 g of 2-(2,5-dibromobenzyloxy)-tetrahydro-2H-pyran dissolved in 1.5 mL of THF in a Schlenk tube. To the mixture was added 0.091 g of Pd(PPh$_3$)$_4$ (0.079 mmol, 0.10 equiv.). The flask was sealed and heated to
60°C for 12 h. The reaction was allowed to cool to ambient temperature, transferred to a separatory funnel, and 25 mL of a saturated solution of NH₄Cl was added. The aqueous layer was extracted 3 times with 10 mL of diethyl ether. The combined organic layers were washed with 10 mL of brine, dried over MgSO₄, filtered, and the solvent was removed in vacuo. The crude product was purified by column chromatography, eluting with 5% diethyl ether/hexanes to yield 0.18 g of a white solid (86% yield).

2-(2,5-di(prop-1-ynyl)benzyl oxy)-tetrahydro-2H-pyran, R_f = 0.4, 1:4 EtOAc/Hexanes; mp: 56 – 58°C IR: 2943, 2868, 1486, 1201, 1130, 1033; ^1H-NMR (500 MHz CDCl₃): δ 1.49-1.68 (m, 3H), 1.69-1.82 (m, 2H), 1.86-1.96 (m, 1H), 2.05 (s, 3H), 2.08 (s, 3H), 3.53-3.59 (m, 1H), 3.90-3.97 (m, 1H), 4.60 (d, J = 13.2, 1H), 4.76-4.79 (m, 1H), 4.85 (d, J = 13.2, 1H), 7.21 (dd, J = 8.5, J = 1.8, 1H), 7.28 (d, J = 8.5, 1H), 7.50 (d, J = 1.8, 1H); ^13C-NMR (75 MHz CDCl₃): δ 4.4, 4.6, 19.2, 25.4, 30.5, 61.8, 66.9, 77.1, 79.7, 87.1, 91.8, 98.2, 121.4, 123.2, 129.92, 129.93, 131.8, 140.2; HRMS (C.I.) m/z (M+H)⁺ calculated: 269.1542. Found: 269.1548.

2,5-di(prop-1-ynyl)benzyl 3-(triethoxysilyl)propylcarbamate

To a 25 mL flame dried round bottom flask was dissolved 0.14 g of 2-(2,5-di(prop-1-ynyl)benzyl oxy)-tetrahydro-2H-pyran (0.54 mmol, 1.00 equiv) in 2.5 mL of MeOH and 1 mL of dichloromethane. To this solution was added 0.020 mg of TsOH·H₂O (0.11 mmol, 0.20 equiv.) and the reaction mixture was allowed to stir for 12 h under a N₂ atmosphere at room temperature. The reaction mixture was transferred to a separatory funnel and diluted with 25 mL of a saturated solution of NaHCO₃. The aqueous layer was extracted three times with 10 mL of dichloromethane. The combined extracts were washed once with 10 mL of brine, dried over MgSO₄, filtered, and the solvent was removed in vacuo to yield a white solid. The solid was dissolved in 3 mL of dry THF and placed under a N₂ atmosphere. To this solution was added 0.17 mL of triethoxy(3-isocyanatopropyl)silane (0.70 mmol, 1.30 equiv.) and 3.2 µL
of dibutyltin dilaurate (0.0054 mmol, 0.010 equiv.) via syringe. A condenser was attached to the flask, and the reaction mixture was heated to reflux under a N₂ atmosphere. After 18 h, the reaction mixture was cooled to ambient temperature and the solvent was removed in vacuo. The crude material was purified by column chromatography eluting with 10% acetone/hexanes to yield 210 mg of a white solid (86% yield over two steps).

2,5-di(prop-1-ynyl)benzyl 3-(triethoxysilyl)propylcarbamate, Rₓ = 0.4, 3:7 EtOAc/-Hexanes; mp: 54 – 56 °C; IR: 3328, 2974, 2927, 2884, 1696, 1540, 1282, 1259, 1082; 

1H-NMR (500 MHz CD₂Cl₂): δ 0.57 (m, 2H), 1.20 (t, J = 7.1, 9H), 1.54-1.66 (m, 2H), 2.04 (s, 3H), 2.08 (s, 3H), 3.13-3.21 (m, 2H), 3.80 (q, J = 7.1 6H), 5.06-5.13 (bs, 1H), 5.16 (s, 2H), 7.22 (d, J = 8, 1H), 7.29 (d, J = 8, 1H), 7.37 (s, 1H); 

13C-NMR (75 MHz CD₂Cl₂): δ 4.4, 4.6, 7.9, 18.4, 23.7, 43.9, 50.6, 64.5, 76.9, 79.5, 87.8, 92.9, 122.3, 123.7 130.65, 130.74, 132.2, 139.0, 156.4; HRMS (C.I.) m/z (M)⁺ calculated: 432.2206. Found: 432.2205.

3,3-diethyl-1-(2,4,5-tribromophenyl)triaz-1-ene

![3,3-diethyl-1-(2,4,5-tribromophenyl)triaz-1-ene](image)

To a stirred solution of 0.93 g 2,4,5-tribromoaniline (2.80 mmol, 1.00 equiv.) dissolved in 6 mL of acetonitrile, 2 mL of THF, and 3 mL of water in a 100 mL round bottom flask, was added with 2.4 mL of concentrated HCl (28.3 mmol, 10.0 equiv.) to form a light orange slurry. The mixture was cooled to −10 °C and a solution of 0.41 g of NaNO₂ (5.90 mmol, 2.10 equiv.) dissolved in 2 mL water and 1 mL acetonitrile was added dropwise via syringe over 20 min maintaining a temperature below −5 °C. The mixture was stirred for an additional 15 min at −10 °C and then transferred via cannulation to a solution of 2.1 g diethylamine (28.3 mmol, 10.0 equiv.) and 19.6 g of K₂CO₃ (14.2 mmol, 10.0 equiv.) dissolved in 6 mL of acetonitrile and 12 mL of water maintaining a temperature below 0 °C. This mixture was allowed to warm to room temperature and stir for 4h. The mixture was transferred to a separatory funnel, diluted with 100 mL of diethylether and washed twice with
100 mL of brine. The organic layer was dried over MgSO$_4$, filtered, and the solvent was removed in vacuo. The crude material was purified by column chromatography eluting with 3% DCM/hexanes to yield 0.70 g of an orange solid (60% yield).

3,3-diethyl-1-(2,4,5-tribromophenyl)triaz-1-ene, $R_f = 0.42$, 1:4 DCM/Hexanes; mp: 46 – 50 °C; IR: 3079, 2973, 2930, 2867, 1440, 1401, 1328, 1109, 1042, 884; $^1$H-NMR (500 MHz CDCl$_3$): $\delta$ 1.2-1.5 (bd, 6H), 3.80 (bs, 4H), 7.66 (s, 1H), 7.80 (s, 1H); $^{13}$C-NMR (75 MHz CDCl$_3$): $\delta$ 10.6, 14.4, 42.3, 49.5, 118.7, 119.8, 122.4, 123.8, 136.4, 148.4; HRMS (E.I.) m/z (M)$^+$ calculated for C$_{10}$H$_{12}$Br$_3$N$_3$: 410.8581. Found: 410.8585.

3,3-diethyl-1-(2,4,5-tris((trimethylsilyl)ethynyl)phenyl)triaz-1-ene

To a 100 mL sealed flask equipped with a stir bar under an argon atmosphere was dissolved 1.7 g of 3,3-diethyl-1-(2,4,5-tribromophenyl)triaz-1-ene (4.0 mmol, 1.0 equiv.), 1.8 g of trimethylsilyl acetylene (18.0 mmol, 4.5 equiv.), 0.14 g Pd(PPh$_3$)$_2$Cl$_2$ (0.20 mmol, 0.050 equiv.), 0.21 g PPh$_3$ (0.80 mmol, 0.20 equiv.), and 76.0 mg CuI (0.4 mmol, 0.1 equiv.) in 40 mL of a 1:1 mixture of TEA/THF. The flask was sealed and heated to 70 °C for 12 h. The mixture was allowed to cool to room temperature, filtered, and the solvent was removed in vacuo. The crude material was purified by column chromatography eluting with 5% Et$_2$O/hexanes to yield 1.7 g of a light yellow solid (94% yield).

(3,3-diethyl-1-(2,4,5-tris((trimethylsilyl)ethynyl)phenyl)triaz-1-ene), $R_f = 0.68$, 1:5 EtOAc/Hexanes; mp: 104 – 108 °C; IR:2960, 2152, 1379, 1249, 841; $^1$H-NMR (400 MHz CDCl$_3$): $\delta$ 0.22 (s, 9H), 0.25 (s, 9H), 0.26 (s, 9H), 1.22-1.38 (bm, 6H), 3.72-3.86 (bs, 4H), 7.51 (s, 1H), 7.60 (s, 1H); $^{13}$C-NMR (75 MHz CDCl$_3$): $\delta$ -0.04, 0, 0.1, 11.0, 14.5, 42.0 49.4, 97.9, 99.1, 100.1, 102.1, 102.9, 103.4, 118.2, 120.2, 121.5, 125.9, 137.3, 151.8; HRMS (E.I.) m/z (M)$^+$ calculated for C$_{25}$H$_{39}$N$_3$Si$_3$: 465.2452. Found: 465.2447.
5-iodobenzene-1,2,4-triyl)tris(ethyne-2,1-diyl)tris(trimethylsilane)

A solution of 0.28 g of (3,3-diethyl-1-(2,4,5-tris((trimethylsilyl)ethynyl)phenyl)triaz-1-ene) (0.59 mmol) dissolved in 5.9 mL of iodomethane was placed in a sealed flask under a nitrogen atmosphere and heated to 125 °C for 14h. The mixture was allowed to cool to room temperature and a small amount of silica was added. The solvent was removed in vacuo and the crude material was purified by column chromatography eluting with 2% DCM/hexanes to yield 0.26 g of a yellow solid (88% yield). (5-iodobenzene-1,2,4-triyl)tris(ethyne-2,1-diyl)tris(trimethylsilane), R_f = 0.76, 1:4 EtOAc/Hexanes; mp = 85 – 88 °C; IR: 2957, 2897, 2159, 1462, 1248, 841, 761; ^1^H-NMR (400 MHz CDCl_3): δ 0.22 (s, 9H), 0.25 (s, 9H), 0.26 (s, 9H), 7.54 (s, 1H), 7.92 (s, 1H); ^13^C-NMR (75 MHz CDCl_3): δ -0.34, -0.14, 98.9, 100.4, 101.2, 101.3, 101.5, 101.7, 125.5, 126.5, 129.5, 135.6, 141.9; HRMS (E.I.) m/z (M)^+ calculated for C_{21}H_{29}ISi_3: 492.0622. Found: 492.0671.

(2,5-bis((2,4,5-tris((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl) methanol

To a 20 mL sealed flask equipped with a stir bar under an argon atmosphere was dissolved 0.11 g of 2-(2,5-diethynylbenzyloxy)-tetrahydro-2H-pyran (0.45 mmol, 1.00 equiv.), 0.49 g of (5-iodobenzene-1,2,4-triyl)tris(ethyne-2,1-diyl)tris(trimethylsilane) (1.00 mmol, 2.20 equiv), 0.016 g Pd(PPh_3)_2Cl_2 (0.023 mmol, 0.050 equiv.), 0.012 g
PPh₃ (0.045 mmol, 0.10 equiv.), and 8.6 mg CuI (0.05 mmol, 0.1 equiv.) in 3 mL of triethylamine and 2 mL of THF. The flask was sealed and stirred at room temperature for 8 h, then heated to 45 °C for 12 h. The mixture was allowed to cool to room temperature, filtered, and the solvent was removed in vacuo. The crude material was purified by column chromatography eluting with 10% EtOAc/hexanes then 7% acetone/hexanes to produce a light yellow solid that was not be purified further. To the crude solid was added 6 mL of MeOH and ca. 2 mL DCM followed by 17.0 mg TsOH-H₂O (0.09 mmol, 0.2 equiv.). The mixture was allowed to stir overnight at room temperature under a N₂ atmosphere. The reaction mixture was transferred to a separatory funnel, diluted with 30 mL of a saturated solution of NaHCO₃, and extracted three times with 15 mL of DCM. The organic extracts were combined and washed one time with 10 mL of brine, dried over MgSO₄, filtered, and the solvent was removed in vacuo. The crude product was purified by column chromatography eluting with 4% acetone/hexanes to 15% acetone/hexanes to yield 0.27 g of a light yellow solid (68% yield over two steps). All chromatography solvents contained ca 0.5% triethylamine.

(2,5-bis((2,4,5-tris((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)methanol, Rf = 0.36, 1:4 DCM/Hexanes; mp: dec. 135 °C; IR: 2959, 2899, 2157, 1250, 879, 842, 760;¹H-NMR (500 MHz CDCl₃): δ 0.26-0.32 (m, 54H), 4.89 (s, 2H), 7.44 (dd, J = 7.9, J = 1.7, 1H), 7.52 (d, J = 7.9, 1H), 7.59-7.66 (m, 5H); ¹³C-NMR (75 MHz CDCl₃): δ -0.1, 0, 63.6, 89.5, 92.7, 94.0, 95.4, 101.5, 101.6, 101.7, 101.75, 101.8, 101.9, 102.1, 102.15, 102.2, 102.25, 102.3, 102.5, 125.1, 125.4, 125.6, 125.7, 125.8, 125.9, 126.0, 130.5, 130.9, 132.8, 135.8, 135.9, 136.4, 136.9, 143.9; MS (E.I.) m/z (M)⁺ calculated for C₅₃H₆₄OSi₆: 884.3573. Found: 884.3577.

2,5-bis((2,4,5-triethynylphenyl)ethynyl)benzyl 3-(triethoxysilyl)propylcarbamate

![Chemical structure image]

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To a solution of 0.24 g of (2,5-bis((2,4,5-tris((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)methanol (0.27 mmol, 1.00 equiv.) dissolved in 3 mL of MeOH and 3 mL of THF was added 0.33 g K$_2$CO$_3$ (2.44 mmol, 9.00 equiv.). After stirring for 8 h at room temperature, the slurry was transferred to a separatory funnel, diluted with 25 mL of brine, and extracted three times with 15 mL of THF. The organic extracts were combined and washed with 10 mL of brine, dried over MgSO$_4$, filtered through a plug of silica, and the solvent was removed in vacuo. The crude solid was dissolved in 5 mL of THF in a 25 mL Schlenk flask under a nitrogen atmosphere. To the flask was added 0.087 mL triethoxy(3-isocyanatopropyl)silane (0.35 mmol, 1.30 equiv.) and 1.6 µL of dibutyltin dilaurate (0.002 mmol, 0.01 equiv.). The flask was sealed and heated to 55°C for 18 h. The solvent was removed in vacuo and the crude material was purified by column chromatography eluting with 40% DCM /hexanes then 40% DCM/10% acetone/hexanes all containing ca. 0.5% TEA to yield 116 mg of a light yellow solid (60% yield over two steps).

2,5-bis((2,4,5-triethynylphenyl)ethynyl)benzyl 3-(triethoxysilyl)propylcarbamate, R$_f$ = 0.65, 1:1 acetone/Hexanes; mp: dec. 125°C; IR: 3286, 2973, 2926, 2884, 1685, 1498, 1252, 1078; $^1$H-NMR (500 MHz CDCl$_3$): δ 0.55-0.71 (m, 2H), 1.21 (t, J = 6.9, 9H) 1.60-1.70 (m, 2H), 3.19-3.27 (m 2H), 3.42-3.46 (m, 4H), 3.50 (s, 1H), 3.72, (s, 1H), 3.81 (q, J = 6.9, 6H), 5.12-5.19 (bs, 1H), 5.39, (s, 2H), 7.47 (d, J = 8.1, 1H), 7.50 (d, J = 8.1, 1H), 7.63 (s, 1H), 7.65-7.70 (m, 4H); $^{13}$C-NMR (75 MHz CD$_2$Cl$_2$): δ 7.9, 18.5, 23.6, 43.9, 58.7, 64.7, 80.75, 80.80, 80.85, 80.9, 81.0, 83.69, 83.71, 83.75, 83.8, 84.0, 85.1, 89.0, 92.9, 93.7, 95.6, 121.9, 123.7, 125.13, 125.15, 125.2, 125.22, 125.5, 125.6, 126.4, 126.5, 130.9, 131.2, 132.9, 136.1, 136.2, 136.8, 136.9, 140.0, 156.4; MS (FAB) m/z (M)$^+$ calculated for C$_{45}$H$_{37}$NO$_5$Si: 699.2441. Found: 699.2442.
AUTHOR’S BIOGRAPHY

Sakulsuk Unarunotai was born in Bangkok, Thailand in 1981. He received his Bachelor of Science degree (with 1st class honor) in Chemistry from Chulalongkorn University in 2004. He received a full scholarship from the Development and Promotion of Science and Technology Talents Project (DPST) during his undergraduate study. He pursued a Ph.D. degree in Materials Chemistry at the University of Illinois at Urbana-Champaign in 2004 under the supervision of Professor John A. Rogers. He was also a recipient of Anandamahidol Foundation Scholarship from 2004 to 2009. On completion of his degree, he decided to return to Thailand and become a faculty member at the Department of Chemistry, Chulalongkorn University.

Publications


