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THE USE OF ARRAYED NANO-DIMENSIONAL TEMPLATE STRUCTURES
FOR CONTROLLED GROWTH

A Thesis in
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by
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ABSTRACT

The objective of this research is to develop a fabrication procedure for producing nanowires and nanoribbons in arrays and circuits without the need for any post-synthesis pick-and-place processing. A general procedure for the fabrication of nano-dimensional channels and their use as templates for the formation of nanomaterial arrays is presented in this thesis. The approach developed uses nanodimensional channels as permanent templates for the formation of nanomaterial arrays with precise dimensional, positional, and orientational control as well as with built-in electrical access, when appropriate. The procedure is general, allowing the synthesis of different materials inside the nanochannels, and opens the door to “grow-in-place” manufacturing.

Two versions of nanochannels for the nanomaterial growth were fabricated, and different nanomaterials grown in the nanochannels were demonstrated. The first version of the template is a nanochannel without the built-in electrodes. The nanochannel template can be completely open and allows nanowire growth, alignment, precise positioning, and geometrical confinement. In the case of polymers this template approach allows different kinds of chain-growth polymerization, such as poly(methyl methacrylate) (PMMA) by radical polymerization, polythiophene (PT) by photopolymerization. It was also shown that polymer nanofilaments can even be released without breaking. The oxygen plasma etching and atomic force microscope tip cutting were used to verify the presence of polymer material. We also demonstrated the carbon nanofiber growth in this first version of the nanochannels using a catalyst metal in the middle in a chemical vapor deposition (CVD) system. Carbon nanofibers can grow inside and even grow out of the
nanochannels, and the dimension, location and orientation of carbon nanofibers followed
the pre-designed nanochannels which establish that the nanochannel is also an effective
growth template for carbon nanofibers.

Fully enclosed horizontal nanochannels, in a pre-arranged array with built-in
electrical contacts and chemical access regions, were used as the second version of
templates for electrochemical synthesis of conducting polymer nanoribbons. In this
“grow-in-place” approach, the nanochannel templates are part of the final array structure
and remain after fabrication of the nanoribbons. The built-in electrical contacts, which
provide the electrical potential for electrochemical polymerization, also remain and
become contacts/interconnects to the array components. The “grow-in-place” architecture
and methodology removes the need for template dissolution, any post-synthesis
nanoribbon “grow-and-then-place” manipulation, and any post-synthesis electrical
contacting. The fact that the templates are fully enclosed prohibits dendrite formation
during growth, ensures precise dimensionality, and provides the encapsulation needed in
any real device application. Polyaniline nanostructures electrochemically polymerized in
the nanochannels were found to be fibrils that grow from the central region of the
growth-template cross-section. Two-point and four-point electrical characterization of
these polyaniline nanoribbons, obtained using the built-in electrodes, was employed to
yield the true polyaniline conductivity and to assess the ohmicity of the contacting
approach. Conductivity studies show conductivity increases as the width decreases. We
also show that electrochemical polymerization is superior to the chemical polymerization
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To My Husband and My Late Grandfather
Chapter 1

Introduction

1.1 Background

Nanotechnology is an emerging field of the scientific and engineering research that has roots that have been developing for decades. It leads to unprecedented understanding and control over the fundamental building blocks of the physical world. Since Richard Feynman’s prescient lecture, “There is Plenty of Room at the Bottom,” 40 years ago about the opportunities harbored in small scale science and engineering, thousands of scientists have been devoting themselves to the knowledge and means to intervene on the nanoscale. In the language of science, the prefix “nano” means one-billionth of something like a second or a meter. A nanometer is one-billionth of a meter, and the world of things is built up from the tiny scale of nanometers. Nanoscience and nanotechnology generally refer to a world whose characteristic dimensions are from one nanometer to several hundred nanometers. Compared to the behavior of isolated molecules and of bulk materials, the behavior of structural features in the range of the nanoscale exhibits important changes. The most important changes in properties of nanomaterials are caused by newly observed phenomena intrinsic to or becoming predominant at the nanoscale, such as quantum confinement effects, predominance of surfaces and predominance of physical optics. Important material properties, including
electrical conductivity, optical properties, mechanical strength, and so on, are determined by the way molecules of various shapes and surface features organize into patterns on the nanoscale. By controlling how the nanoscale patterning unfolds, researchers can design new materials with new sets of properties. With these new materials as basic building blocks, researchers can build macroscopic structures with novel and significant physical, chemical, biological properties, phenomena, and processes. The aim of nanotechnology is to exploit these properties by gaining control of structures and devices at atomic, molecular, and supramolecular levels and to learn to efficiently manufacture and use these devices and integrate these “nanostructures” at the micron-length scale or macroscopic scale. Nanotechnology - in its various forms such as nanoelectronics, nanoelectromechanical systems, ultrasmall and highly sensitive sensors, multifunctional materials, biologically inspired materials, systems and architectures, and possibly many others that scientist has not yet thought of - is expected to play a strong and critical role in future. The intersection of nano, bio, and information technologies also provides rich possibilities for exploring useful concepts and breakthroughs.

1.2 Research motivation

Nanotechnology offers the promise of letting us fabricate an entire new generation of products that are cleaner, stronger, lighter, and more precise by using nanoscale fundamental building blocks. Novel fabrication techniques permit precise control of the structure, properties, size, and position of nanoscale elements allowing us to overcome the scaling constrains inherent in conventional photolithography. A
promising approach where nanotechnology can lead the way is in the fabrication of nanowires and their assembly into nanoelectronic devices by nanotechnology. Potential application for such processing and devices in electronics could involve nanowires of sizes ranging from few to hundreds of nanometers as the fundamental building blocks. Devices based on the nanowires, may find use in applications ranging from molecular electronics to chemical sensors.

To realize the full potential of nanoscience and nanotechnology, nanostructured materials must be manufacturable and applicable in useful devices by suitable manipulation.[1] Over the past few years, one-dimensional nanostructures of different materials, including nanotubes,[2-4] nanorods,[5-11] nanofibers,[12] and nanowires,[13-17] have attracted much attention, and considerable progress has already been made in their synthesis and their application in devices. However, a significant obstacle in the application of these nanostructures has been the difficulty in handling, maneuvering, and integrating them to form a complete system.[18-22] The challenge still has to be faced due to the lack of post-synthesis process suitable for the hierarchical organization of these nanoscale building-blocks into functional assemblies and, ultimately, useful systems. Additional processing and self-assembly techniques are needed to contact the nanowires and form interconnected structures which increase complexity. If nanowires could be easily aligned, arranged into patterns, and contacts and interconnects set-up, the impact would be tremendous in many areas, from nanoscale electronics and optoelectronics to molecular sensing. As one example, we note that discovering new ways of making and manipulating materials at nanometer scale should help to maintain the computer industry’s relentless drive towards ever greater miniaturization and performance. Current
lithographic techniques, including dip-pen lithography, allow precise positioning; however, the range of materials that can be synthesized is limited.[23-24] Among the most frequently used synthesis methods used to gain some control of creating nanostructures is the approach to forming nanoscale structures in templates which define the diameter and length of the nanowires. The syntheses of nanowires by templates have been demonstrated by many groups including Martin’s,[25-27] Bein’s,[28] and others.[29-32] Most of these efforts used commercially available track-etch polymeric membranes or alumina porous membranes as the growth templates. The produced nanowires synthesized in growing membrane template are generally separated and collected by dissolving the membrane in the solution by the so-called two-step synthesizing-and-then-positioning procedure. A variety of nanomaterials can be synthesized by these two-step synthesizing-and-then-positioning procedures, but the approach seriously limits the ability to control location, and orientation on the nanoscale.[26, 33-37] Once the membrane is removed and the nanowires liberated from the membrane, the nanowires are either floated free in a solution and then stacked into disorganized forms after the solution dries out, or they remain attached to a substrate forming a vertical array. In the vertical array alternative one has the difficulties of electrically contacting and using vertically positioned elements on a substrate. In the free floating alternative, one must employ some pick-and-place technique to capture the nanostructures and to position them at the point of use. Such manipulation can be very time-consuming and arduous.[18, 38-41] Examples include:

(a). Using an atomic force microscope to manipulate individual nanowires onto pre-patterned electrodes and then do the characterization.[42]
(b). Random dispersion and adsorption on substrate followed by microscopic search.\cite{43-49} In this situation the characterization of the nanomaterials was carried out by patterning contact electrodes onto the individual nanomaterials after the nanomaterials were randomly dispersed on an insulating substrate.

(c). Post-growth electrical field induced orientation,\cite{19, 50-52} where the nanomaterials are aligned to two electrode pads by the electrical field strength between the electrodes and the nanomaterial tips.

(d). Fluid flow induced orientation,\cite{20, 53-56} where the nanomaterials are aligned by passing suspensions of the nanomaterials through fluidic channel structures, then the electrodes were patterned by lithography and deposition after the microscopic search.

(e). Langmuir-Blodgett technique,\cite{57-59} which adopted a “logs-on-a-river” approach on a nanoscopic level to align nanomaterials into large-scale assembly on a water surface by Yang’s group.

(f). A nano-imprinting technique using semiconductor superlattices as templates for aligning nanowire arrays of high density by translating thin film growth thickness control into planar nanowire arrays.\cite{60}

(g). Lithographically patterning catalysts on electrodes as nanowire nucleation sites\cite{61-62} thereby producing growth at the final use (electrodes) sites. Characterization is then easily carried out by using the electrodes.

(h). Applying an electrical field for alignment during the growth,\cite{63} where the field helps the alignment as the nanomaterials grow.
(i). Using permanent but open-channel template structures which are created between electrical-contact metal pads by e-beam lithography and etching on an insulating layer.[64]

(j) A simultaneous lateral growth of a high density of highly oriented, metal-catalyzed silicon nanowires on a patterned silicon substrate and bridging of nanowires between two vertical silicon sidewalls.[65]

However, these approaches may not be suitable and economically feasible for assemblies of more complex geometry and integration, as is required for usable devices and circuits. Also the post-synthesis processing step usually required in devices, such as encapsulation or electrode deposition, open the door to possible property changes due to the processing itself. Device fabrication with controllability, reproducibility, and yield suitable for large-scale circuits built from nanomaterials remains a significant challenge. There is an urgent need for an engineered approach for better control of manufacturing and assembling of oriented nanomaterials in order to advance to the next stage of nanoscience and nanotechnology.

1.3 Research objectives

The realization of the full potential of nanotechnology for electronics, displays, and sensing demands the ability to accurately position, contact, and interconnect a wide variety of nanomaterials to construct complex structures and devices. The main goal of this research is to develop an innovative method to accomplish the synthesis of well-aligned nanowires, and at the same time, the precise control of the nanowire orientation,
dimension, position, assembly, and even contacting/interconnecting in a single integrated step. To accomplish this, we will utilize the geometric confinement effect of nanochannels to orient, precisely position, and assemble nanowires as they are synthesized.[66] We will also take the unique step of building contacts and interconnects into these templates so that the array is completed when nanowire fabrication is completed. There is no “two-step synthesizing-and-then-positioning procedure” in the approach of this thesis. For this research work, we will demonstrate our approach using individual devices and not construct actual circuits; hence, the built-in contacts in this study are used for characterization.

In summary, herein we propose and demonstrate a general procedure for the fabrication of nanodimensional channels and their use as templates for the formation of nanomaterial arrays with precise dimensional, positional, orientational control, and even contacting/interconnecting in a single integrated step. There is no destruction of the template in our approach; rather it becomes part of the finished array. Our approach offers a number of distinct advantages over alternative nanowire fabrication and array construction technologies. In this work two versions of nanochannels are proposed and fabricated as shown in Figure 1-1. In the first version as shown in Figure 1-1(a), the nanochannel template are fabricated without built-in electrodes. These structures can be open their whole length for general nanomaterial synthesis by chemical means or have a catalyst inside the channels for nanowire growth in a chemical vapor deposition (CVD) system. In the second version as shown in Figure 1-1(b), the nanochannels of the template use built-in electrodes to drive electrochemical synthesis. Contacts are built-in for all
cases where the nanowires are to have electrical use. These contacts allow for the completion of arrays with built-in contacts and interconnects. Of course, in this research work, these contacts also allow for interrogation of individual nanowire electrical properties. The overall procedure presented in this thesis is general, allowing the synthesis of different materials inside the nanochannels and allowing for “grow-in-place” nanoscale structures.[67-68] Our approach based on nanoscale control provides unique advantages and capabilities. As we demonstrate in this work, the nanomaterials fabricated can be organic, metallic, and semiconducting materials, and even combinations of these.

Figure 1-1: Nanochannel template (a) without and (b) with built-in electrodes.
The realization of the research outlined above requires completing the following tasks:

(1). Fabrication of the first version, nanochannel templates without built-in electrodes and their use in nanowire growth, alignment, precise positioning, and geometrical confinement inside the channels.

(2). Production of aligned, position-controlled and geometry-controlled organic nanowires grown in the first version of empty nanochannel templates using initiator-based polymerization or carbon nanofibers in the first version of nanochannel templates with catalyst inside.

(3). Fabrication of the second version of the open nanochannel template with built-in electrodes and channel access regions structure.

(4). Electrochemical synthesis of the conducting polymer nanoribbons by second version of nanochannels and characterization of the individual addressable nanoribbons using the same built-in electrodes.

Polymer nanowires and carbon nanotubes were mainly used to demonstrate the use of the first version of nanochannel permanent templates in this research. However, the nanochannel template with catalyst inside is not limited to synthesizing conducting carbon nanofibers. The use of nanochannel templates with catalysts can be expanded to other semiconducting materials such as silicon nanowires, germanium nanowires, Si-Ge alloy nanowires, etc, with proper catalyst, feed gas, and temperature by the CVD growth. We have already very successfully applied this “grow-in-place” approach to produce silicon nanoribbons and nanowires by the vapor-liquid-solid (VLS) technique[67].

Conducting polyaniline was used to demonstrate the use of the second version of nanochannel permanent templates with built-in electrodes and channel access regions by
electropolymerization. The second version of nanochannels is not limited to electrochemically synthesizing conducting polymers, but can expand to different electrochemical synthesizable materials inside nanochannels, including metals, alloys, metal oxides, etc. Of course, as noted, the creation of a technology with built-in contacts/interconnects in place with the nanowires has very general, key implications for fabricating economically viable nanowire-based circuitry and arrays.

1.4 Thesis organization

The organization of this thesis is as follows:

Chapter 1 describes the background and motivation of the research, and an outline of the research.

Chapter 2 describes the fabrication process flow of the first version of the nanochannel templates which are without the built-in electrodes, and of the second version of the nanochannel templates which are with the built-in electrodes and channel access regions. The verifications of open and continuous nanochannels for both versions of template are also demonstrated.

Chapter 3 describes the growth of aligned, position-controlled, geometry-controlled polymer nanowires in the empty nanochannel templates and carbon nanofibers in the nanochannel template with catalyst inside. The potential extended application of this first version of our nanochannel template for structures such as nanobridges is also described.
Chapter 4 describes the electrochemical synthesis and electrical characterization of individual addressable conducting polyaniline nanoribbons made using the nanochannel templates with built-in electrodes and channel access regions.

Chapter 5 gives a summary and discussion of the results obtained throughout the entire thesis research and suggests future research.

1.5 Publications for this work

Publications related to this thesis include:


References


Chapter 2

Fabrication of the nanochannel templates without and with built-in electrodes

2.1 General

The use of template structures with nanochannels to synthesize nanoscale structures with defined geometry is common as pointed out in Chapter 1; however, generally these templates are destroyed when liberating the nanowires and a “two-step synthesizing-and-then-positioning procedure” is used to fabricate circuits and arrays. This chapter presents the design and fabrication of the horizontal, encapsulated nanochannel templates structure without and with built-in electrodes and access regions which we conceived to avoid this “two-step synthesizing-and-then-positioning procedure”. The verification of the healthy channels made by our approaches will also be demonstrated. The nanobridge, a structure which can be obtained by modifying our nanochannel template approach, is also introduced as an extended application of the fabrication.

The nanochannel templates structure without built-in electrodes which is either open all the way by completely etching or has catalyst in the nanochannel positioned by partially etching the sacrificial metal, has nanochannels which have nanoscale cross-
sectional dimensions and can be of any prescribed length. We use the structure to produce polymer nano-filaments which were synthesized in the nanochannels or to produce carbon nanofibers in nanochannels which have a catalyst positioned inside for chemical vapor deposition (CVD) growth. The applications of nanochannel templates for production of polymer nanofilaments and carbon nanofibers with precise control of the nanofilament dimensions, position, separation, and orientation will be demonstrated in Chapter 3.

Fully enclosed horizontal nanochannels, in a pre-arranged array on a substrate and with built-in electrical contacts and chemical access regions, were used as growth templates for electrochemical synthesis of conducting polymer nanoribbons. In the “grow-in-place” approach, the nanochannel templates are part of the final array structure and remain after fabrication of the nanoribbons. The built-in electrical contacts, which provide the electrical potential for electrochemical polymerization, also remain and become contacts/interconnects to the array components for direct characterization or electrical circuit use. The grow-in-place architecture and methodology removes the need for template dissolution, any post-synthesis nanoribbon “grow-and-then-place” manipulation, and any post-synthesis electrical contacting. The fact that the templates are fully enclosed prohibits dendrite formation during growth, insures precise dimensionality, and gives the encapsulation needed in any real device application. We report the “grow-in-place” approach to electrochemical polymerization used to produce conducting polyaniline nanoribbons in Chapter 4.
2.2 Nanochannel template without built-in electrodes and access regions

Our first version of nanochannel templates was fabricated by the combined use of electron-beam lithography and a sacrificial metal nanowire etching technique. The use of electron-beam lithography allowed nanoscale control of the channel dimension, interchannel separation, and orientation, which eventually transformed into the control of the nanofilament dimension, separation, and orientation. The sacrificial metal nanowire etching technique allows the creation of a channel of desired dimension. In brief, our nanochannel template fabrication technique consists of first forming parallel lines of desired width and length in a patterned in a resist film on an insulating layer on a silicon substrate. These trenches in the resist are then filled with sacrificial metal to a desired height. After resist lift-off, only sacrificial metal lines remain on the substrate. A thick capping layer was next deposited over the substrate and finally the sacrificial metal lines were etched away from channel access thereby creating empty nanochannels embedded in the capping layer.

2.2.1 Process flow of nanochannel template without built-in electrodes fabrication

Figure 2-1 describes schematically the process flow steps used to fabricate this first version of the nanochannel templates of this research. To begin, a (100)-oriented silicon wafer is cleaned with standard RCA cleaning. Then a 40 nm thick hydrophilic SiO₂ film was grown on a silicon wafer by thermal oxidation at 1100 °C for 4 hours in a furnace. The hydrophilicity of SiO₂ floor in nanochannels will assist solution filling into
the nanochannels by capillary force, and the thickness of SiO₂ film is flexible. In order to achieve controlled nanoscale dimensions of channels, we use e-beam lithography to pattern. Since the insulating SiO₂ film is not very thick, we can ignore the substrate charging which causes pattern distortion during e-beam lithography, so the deposition of thin metal film on resist for charge dissipation can be skipped. To undertake the e-beam lithography, the 120 nm single layer e-beam positive resist 3% 950K molecular weight poly(methyl methacrylate) (PMMA) in a casting solvent anisole was spun on the wafer with spin speed 4000 rpm for 60 seconds. Then PMMA was baked on hot plate at 180 °C for 3 minutes to remove the solvent. For clean lift-off processing, the resist film should be few times thicker than the metal deposition thickness. Since the sacrificial metal is only 20 nm thick for this research, 120 nm single layer PMMA was found to be thick enough. Electron beam exposures were performed using a Leica EBPG-5HR with a beam energy of 100 KV as shown in Figure 2-1(a) to define the region that will be occupied by the sacrificial material later. As the electrons penetrate the resist, they experience very small angle scattering events (forward-scattering), which tend to broaden the initial beam diameter and leave the resist with a negative slope which is advantageous for a successful lift-off process. Figure 2-2 shows the Monte Carlo simulation of electron scattering in resist on a silicon substrate at a) lower voltage 10 KV and b) higher voltage 20 KV.[2] Higher beam voltages minimize forward scattering thus provide better width resolution, so we chose the highest voltage, 100 KV, in Leica EBPG-5HR for e-beam writing to push the limitation of the width dimension. Different line widths were designed from 200 nm to 20 nm for e-beam writing. A group of five lines with the same width were placed
in a row with equal spacing (200 nm) within a set. As the electrons penetrate through the resist into the substrate, they occasionally undergo large angle scattering events (backscattering). The backscattered electrons cause the proximity effect, where the dose that a pattern feature receives is affected by electrons scattering from other features nearby. Different line width grouping sets were separated by 10 µm to reduce the proximity effect caused by e-beam scattering. The dose for reliable removal of the PMMA with a resolution of 20 nm was 4000 µC/cm². The electron beam exposure breaks the polymer molecule into fragments that are dissolved preferentially by a developer such as Methyl iso-Butyl ketone (MIBK). Because MIBK alone is too strong a developer and removes some of the unexposed resist, the MIBK is usually diluted by mixing in a weaker developer such as isopropyl alcohol (IPA). A mixture of 1 part MIBK to 7 parts IPA at 20 °C produced high contrast and low sensitivity, and resulted in a developed pattern is not too sensitive to the development time. Wet development was made with the mixture solution of one part of MIBK and seven parts of IPA at 20 °C for 2 minutes with subsequent IPA rinse for 1 second and then drying with nitrogen gas. Figure 2-1(b) schematically shows the PMMA pattern after development.

Before the deposition, a descum process to remove a thin layer of resist scum which may occlude open regions in pattern is necessary for good lift-off, especially in small features. E-beam resist etches very fast in oxygen, so we descum the PMMA in oxygen reactive ionic etching (RIE) for 6 seconds in Plasma Therm 720 RIE system. Our approach to form the nanowires by patterning a “resist” is not limited to e-beam lithography. Our approach can use probe, stamping, photo, ion, step and flash[3], nano-
imprinting[4] or any other “soft” or “hard” lithography process that will chemically modify a controlled nano-scale width region of the resist.

After the defining of the channels, nickel, the sacrificial material used to create the channels, was then deposited to a prescribed thickness of 20 nm as shown in Figure 2-1(c) by evaporation (Kurt Lesker E-gun/Thermal Evaporator), and then lift-off was done in acetone using ultrasonic agitation at 40 °C. After lift-off, fine lines, 20 nm to 200 nm in width, and 20 nm in thickness, of nickel remained only in the areas not covered by the resist as shown in Figure 2-1(d). Next, a silicon nitride layer of 500 nm was deposited at 100 °C in electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD) from a SiH₄+N₂+Ar gas mixture. This silicon nitride was used to form a transparent, non-collapsing channel capping layer. Subsequent photolithography steps and RIE were used to define regions that gave access to the ends of the channels. The standard steps in the lithography module for patterning are (in sequence): dehydration bake at 110 °C for 2 minutes to aid resist adhesion on substrate, a thin layer of hexamethyldisilazane (HMDS) coating by spinning at 4000 rpm for promoting adhesion with subsequent baking at 110 °C for 15 seconds to remove solvent, coating Shipley 1813 photoresist uniformly by spinning at 4000 rpm, driving off some of the solvent in the resist by soft baking at 110 °C for 90 seconds, aligning pattern on mask to features on wafer on Karl Suss MA6 Contact Aligner, exposure at 12mW/cm² for 6 seconds to cause selective chemical property change at certain regions on photoresist, developing in MF-CD-26 for 50 seconds to remove exposed resist and hard bake at 115 °C for 2 minutes. The RIE process to etch the nitride for channel opening was performed in CF₄+Ar+O₂
gas mixture and was terminated when the nickel lines were exposed as shown in Figure 2-1(e). In the finishing step, the samples were immersed in organic-removing solution ACT-935 to remove any photoresist and RIE residue as shown in Figure 2-1(f), and the sacrificial nickel was etched by Transene Nickel Etchant TYPE I at 40 °C thereby creating the nanochannels as shown in Figure 2-1(g-1) by completely etching or Figure 2-1(g-2) by partially etching to leave some sacrificial nickel in the middle of the nanochannels. Figure 2-3 shows the optical microscope picture of a template with partially etched sacrificial material remained in the middle of nanochannel. The etching time is only 10 seconds, so we have two regions in the channels, one is the empty part, which is about 5 µm long near the channel opening, and the other is the remaining part with the sacrificial metal remaining part, which is about 90 µm long in the middle of the channel. The empty channel part is in the background color, and the sacrificial metal remaining part is in the light orange color. There are 11 sets in Figure 2-3: each set has 5 lines with equal width and 200 nm spacing apart, and the width ranges from 20 nm to 500 nm. Individual nickel metal lines cannot be resolved in the optical image. The sacrificial metal can be changed to other easily removable materials for different uses, as long as the etching process does not damage the template. For example, gold can be used since it is advantageous for nanosilicon vapor-liquid-solid (VLS) growth which is successfully applied to produce silicon nanoribbons and nanowires in our group.[5] The remained length of sacrificial metal in the nanochannels can be controlled by the etching solution, etching temperature, and the etching time. The shorter the etching time, the longer the sacrificial metal length and the short the distance between the channel opening and the
edge of the sacrificial metal. The distance between the sacrificial metal and channel opening is critical in some cases. For example, if the nanochannels with sacrificial (also the catalyst) metal inside are used as the VLS nanomaterial growth templates, the careful choice of reaction parameters is required to ensure that the vapor phase species diffuses far into the channel and preferentially reacts with the metal catalyst rather than with the internal walls of the channel. If the distance between the sacrificial metal and channel opening is too long, the channel may close up due to clogging and then the VLS reaction terminates because the vapor is unable to diffuse into the catalyst.
(a) e-beam direct writing on oxide

(b) e-beam resist development

(c) Sacrificial metal deposition

(d) Metal nanowire remain after lift-off

(e) Anisotropic Reactive Ion Etching

(f) Removing the patterning resist

(g-1) completely empty nanochannels

(g-2) nanochannels with catalyst inside

Figure 2-1: Schematic representation of the procedure used to fabricate the nanochannel template without built-in electrodes and access regions.
Figure 2-2: Monte Carlo simulation of electron scattering in resist on a silicon substrate at a) 10 KV and b) 20 KV.

Figure 2-3: Optical microscope picture of nanochannels with sacrificial material inside.
2.3 Verification of open nanochannels

In order to successfully apply our nanochannels as nanomaterial growth templates with controlled orientation, location, dimension, and separation, we have to verify that the nanochannels fabricated in 2.2.1 have the designed orientation, position, and geometry. And also we must verify that the nanochannels we fabricated are open without any collapsed area and blockage. In such small dimensions, the capillary force is strong enough to possibly be able to result in capping layer collapse during any process with wet solution or in any vacuum system. Also, the diffusion of etchants in the nanochannels is a factor that must be considered. For example if the efficiency of etchant diffusion is not good enough, it may not be able to remove the sacrificial metal to form the open and continuous nanochannels. If the capping layer collapses, or the sacrificial metal is not completely removed by the etchant due to the limitation of diffusion, the nanomaterials can not successfully grow in the template or at least they can not follow the controlled dimensions of nanochannels. So it is very important to investigate the nanochannels, after the processing of the last section, to determine their state and, most importantly, to determine if they are open (i.e. empty).

2.3.1 Determination of dimensions of sacrificial metal nanowires

Before being able to achieve precise dimensional control of the nanochannels, we have to make sure we have precise control of the dimensions of the sacrificial metal nanowires since they establish the dimensions of the nanochannels after the sacrificial metal is etched away. The field emission scanning electron microscope (FESEM
LEO1530) top-view picture of 20 nm wide, 20 nm high (which can not be determined by a top-view FESEM picture, but by the deposited metal thickness), 200 nm spacing nickel nanowires patterned by e-beam lithography is shown in Figure 2-4. The FESEM LEO 1530 is used because it is capable of imaging features down below 25 nm. The wafer was coated with a thin conducting gold layer deposited in a sputter before loading to the FESEM chamber for charge dissipation. From this FESEM picture, we determined that the location, orientation, interspacing, length of sacrificial metal nanowires are exactly as we designed for the pattern. This is the basis of the successful fabrication of nanochannels with designed dimensions for the following process. Because the sacrificial metal is evaporated on the whole sample at the same time, the thickness is identically 20 nm for different widths of sacrificial metal nanowires. This was demonstrated by investigating other widths, from 30 nm to 200 nm, with the same height 20 nm and the same spacing 200 nm by FESEM. The thin sputtered conducting gold is not to be confused with the sacrificial metal forming the metal nanowires. The gold layer is for charge dissipation in FESEM so the electrons do not accumulate on the substrate and blur the image detected. Since the substrate we have is insulating silicon oxide layer, the conducting gold layer is necessary especially for imaging such small features. Gold is the generally used metal for change dissipation in FESEM in this thesis because it is easily removed by etchant solution, and does not react with the sacrificial material. This thin gold layer generally appears patterned in Figure 2-4 because the gold is not thick enough to form a uniform film. The scale bar in the picture is 200 nm.
2.3.2 Verification of open channels: scanning electron microscopy

Figure 2-5 shows five empty, 20 nm wide by 20 nm high channels in cross-section in a FESEM micrograph. These are the first such channels fabricated by our method in the world.[6] The sample was obtained by cutting in the middle of 200 µm long nanochannels, perpendicular to the channel length direction, under the capping layer, to create this cross-section. The cutting is done by breaking the substrate with a blade along the silicon crystal direction (100). The scale bar in Figure 2-5 is 100 nm. It can be seen from Figure 2-5 that the sacrificial nickel was etched away completely leaving open channels and very importantly that the capping layer did not collapse and that there is no
nanochannels blockage. We noted that the nanochannels must be open all the way for the middle of the nanochannels to be open. Other channels with the same height 20 nm but different widths, from 30 nm to 200 nm, were seen to be open as well by FESEM examination. Figure 2-6 shows the FESEM picture of another set of five empty, 70 nm wide by 20 nm high channels in cross-section. The scale bar in Figure 2-6 is 200 nm.

Figure 2-5: FESEM cross-section picture showing five 20 nm wide, 20 nm high nanochannel templates, which are spaced 200 nm apart.
Verification of open channels: fluorescent imaging microscopy

Fluorescence imaging was also used to establish that the nanochannel templates are fabricated without any collapsed regions, are open, and can be completely filled with monomers without any trapped bubbles. For this, a homogeneous solution of fluorescence-active 1-pyrenylmethyl methacrylate and initiator AIBN in toluene were introduced and filled into the nanochannel templates and then polymerized by heating to 80 °C. The template surface was washed clean after the 1-pyrenylmethyl methacrylate and AIBN were filled into the nanochannels so there was no fluorescence-active material on the surface to interfere with the real signal from the channels. The fluorescence from ten different fluorescence-active polymer line sets with members with designed line
widths ranging from 200 nm to 20 nm was detected by a confocal fluorescence microscope with the different line width sets separated by the expected 10 µm as shown in Figure 2-7. Individual polymer filaments cannot be resolved in the optical image. The UV-transparent capping layer was not removed so the fluorescence-active material had to fill into the nanochannels. The radiation was passed through a 365 nm excitation filter, and the fluorescence light was filtered by a 395 nm long pass emission filter. The continuity of the fluorescent poly(1-pyrenylmethyl methacrylate) lines seen in fluorescence images confirmed that the channels were initially and completely open all the way without any void or collapsed region and hence filled with continuous fluorescent polymer filaments after polymerization. As the fluorescent polymer was exposed for longer times under light, the efficiency to emit fluorescent light decreases due to photo-bleaching effect as shown in the central rectangular area in Figure 2-7 which indicates the polymerization did take place in the channels[7].
A concept diagram of our permanent nanochannel template structure with built-in contacts is schematically shown with two nanochannels in Figure 2-8. These channels are seen to be fully encapsulated by a bottom floor layer and top capping layer. They are seen to have two access regions to allow polymer precursor solution entry before the electrochemical polymerization driven by the built-in electrodes. These access regions also allow oxidant and monomer entry, respectively, in the case of chemical polymerization. One can envisage that the electrode positions and nanoribbon lengths and
positions in an array would be dictated by the actual device application. These nanochannel templates with built-in electrodes and solution access regions are fabricated by the combined use of top-down process and the sacrificial material approaches.

2.4.1 Process flow for nanochannel templates with built-in electrodes fabrication

In the specific demonstration reported here, the starting substrate was an RCA-cleaned, (100)-oriented silicon wafer covered with an electrically insulating 1 μm thick silicon oxide layer grown by thermal oxidation at 1100 °C for 14 hours in a furnace. Because the silicon oxide will be etched in the access region patterning, the silicon oxide layer must be thick enough to prevent the electrical current flowing through silicon substrate in the case of electrochemical polymerization. The substrate was dehydrated before the lithography process. Bi-layer resist was spun onto the silicon oxide and

Figure 2-8: Schematic concept diagram showing two nanochannel templates with built-in electrodes for electrochemical polymerization and electrical contacting.
patterned by e-beam for narrower lines or photo-lithography for wider lines to define the parallel lines of desired width and length which will be the growth-nanochannel template regions. The reason to use bi-layer resist is for successful lift-off for thicker deposited metal layer, which is 55 nm in this case. For e-beam lithography, a high sensitivity copolymer of methyl methacrylate and methacrylic acid \([P(MMA-MAA)]\) is spun with PMMA on top. The 5.5 % 120 nm thick \([P(MMA-MAA)]\) in a casting solvent anisole was spun on the wafer uniformly with spin speed 5000 rpm for 60 seconds and baked on hot plate at 180 °C for 3 minutes to remove the solvent. Then the 2 % 950K 50 nm thick poly(methyl methacrylate) (PMMA) was spun on the wafer with spin speed 5000 rpm for 60 seconds and baked on hot plate at 180 °C for another 3 minutes. A common problem is the exposure of resist on thick insulating substrates. Substrate charging causes considerable distortion when patterning features on thick insulators and may contribute significantly to overlay errors. A simple solution for exposure at higher voltages (>10 KV) is to evaporate a thin (~15 nm) layer of gold on top of the resist by thermal evaporation. The e-gun evaporator is not suitable because x-rays and electrons in the evaporator will expose the resist. Electrons travel through the metal with minimal scatter, exposing the resist. The gold film is removed by gold etchant before developing the resist. Electron beam exposures were performed by Leica EBPG-5HR using beam energy of 100 KV to define the region that will be occupied by the sacrificial material later. The dose for reliable removal of the bi-layer resist of 120 nm thick \([P(MMA-MAA)]\) with 50 nm thick PMMA on top was 4000 \(\mu\)C/cm\(^2\). Wet development was made with the mixture solution of one part of MIBK and seven parts of IPA at 20 °C for 2 minutes with subsequent IPA rinse for 1 second and drying with nitrogen. The development giving a large undercut is
ideal for clean lift-off for thick deposition which is shown in Figure 2-9. Descum the e-beam resist in oxygen RIE for 6 seconds is also applied for clean lift-off.

For photo-lithography, we also use bi-layer resist for clean thicker metal layer lift-off. LOR-1A is spun with SPR3012 on top as imaging resist. MicroChem’s lift-off resist LOR-1A has relatively low dissolution rates and offers superb undercut control. LOR-1A was spun on the wafer with spin speed 2500 rpm for 60 seconds and baked on hot plate at 170 °C for 2 minutes. SPR3012 was spun on the wafer with spin speed 4000 rpm for 60 seconds and baked on hot plate at 95 °C for 1 minute. The combination of the bi-layers must be chosen well because resists used may intermix with each other which may influence the pattern after exposure and development. Then we align the pattern on mask to features on wafers on Karl Suss MA6 Contact Aligner and expose at 12 mW/cm² for 5 seconds followed by post-exposure back 115 °C for 1 minute. The wet development was done by MF-CD-26 for 70 seconds followed by DI water rinse and nitrogen drying. The use of combination of LOR-1A and SPR3012 as the imaging resist gave an ideal undercut for clean lift-offs as shown in Figure 2-10. The SEM picture of the cross-section of bi-
layer resists based on the photo-lithography parameters described above is shown in Figure 2-11.

Figure 2-10: Bi-layer of LOR-1A and SPR3012 for clean lift-off.
The use of lithography allows control of the channel dimension, position, inter-channel separation, and orientation, which eventually transforms into control of the dimension, position, separation, and orientation of the nanoribbons synthesized in the growth-nanochannels. As discussed in 2.2.1, while e-beam and photo lithography were used for the features, other techniques such as step and flash or nano-imprinting can also be employed.

After this patterning, the channels in the resist as well as the remainder of the surface were covered with sacrificial metal to a desired height (55 nm high nickel was used here) by e-gun evaporation. After the bi-layer resist lift-off by NanoRemover solution at 70 °C for 30 minutes, only sacrificial metal lines, defining what will become the growth-nanochannel templates and then the synthesized nanoribbons, remained on the
substrate. The built-in contacts, which will provide electrical access to the nanoribbons to be grown in the growth-nanochannel templates, were defined next. The contacts were designed to be four parallel equal-width and equally spaced electrical probes which were perpendicular to the direction of nanochannels. They were located as desired on the top of the sacrificial metal lines and oxide substrate layer. They are fabricated in this manner so that they will be on the sides and top of the polymer nanoribbons grown in the channel. This was done to insure that the contacts do not impede nanoribbon growth. These contact/interconnect structures, 85 nm thick platinum with a thin adhesion layer of 2 nm titanium, were defined by photo-lithography, metal deposition and lift-off. The photo-lithography steps used to define the contacts were identical to those we used to define the 55 nm thick nickel lines because the thickness of bottom resist LOR-1A, 230nm, is thick enough for the clean lift-off for the 90nm thick contacts. The metal depositions of platinum and titanium were done by e-gun evaporation subsequently without breaking vacuum to prevent the formation of titanium oxide between platinum and titanium. The lift-off was accomplished in NanoRemover solution at 70 °C for 30 minutes. Nitrogen drying or ultrasonic agitation were avoided here to prevent electrodes from peeling off. The clean lift-off of nickel lines is important because if there is nickel deposition step coverage on the sidewall of the resist forming sharp “rabbit-ears” on the nickel lines resulting from bad lift-off, the contacts we formed in this step will be discontinuous which will result in open circuits as shown in Figure2-12. The open circuit can not provide adequate electrical current to drive the electrochemical polymerization nor can it to be used to get the electrical signal needed for characterization or device operation.
A silicon nitride capping layer of 500 nm was next deposited over the whole substrate by ECR-PECVD from a SiH$_4$+N$_2$+Ar gas mixture at 100 °C. This use of nitride for the “roof” on the growth channels allowed optical techniques to be used to assess the nanoribbons and their growth process. In particular, this capping layer is transparent to both the excitation and fluorescein emission used in our nanomaterial growth in the channel studies. Using subsequent lithography patterning, the deposited silicon nitride was selectively etched with RIE to define the access regions. The access regions were defined on either side of the channel to facilitate movement of the solution and to avoid flooding of solution on the electrodes. The standard steps in the lithography module for patterning in the RIE for etching nitride are identical to what we used in 2.2.1. Finally the sacrificial nickel lines were removed by Transene Nickel Etchant TYPE I solution attack.

Figure 2-12: Discontinues platinum contact on nickel lines with “rabbit-ears” due to bad lift-off.
from the access regions at 40 °C to form the nanochannel (empty) templates. Any remaining titanium adhesion layer under the platinum contacts in the roof and walls of the nanochannel templates was removed by wet etching directly after removal of the sacrificial nickel. This step insures that the titanium will not form insulating titanium oxide to hinder the electrical functions (electropolymerization and subsequent electrical contacting to the polymer) carried out by the platinum contacts. Before nickel etching, the conductivity of sacrificial nickel nanowires was determined to be 1/4 of conductivity of bulk nickel by I-V measurement through built-in electrodes. After nickel etching, the conductivity was measured to be zero which indicates empty channels were formed. With this process flow, encapsulated, empty growth-channels with built-in electrode contacts and access regions were created. In this thesis we fabricated multiple groups of five empty growth-nanochannels on a substrate. All had a 55 nm nanochannel height. Each group of five had the same nanochannel width which ranged from 50 nm to 4.5 µm. The length of the nanochannels was 40 µm - 100 µm from access region to access region. For this study, four parallel, equally spaced contacts were positioned in each channel to accomplish the multiple tasks of electrochemical polymerization, material conductivity determination, and ohmic contact studies. An optical image showing an actual growth-nanochannel template region with built-in electrode contacts and access regions is presented in Figure2-13
Verification of open channels with built-in electrodes

The nanochannels were checked to determine their status by introducing an ionic solution into the nanochannels from the channel access region and monitoring the electrical current by biasing on the built-in electrodes. The ionic solution was first put in the access region reservoir, and then introduced carefully by micromanipulator to the channel opening. Any solution flooding had to be avoided so the signals detected by the built-in electrodes are from the current response inside the nanochannels. As shown in Figure 2-14, by applying voltage on two built-in electrodes, the electrical current jumped...
up as the ionic solution was introduced into the nanochannels at the 30 second point, and
dropped down as the solution was sucked out at the 90 second point. The response to the
ionic solution in and out the nanochannels was instant and repeatable which verified that
the nanochannels were open all the way without any collapsed region, and the built-in
electrodes can directly contact and monitor the solution inside the nanochannels. The
latter point is critical since we need to remove electrons (oxidize) from the solution via
these electrodes for oxidative electropolymerization.

Figure 2-14: The electrical current response to the ionic solution in and out the
nanochannels with built-in electrodes.
2.6 Extended applications of the templates as nanobridges

The process flow for the first version of our nanochannel templates can be modified for more applications. One of these is the nanobridge structure which can be used for sensors. The process flow is basically the same as the one described in Figure 2-1(a)-(d), except starting from Figure 2-1(e). In this step, the photoresist mask is patterned on the complementary region of Figure 2-1(e) and then, after the RIE, the metal nanowires remain as nanobridges which is shown in Figure 2-15. In other words, the channel forming material in Figure 2-1 is to become the nanobridges in Figure 2-15 by adequately adjusting the process flow. The nanocantilever can also be done using the same approach.

The electrical contact electrodes can be arranged by lithography and lift-off on the nanobridges thereby providing means for detecting chemical, biological, and physical properties by measuring the AC or DC electrical current through a nano-bridge structure[8] or the change in resonance frequency or magnitude due to mass loading.[9] Chemical detection by nanobridges can be very specific by using functionalization, and these miniaturized sensors are highly suitable for parallelization into arrays and integrated devices. The nanobridges can also be used as probes into structures such as cells or manipulators of structures such as cells and other biological entities. Such uses make it possible to examine a living sample in vitro or in vivo with minor perturbation to the system and without laborious sample preparation. While this thesis developed the processing that can produce such nanobridge structures, use of these structures was beyond the scope of this work.
2.7 Conclusion

This chapter presents the design and fabrication of the nanochannel template structures without and with built-in electrodes and access regions which we conceived to avoid the “two-step synthesizing-and-then-positioning procedure”. In addition, the verification of the attainment of the open channels by different methods was also demonstrated.
We have first demonstrated the fabrication of the nanochannel templates without built-in electrodes by the combined use of electron-beam lithography and the sacrificial metal nanowire etching technique. The use of electron-beam lithography allowed nanoscale control of the sacrificial metal nanowire dimension, position, interchannel separation, and orientation, which eventually transformed into the control of the nanochannel and nanomaterial dimensions, position, separation, and orientation. The sacrificial metal and the corresponding formed channel can be as small as 20 nm high by 20 nm wide which was verified by FESEM imaging. Fluorescence imaging was also used to establish that the nanochannel templates are fabricated without any collapsed regions, are open, and can be completely filled with monomers without any trapped bubbles. The nanochannel without built-in electrodes can be empty all the way through or can have a segment of sacrificial metal in the middle by partially etching.

Secondly, the nanochannel templates with built-in electrodes and solution access regions are fabricated by the combined use of top-down process and the sacrificial material etching approaches. Bi-layer resist were used in lithography for clean lift-off for thick deposited materials. The built-in electrodes, which directly contact and provide the electrical potential to the channel, remain and become contacts/interconnects to the array components. The access regions allow the necessary solution entry. The nanochannels were checked to determine their status by introducing an ionic solution into the nanochannels from the access regions and monitoring the electrical current by biasing on the built-in electrodes. The response to the ionic solution in and out the nanochannels was instant and repeatable which verified that the nanochannels were open all the way
without any collapse region, and the built-in electrodes can directly contact and monitor the solution inside the nanochannels.

A class of nano-bridge/cantilever structures which can be obtained by modifying the nanochannel fabrication process flow is also demonstrated as an extended application of the template process flow.
References


7. B. Herman, Fluorescence Microscopy 2nd Ed. (Springer-Verlag, Singapore), **1998**.


Chapter 3

Nanochannel templates for nanomaterial filament formation

3.1 Introduction

The realization of the full potential of nanotechnology demands the ability to accurately position a wide variety of nanomaterials to construct complex structures and devices.[1] Current lithographic techniques, including dip-pen lithography, allow precise positioning; however, the range of materials that can be synthesized is limited.[2-3] Other approaches to forming nanoscale structures involve a two-step synthesizing-and-then-positioning procedure. While a variety of materials, including nanoparticles, nanotubes, and nanorods, can be synthesized in this manner, it seriously limits the ability to control size, location, and orientation on the nanoscale.[4-9] The common approach for nanowire fabrication is to use nano-templates for growth and then dissolve them to release the produced nanowires. These nanowires must then be “caught” and directed to their point of use. In this process, the big challenge that must be overcome for mass production of nanowire-based electronics and sensors is that one must be able to align and assemble these nanowires by design, not by statistics. Once nanowires are released from the template, it is very difficult to obtain spatial and orientational control in nanowire
assembly as well as electrical contacts at a specific location. In order to circumvent this problem, we developed a new nanomanufacturing technology that utilizes carefully designed nanochannel reactor systems to align oriented nanomaterials as they are produced and then the reactor systems become part of the device structure. In this chapter we demonstrate our approach by synthesizing polymer in these nanochannel reactors with controlled size, orientation and location. The procedure is general, allowing the synthesis of different polymeric materials through a variety of chain-growth mechanisms (e.g., radical, metal-catalyzed, photochemical, electropolymerization) inside the nanochannel templates, and it opens up the possibility of directed design of “grow-in-place” nanoscale structures.[10] With the attainment of controlled alignment, nanomaterials with novel properties and functions can be assembled into usable materials and devices that will play a critical role in advancing future technologies.

This chapter includes two parts. The first part describes the use of empty nanochannels without built-in electrodes as templates for the formation of polymer nanofilaments. Different ways of polymerization will be demonstrated to show the broad applications of the nanochannels template use to producing polymer filaments, such as poly(methyl methacrylate) (PMMA) by radical polymerization, polythiophene (PT) by photopolymerization. The second part describes the use of nanochannels with a catalyst inside as the template for the formation of carbon nanofibers. Lateral aligned carbon nanofiber growth inside and even out from the nanochannel templates is also demonstrated. Different verification approaches are done accordingly to prove those nanofilament or nanofiber arrays are produced with precise dimension, position, orientation control in a single integrated step.
3.2 Polymerization in nanochannels without built-in electrodes

The concept diagram of empty nanochannels without built-in electrodes serving as polymer growth templates is schematically shown in Figure 3-1. The detailed fabrication process for the nanochannels was described in Section 2.2.1. The catalyst or monomer solution is introduced from the nanochannel opening to fill the whole nanochannels and then do the polymerization, in this way polymer nanofilaments are formed with predetermined dimensions, location, and orientation.[11] Any excess liquid outside of the nanochannels was removed to ensure the polymerization only takes place in the nanochannels.

We used the nanochannels as growth templates to synthesize poly(methyl methacrylate) (PMMA) by radical polymerization, and polythiophene (PT) by photopolymerization. Different verifications were done for each polymer. The silicon nitride capping layer can be removed for field emission scanning electron microscope (FESEM) or atomic force microscopy (AFM) verification, or remain for optical imaging owing to its transparent properties.

Figure 3-1: Empty nanochannels without built-in electrodes.
3.2.1 Radical polymerization

Poly(methyl methacrylate) (PMMA) was polymerized in the nanochannels by introducing a solution containing the initiator AIBN (0.5 mol%) dissolved in monomer MMA liquid by capillary force. Following initiator and monomer introduction, the sample surface was carefully cleaned with acetone to remove the monomer, and polymerization was performed by heating at 80 °C in atmosphere for 20 minutes.

To measure the dimensions of polymer filaments produced in nanochannels, the capping silicon nitride layer had to be removed and the exposed filaments were imaged with an FESEM. The etching step must be done at room temperature to prevent the polymer from reforming and deforming by heating, and the etchant solution can not attack the formed polymer, so we choose hydrofluoric acid (HF) 50% to etch the capping layer for 10 minutes.

As an experimental control, Figure 3-2 shows the AFM image of a group of empty nanochannels after removing the capping layer. AFM image was obtained on a Digital Instruments Dimension 3000. Since no polymer is formed in the channels, nothing remained after removing the capping layer, thus leaving a 3 µm wide trench. The trench is the region where there was the group of nanochannels. Near the nanochannels, the silicon nitride was deposited with higher stress due to the step of the sacrificial metal wires, thus the silicon nitride around the nanochannels was removed faster than the bulk nitride region, which became the plateau region in Figure 3-2. Even slower, the bulk nitride region was still etched by HF for about 300 nm thick; i.e., a 200 nm height difference was left after removing the nitride around the nanochannels.
Figure 3-3 shows FESEM image of five 173 nm (left group) and five 123 nm (right group) wide filaments of PMMA. The PMMA nanofilaments were located inside the nanochannels before removing the capping silicon nitride layer and then remained in the trench after removing the capping layer near the nanochannels. These filaments were all 20 nm thick and equally spaced (200 nm) as pre-designed nanochannels. As we note, the locations, orientation, separation, and dimension of the PMMA nanofilaments are completely consistent with the pre-determined growth nanochannel template. The continuity of polymer nanofilaments indicates the channels were open all the way so the monomer solution can fill the nanochannels to form the continuous polymer nanofilaments. Groups of different widths of PMMA nanofilaments were also observed as designed (not shown).
In one instance, a twisted PMMA nanofilament with a 170 nm width and a 20 nm height was observed by FESEM as shown in Figure 3-4. The PMMA nanofilament seems to have good flexibility so it can curve and bend with a large angle but not break.

The results in Figure 3-3 and Figure 3-4 show that the polymer filaments are formed with the same location, orientation, separation, and dimension as the corresponding nanochannels. Thus, the nanochannel templates precisely define the location, orientation, separation, and dimension of polymer nanofilaments and, most notably, nanofilaments can be released without breaking.

Figure 3-3: FESEM picture of two sets of PMMA nanofilaments. In the left group are filaments in 173 nm wide, 20 nm thick, and separated 200 nm from others. In the right group are filaments in 123 nm wide with the same thickness and spacing.
An oxygen plasma exposure was utilized to verify the exposed filaments seen in Figure 3-3 were organic polymers, since the oxygen plasma can etch only the organic material but not an inorganic dielectric or metal. Figure 3-5 shows an FESEM of polymer filaments before and after the oxygen plasma etching. This establishes that the filaments in the channel region were the organic polymers. Clearly the silicon lines beyond the channel region were not etched by the oxygen plasma.

Figure 3-4: FESEM picture of a twisted polymer nanofilament having 170 nm width and 20 nm height.
Figure 3-5: FESEM picture of PMMA nanofilaments before (top) and after O₂ plasma etching (bottom).
Solid-like behavior of PMMA wires was confirmed by intermittent contact atomic force microscopy. Figure 3-6 is a scan at low force (ca. 100 nm free-oscillation amplitude, 80 nm scanning oscillation amplitude; tip force constant 0.65 Newton/meter; resonant frequency 43.5 kilohertz) showing a PMMA nanofilament. The filament was then scanned at a single spot for several line scans at large force to perform the cutting (0 nm scanning oscillation amplitude). The original fiber was then re-scanned showing where it was cut by the AFM tip. The underlying silicon surface remained undamaged. Figure 3-6(b) shows line profiles of the nanofilament before and after cutting.

Figure 3-6: AFM of polymer nanofilament cutting, the left picture shows scan of one PMMA nanofilament at low tapping force, the right shows the same nanofilament scanned again at low force after scanning a single line at high force, scale bar is 100 nm. (b) Line profiles of the nanofilament before and after cutting.
3.2.2 Photopolymerization

Photopolymerization is also possible inside nanochannels since the silicon nitride capping layer is UV transparent. Figure 3-7 is a fluorescence microscope image showing the photoluminescence of polythiophene nanofilaments produced via photoinduced coupling of 1,4-diiodothiophene inside nanochannels upon UV irradiation with a 200W Hg lamp. Since the monomer does not fluoresce, what we see is the fluorescent polymer in the channels. Also, the polymer filaments remained intact after tetrahydrofuran (THF) solvent washing, which proves what we have in the channels are polymers, not just oligomers, because polythiophene is insoluble in organic solvents due to the rigid main chains.

Figure 3-7: Fluorescence microscopy image of photoluminescence of polythiophene (PT) produced in nanochannels via photo-induced coupling. Polymer grouping sets are spaced 10 µm apart. Individual polymer filaments cannot be resolved in the fluorescence image.
3.3 Carbon nanofiber growth in the nanochannel templates with catalyst inside

Carbon nanotubes\[12\] (CNT) are of great interest to the scientific and industrial communities due to their astounding properties\[13\] which include ballistic electron transport and high mechanical strength and flexibility. Nearly perfect CNTs can be prepared by a variety of methods including laser ablation,\[14\] arc discharge,\[15-16\] and catalytic chemical vapor deposition (CVD).\[17\] Unfortunately for electrical applications and integration with microelectronics, all of these approaches involve high synthesis temperatures and produce randomly oriented CNTs that must be laboriously separated, purified, and cut to length before use. Even if a CNT can be aligned by applying an electrical field during and after the growth, assemblies of much more complex geometry and integration, as is required for usable devices and circuits, is still not feasible. Recently, carbon nanostructures such as vapor-grown vertically aligned carbon nanofibers (VACNFs) \[18-19\] produced by low substrate temperature (~660 °C) plasma-enhanced chemical vapor deposition (PECVD) has attracted great interest due to its potential applications in areas such as tips for scanning microscopy and field-emission devices\[20\], local electrochemical probes\[21\], nanoelectrodes and interconnects for nanoelectronics, etc. However, those vertically grown carbon nanofibers (CNFs) can only align to the direction perpendicular to the substrate. Using our lateral channel deterministic growth template approach with catalyst inside in low temperature CVD, we can obtain lateral aligned carbon nanofibers (LACNFs). It is easier to integrate the LACNFs into the silicon top-down fabrication process than it is to use vertically aligned CNFs to realize more complex microscale devices with functional nanoscale features.
The location, number, dimension, and chemical composition of LACNFs can be controlled by the predetermined channel growth template and CVD synthesis parameters. The addressable LACNFs can be synthesized individually or in an array and can be directly connect to built-in metal contact for further applications like field-emission devices with controlled point of emission, lab-on-chip biological or chemical probes for intercellular characterization, nanoelectrodes and interconnect for silicon-carbon hybrid nanoelectronics, etc.

3.3.1 Carbon nanofibers growth in chemical vapor deposition system

In the CVD method, the carbon nanofibers (CNFs) growth is catalyzed by transition metals such as nickel, iron or cobalt. Parameters controlling growth appear to be numerous: nature of feed gas and composition, flow rate, temperature, type of catalyst, catalyst preparation technique, etc. A schematic experimental CVD system for carbon nanofiber growth is shown in Figure3-8. The carbon nanofiber growth process involves heating a catalyst material in the channel template to moderate temperatures (>500 °C) in a furnace and flowing a hydrocarbon gas through the tube reactor for a period of time. The general carbon nanomaterial growth mechanism in a CVD process involves the dissociation of hydrocarbon molecules catalyzed by the transition metal, and the dissolution and saturation of carbon atoms in the metal. Then the precipitation of carbon leads to the formation of carbon fibers which follows the dimension of our pre-designed nanochannels.
In our experiment, we employ the mixture of feed gas acetylene (C₂H₂, 5 sccm) and carrier gas helium (He, 30 sccm) in the tube, the growth temperature is 700 °C, the pressure is 1 atmosphere, and the reaction time is 30 minutes. The sacrificial metal nickel segment which is formed by partial etching in the nanochannel template, shown in Figure 3-9, is used as the catalyst.

Figure 3-8: APCVD system for carbon nanostructure growth.

Figure 3-9: Nanochannel template with catalyst metal inside.
3.3.2 Optical microscopy and Raman spectroscopy

In the Figure 3-10 optical microscopy shows that the carbon nanofibers were formed in the nanochannel as the black region from catalyst metal, and the material in this black region was verified by the Raman spectroscopy shown in Figure 3-11. Raman spectroscopy is the inelastic scattering of photons (light) by phonons (crystal vibrations) which is produced by irradiating the sample with laser light of a certain frequency coupled with analysis of the scattered radiation. The difference in frequency of the incident and scattered light is equal to the actual vibrational frequencies of the material, thus the Raman spectroscopy can identify and track changes in specific chemical groups. It is a fast, relatively simple, and non-destructive tool for structural characterization of carbons.[22-24] The Raman spectra of all carbons show several common vibration modes in the 800-2000 cm\(^{-1}\) region, the so-called \(G\) (for “graphite”) and \(D\) (for “disordered”) peaks, which are carried out at wavelengths in the blue-green spectral region (488-514.5 nm). The \(G\) mode observed at 1580 cm\(^{-1}\) is related to the highly oriented pyrolytic graphite (HOPG), and the \(D\) mode observed near 1360 cm\(^{-1}\) is related to the microcrystalline graphite and glassy carbon but not in pristine HOPG or single-crystal graphite.[25-26] The dispersion of peak positions and relative intensities of all of these modes can give much information about the structure and domain size of a carbon material. The 488 nm wavelength light was spotted on the black region through the transparent capping layer by using a light microscope. The characteristic peaks of Raman spectrum at 1360 cm\(^{-1}\) and 1580 cm\(^{-1}\) indicate that the material inside the channels is the carbon after the CVD growth. Since the intensity of \(G\) mode and \(D\) mode is comparable,
the carbon nanofibers in the nanochannels are of the combination of crystalline and amorphous carbon.

Figure 3-10: Optical image of nanochannel template after carbon nanofiber growth.

Figure 3-11: Raman spectrum of the black region of nanochannels after 30 minutes, 700 °C CVD growth.
The Raman spectrum of the nitride capping layer region is shown in Figure 3-12 as the control. As seen, it has no such carbon characteristic peaks, which determines that what we detected in the black region in Figure 3-10 is not the residual amorphous carbon all over the surface, but the material inside the nanochannels. The result demonstrates the nanochannel templates are suitable for the carbon nanofiber growth.

![Nitride capping layer](image)

**Figure 3-12**: Raman spectrum of the capping layer of nanochannels after 30 minutes, 700 °C CVD growth.

### 3.3.3 Scanning electron microscopy

In order to investigate the carbon nanofiber growing out of the nanochannel templates during CVD process, we decreased the wet etching time of nickel to 1 second so the distance between the channel opening and the end of the catalyst metal is only 5 µm. Thus the acetylene gas can reach the catalyst metal more easily to dissociate and
form carbon nanofibers before depositing on the channel wall and clogging the nanochannels. Also, a suitable ratio of hydrogen was flowed in the gas so it decreased the decomposition rate of acetylene, thus decreasing the rate that carbon clogs the nanochannels. In this carbon nanofiber growth experiment, we flowed the mixture of feed gas acetylene (5 sccm), hydrogen (10 sccm) and carrier gas helium (35 sccm) into the tube at a growth temperature 700 °C, and for reaction time of 40 minutes.

Before removing the capping layer, the FESEM picture of the grown carbon nanofiber was taken and this is shown in Figure3-13. The carbon nanofiber followed the direction and dimension of the nanochannel growth template at the initial stage of growth out of the nanochannel templates, and then it got thinner and curved. The growth diameters of carbon nanofiber got thinner because the nickel catalyst particle at the tip is consumed and becomes a smaller droplet outside the nanochannels during the CVD process. The carbon nanofiber curved because of the nonuniform stress across the interface of the catalyst particle due to a spatial fluctuation in the carbon precipitation.
After removing the capping layer by HF solution, a FESEM picture was taken and this is shown as Figure 3-14. The carbon nanofibers may stick to the substrate or drift away due to poor adhesion to the substrate. We can see the carbon nanofiber (grey part) grew at the end of the catalyst metal (white part) in the places where the nanochannels were. The dimension, location and orientation of carbon nanofibers followed those of the nanochannels which were designed as five equal width channels a set with the inner set spacing 1 µm and intra set spacing 5 µm. From this work, it can be seen that we have demonstrated that our nanochannel templates are effective growth templates for carbon nanofibers.
3.3.4 Energy dispersive x-ray spectroscopy

Energy dispersive x-ray spectroscopy (EDS) is a chemical microanalysis technique performed in conjunction with a scanning electron microscope (SEM). The technique utilizes x-rays that are emitted from the sample during bombardment by the electron beam to characterize the elemental composition of the analyzed volume. When the sample is bombarded by the electron beam of the SEM, electrons are ejected from the atoms with a sampling depth of 1-2 µm. A resulting electron vacancy is filled by an electron from a higher shell, and an x-ray is emitted to balance the energy difference between the two electrons. The EDS x-ray detector measures the number of emitted x-
rays versus their energy. The energy of the x-ray is characteristic of the element from which the x-ray was emitted. A spectrum of the energy versus relative counts of the detected x-rays is obtained and evaluated for qualitative and quantitative determinations of the elements present in the sampled volume.

Figure 3-15 gives the EDS data which verify the presence of carbon element when detecting the carbon nanofiber region in Figure 3-14 after removing the capping layer. The element carbon has a signature located at 0.3 KeV, while that of the background silicon is located at 1.8 KeV. From this qualitative analysis, we can determine that carbon is present in the sample. The intensities of the peaks do not reflect the actual concentration of the element in the sample since the lower the atomic number of the elements, the lower the intensity of the reflected or transmitted x-ray radiation.

Figure 3-15: EDS of the carbon nanofiber region.
3.4 Conclusion

We have demonstrated the combined use of standard top-down silicon process and sacrificial metal etching technique to create empty nanoscale templates with precise dimensional and orientational control in Chapter 1, and their use in the production of polymer nanofilaments in this chapter. The procedure is general as illustrated by the radical, and photochemical polymerizations that were performed in these empty nanochannels template, and poly(methyl methacrylate) (PMMA) and polythiophene (PT) nanofilaments were produced, respectively. Different verification approaches including FESEM, AFM cutting and probing, oxygen plasma treatment, and fluorescent microscope imaging were done to establish that the nanochannel templates precisely define the orientation, separation, dimension, and location of polymer nanofilaments grown inside.

We also demonstrated the carbon nanofiber growth in the nanochannels with catalyst metal segment in the middle by introducing the mixture of feed gas acetylene and carrier gas helium in CVD system at 700 °C. Optical microscopy shows that the carbon nanofibers were formed in the nanochannel from catalyst metal and it was verified by the Raman spectroscopy. EDS was also used to verify the presence of the element carbon in the carbon nanofiber region. It was seen that carbon nanofibers can grow inside and even grow out of the nanochannels, and the dimension, location and orientation of carbon nanofibers followed the pre-designed nanochannels which establish that our nanochannels with a catalyst are an effective growth template for carbon nanofibers.
The polymers nanofilaments and carbon nanofibers grown follow the dimensions of the pre-designed nanochannels, allowing the precise control of the dimension, location and orientation of polymer and carbon nanostructures. The approach opens up the possibility of “grow-in-place” manufacturing and processing of patterns and devices from nanostructured polymers using well-established polymer chemistry and from nanostructured carbon using the CVD technique.
Reference


Chapter 4

Electrochemical synthesis and direct characterization of an array of individual conducting polymer nanoribbons using permanent nanochannel templates with built-in electrodes and channel access regions

4.1 Introduction

In the mid 1970s after the first polymer capable of conducting electricity – polyacetylene – was reportedly prepared accidentally by Shirakawa,[1] chemists began to prepare new types of organic polymers that are good electronic conductors, a number of conducting polymers, namely polypyrrole, polythiophene, and polyaniline, have become the focus of much study.[2] A characteristic feature of these polymers is that they are conjugated along the polymer chain. Conjugation in simple carbon-containing compounds means the presence of alternating single and double carbon-carbon bonds in the molecule. Conjugated polymers are insulators in their neutral state due to a large band gap, but by adding some charge carriers, conjugated polymers can have their conductivity increased by more than a million times. For example, it was found that the conductivity of polyacetylene increased by up to 15 orders of magnitude when reacted with iodine (from $10^{-10}$ S/cm to $10^5$ S/cm); this phenomenon, known as doping, is a result of the
formation of charge carriers in the polymer. As the conducting polymers may be doped to varying degrees, there is an element of control in the doping level and hence in the conductivity. It was discovered that varying the level of doping yielded polymers exhibiting a wide range of electrical properties, from insulator, or semi-conductor, to metal. This ability to tailor the polymer’s electrical properties exemplifies the versatility of conducting polymers. Thus conjugated polymers are promising materials for future applications in electronics and sensors due to their improved and tunable electronic properties, low cost, environmental stability, flexibility, light weight, easy disposability and processibility.[3-5] The importance of conducting polymers is recognized by the awarding of the 2000 Nobel Prize in Chemistry to MacDiarmid, Shirakawa, and Heeger, for the discovery and development of conducting polymers.

Besides the doping level control by charge carriers, the enhanced electronic conductivities can be obtained if polymers with enhanced molecular order can be prepared[6-7] due to fewer conjugation-interrupting defects and easier intermolecular communication. The template synthesis approach has been found to be a route for achieving this order. The syntheses of polymer nanostructures by templates have been demonstrated by many groups [8-13] The basic methodologies of these groups are either (1) to use temporary but enclosed template structures or (2) to use permanent but open-channel template structures. In method (1), the temporary templates are usually commercially available track-etched polymeric membranes or porous alumina membranes. In this approach, after polymer nanostructure formation, the template material is usually etched away. As a result, the nanostructures either remain in a vertical array due to attachment to a substrate added to one side of the template or are floating
free in the solution. In the vertical array alternative one has the difficulties of electrically contacting and using vertically positioned elements on a substrate. In the free floating alternative, one must employ some pick-and-place technique to capture the nanostructures and to position them at the point of use. Such techniques can be very time-consuming and arduous.[14-17] Such approaches do not appear suitable for assemblies of much more complex geometry and integration as is required for usable devices and circuits as we discussed in Chapter 1. In method (2), the permanent but open template that has been employed is an open channel defined in SiO₂. This open channel is created between electrical-contact metal pads by e-beam lithography and etching.[18-19] The mixture of monomer and electrolyte is then added onto the sample to produce electrochemical polymerization in the template open channel region between the electrical contact pads. These template channels have no top covering and hence the approach offers no control of one dimension of the nanoribbons and, therefore, no control of dendrite formation. In both methods (1) and (2), an encapsulation step, which must be done on at least part of any practical sensor or electronic device, would have to be undertaken after nanoribbon formation. This requires deposition onto at least some regions of the polymer which can be problematic.

As has been shown,[8-13] conducting polymers synthesized in nanochannels have significantly higher conductivity due to higher order with the chains preferentially oriented parallel to the channel axis, which means that nanochannels provide unique opportunities for novel polymer synthesis. Herein, we demonstrate a “grow-in-place” architecture and fabrication approach[20-21] for producing conducting polymer nanoribbons which is based on employing enclosed, horizontal-growth nanochannel-
templates with built-in contacts. Our templates are permanent and give precise
dimensional, positional, and orientational control, and direct electrical access to
individual addressable conducting polymer nanoribbons in arrays. These features are all
obtained in an integrated step. Our permanent template with the built-in contacts
approach allows the synthesis of different electrochemically produced materials inside
nanochannels, and direct electrical access to an individual nanoribbon without destroying
the template. These templates become the permanent encapsulation, and
contact/interconnect structures of the finished devices. Our group has very successfully
applied this “grow-in-place” approach to produce silicon nanoribbons and nanowires by
the vapor-liquid-solid (VLS) technique.[21] Herein we specifically apply the method to
the fabrication of polyaniline nanoribbons by electrochemical polymerization. The built-
in electrodes of our template structures are used to drive the polymerization and then they
are used to directly obtain, by both two-point and four-point measurements, the resulting
polymer conductivity. In actual array applications, these electrodes would be the final
contact/interconnect structures of the array. Using these same permanent template
structures, we also undertake chemical polymerization of polyaniline allowing
comparison with the electrochemical case. Also we apply this methodology to synthesize
another conducting polymer polypyrrole and compare the result with polyaniline.
4.2 Conducting polymers

4.2.1 Structure of conducting polymers

As noted, conjugation in simple carbon-containing compounds means the presence of alternating single and double carbon-carbon bonds in the molecule. Hence, the simplest conjugated polymer is polyacetylene, but nearly any aromatic or heteroaromatic ring has been used as a monomer unit in conjugated polymers like polypyrrole, polythiophene, polyaniline (Figure 4-1), and their derivatives. Owing to its structural and electronic simplicity, polyacetylene has played a critical role in the theoretical aspects of conducting polymers, but polyacetylene is easily oxidized by the oxygen in air and is also sensitive to humidity. Polypyrrole and polyaniline differ from polyacetylene most notably in that they may be synthesized directly in the doped form and are very stable in air. The reported conductivities of various doped and undoped polymers and metals are presented in Table 4-1.[22]

In a conjugated polymer, the chemical bonding between two carbon atoms in the hybridization state $2sp^2 2p_z$ leads to one unpaired $p$ orbital electron (the $\pi$-electron) per carbon atom, and the unpaired $p$ orbitals of successive carbon atoms overlapped along the backbone leads to electron delocalization. This $\pi$-electron delocalization is what provides the electric pathway for charge mobility along the backbone of the polymer. The essential structural characteristic of all conjugated polymers is this kind of quasi-infinite $\pi$-electron system extending over a large number of recurring monomer units. This feature results in materials with directional conductivity, strongest along the axis of the chain.[3]
Figure 4-1: Some common conjugated polymers (undoped form).

Table 4-1: Conductivity of various conducting polymers and metals.

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold, silver, copper</td>
<td>$\sim 10^7$</td>
</tr>
<tr>
<td>Doped polyacetylene</td>
<td>$\sim 10^5$</td>
</tr>
<tr>
<td>Doped polypyrrole</td>
<td>$\sim 10^2$</td>
</tr>
<tr>
<td>Doped polyaniline</td>
<td>$\sim 10^2$</td>
</tr>
<tr>
<td>Undoped polyacetylene</td>
<td>$\sim 10^{-10}$</td>
</tr>
<tr>
<td>Updoped polyaniline</td>
<td>$\sim 10^{-10}$</td>
</tr>
</tbody>
</table>
4.2.2 Electrochemical polymerization

Among the conductive polymers, polyaniline have drawn considerable interest because of its good environmental stability and satisfactory electrical conductivity when doped. Conducting polyaniline can be formed by the oxidation of aniline at a suitable anode upon application of an adequate positive potential, the mechanism of electropolymerization can be divided into several steps,[23] which are depicted in Figure 4-2. The first step is the formation of the radical cation of aniline by oxidation on the electrode surface which is considered to be the rate-determining step. This is followed by coupling of radicals and elimination of two protons (step 2). The dimer (or oligomer) formed then undergoes oxidation on the electrode surface along with aniline. The radical cation of the oligomer couples with an aniline radical cation, resulting in propagation of the chain. Polymerization proceeds via the radical-radical coupling mechanism, wherein the natural repulsion of the radicals is negated by the presence of other species, such as the solvent, the counter ion, and even the monomer. The oxidized form of polymer contains positive charge carriers, at the same time the positive charge should be compensated by a corresponding amount of negative charge for charge neutrality. This is commonly done by incorporating of anions from the electrolyte solution during the polymerization process which is shown in step 4 which shows the formed polymer doped by the acid (HA) present in solution. Eventually, as the polyaniline chain exceeds a critical length, the solubility limit is exceeded and the insoluble polyaniline precipitates on the electrode surface.
Figure 4-2: Mechanism of electropolymerization of aniline.
In an electrochemical polymerization setup, two or three electrodes are generally used in a solvent with dissolved electrolyte and monomer. As current flows, the polymer is deposited on the anode by oxidation. Owing to the method of preparation, the polymer synthesized by electrochemical polymerization is formed in its conductive form. If it were insulating, the current would stop quite early when the electrode surface is covered with a very thin layer.

The oxidized form of a polymer contains positive charge carriers. At the same time this positive charge in the polymer resulting from oxidation is compensated by a corresponding amount of counter ions $A^-$ to maintain electroneutrality. The counter ions, which are generally called the dopants, are commonly the anion from the electrolyte solution during the oxidation polymerization process. It is to be expected that the size and character of the anion may have a pronounced effect on the quality of the polymer.

Electrodes used for electrochemical polymerization must be selected carefully to prevent electrode oxidation during the experiments. Platinum is often employed as anodes, where the polymerization occurs, due to its resistance to oxidation. That is the reason we choose platinum as our built-in electrode material because the polymerization will occur on the built-in electrode surface in the nanochannels. The adhesion thin titanium layer is not a problem in our structure because it is removed by wet etching right after we removed the sacrificial nickel; hence, the titanium does not have the opportunity to form the wide band gap material titanium oxide to hinder the electropolymerization at our built-in platinum electrode.
4.3 Electrochemical polymerization of polyaniline in nanochannels template

The concept diagram of our permanent nanochannel template structure schematically shown with two nanochannels is in Figure 4-3, and the actual empty nanochannel with built-in electrodes contacts and access regions is presented in Figure 4-4 whose fabrication process detail was described in Section 2.4.1. Conducting polyaniline was synthesized electrochemically in these empty growth-nanochannels of Figure 4-4 by introducing a mixture of monomer and electrolyte into the growth-nanochannels via the access regions and applying an electrochemical polymerization potential through the built-in contacts in the growth-nanochannels. Multiple channels can be created in the form of arrays to provide formation of any number of individual nanoribbons. And multiple-nanoribbon arrays of different materials can be deposited in different channel sets on the same wafer.

Figure 4-3: Schematic concept diagram showing two nanochannel templates with built-in electrodes for electrochemical polymerization and electrical contacting.
4.3.1 Experimental procedure

The deposition and growth of the polyaniline are based on the well-known electrochemical oxidative polymerization, starting with monomer and electrolyte. Aniline monomer was purified by distillation under reduced pressure prior to use and all solutions were made up with Milli-Q grade water right before use. In a typical experiment, the nanochannel template was mounted on a probe station and the contact is established using a platinum probe in the access region serving as the cathode and a built-in electrode.

Figure 4-4: Optical image of an actual nanochannel template region with built-in contacts. Shown are fluid access regions, electrical connections, and a group of five empty channels.
serving as the anode. The probe was precleaned with 2-propanol. A two-electrode setup was used for the deposition. A drop of 5 microliters of aqueous solution containing 0.3 M aniline monomer in 0.75 M HCl electrolyte was placed into each fluid access region by micropipette after mixing the solution in ultrasonic agitation. Then the solution was introduced into channels from the fluid access regions by moving the solution front with micromanipulator. The solution was sucked into the channels by capillary force as soon as the solution front touched the channel opening and the channels remain filled as long as the solution front still touches the channel opening. Special precautions were taken to avoid having the solution flood over the substrate thereby forming conducting polymer on the electrical contacts. Water is more suitable than acetonitrile to be used as the solvent in our template because water has lower vapor pressure and thus the solution will not dry out in the fluid access region immediately due to the large surface area. Electrochemical polymerization was accomplished potentiostatically at +0.45 V by using an HP 4145 semiconductor parameter analyzer, at room temperature, through using Electrode 1 as the anode in Figure 4-4, and the electropolymerization current was monitored simultaneously. A platinum probe placed in the solution in the fluid access region was served as the cathode for the figures of this thesis. However, another built-in electrode can be used for the cathode for more spatially controlled polymerization. The evaporation of water in fluid access region was minimal and did not affect the process at least up to 20 minutes. The solution in access region can be replenished by adding more solution. After electropolymerization, the sample was rinsed with deionized distilled water to remove excess chemicals and then dried in air.
4.3.2 Electropolymerized polyaniline in nanochannels

As the electropolymerization potential +0.45 V was applied to the built-in electrode with the channels filled with the monomer aniline and electrolyte HCl, the conducting polyaniline grew and deposited from the anode electrode and elongated in the channel with time. The heights and widths of the grown polyaniline nanoribbons were predetermined by the heights and widths of channels due to geometric confinement, thus the channels block any dendrite branching during growth. Figure 4-5 and Figure 4-6 show the optical and fluorescent images, respectively, of polyaniline grown electrochemically in five 2.2 µm wide, 55 nm high, 100 µm long channels with four built-in electrodes. These images were seen through the transparent silicon nitride capping layer.

In Figure 4-5, polyaniline nanoribbons, which are shorter than their corresponding channels due to the growth time used, appear in the darker shade because of the higher light impedance than the empty channels under optical microscope. To further visualize the nanoribbon growth, a fluorescein solution was introduced into the channels through the access regions after electropolymerization. Any excess liquid wetting of the capping layer was removed to ensure minimum background fluorescence from the capping layer outer surface. The remaining fluorescein, present in the nanochannels due to capillary action, was then excited by 488 nm laser light in confocal fluorescent microscope. The fluorescein used herein does not stain polyaniline, and the resulting fluorescence was seen in Figure 4-6. The green domains seen in this figure are the emission from fluorescein. A comparison of Figure 4-5 and Figure 4-6 shows that the fluorescein can only fill the empty regions in the nanochannels. Therefore, the green domains correspond
to the regions of the nanochannels unoccupied by polyaniline. Figure 4-6 is seen to perfectly match its optical counterpart shown in Figure 4-5.

Figure 4-5 and Figure 4-6 give insight into the polyaniline electrochemical growth in our Si₃N₄ capping and SiO₂ floor encapsulated growth-channels. The absorption coefficient of polyaniline in thin solid film form has been measured to be less than $5 \times 10^4$ cm⁻¹ across the entire visible range.[24-25] Accordingly, if the polyaniline were in tubular form in Figure 4-6, it would absorb no more than ~12% of either the excitation or emission assuming the most absorptive situation; i.e., the fluorescein is in the middle of the polyaniline tubule. Since no fluorescence is seen where there is polyaniline, the electropolymerized polyaniline cannot be in a hollow tubular structure; i.e., it must be in a solid fibril-form. This is contrary to the tubular structures reported for template-assisted electropolymerization of polyaniline inside the pores (i.e., nanochannels) of porous anodic aluminum oxide (AAO)[26] and track-etched polycarbonate[9, 11] membranes. Formation of tubes in these structures has been attributed to the preferential nucleation and growth of the polymer on the pore walls.[9, 11] In our nanochannel templates, electropolymerization initiates at the anode in the nanochannel and gradually proceeds down the channel in the form of an elongating solid nanoribbon.

Whether a solid nanoribbon or a hollow nanotube is formed is highly related to the interaction between the polymer component and the pore wall where the surface chemistry of the pore wall plays an important role. Martin et al. illustrated an important point: if a “molecular anchor”[27] that interacts with the material being deposited is present on the pore wall, a hollow nanotubule (as opposed to a solid nanoribbon) will be
obtained. For example, Martin et al. showed that Au nanotubules can be electrochemically deposited into the pores of AAO template membranes if a silane that contains a –CN functionality is first bonded to the alumina pore wall.[27] If the –CN containing silane is not attached to the pore wall prior to Au deposition, solid Au nanofibers are obtained in the pores where the –OH groups are on the pore walls. This is due to a weak interaction between Au and the –OH groups. This molecular anchor concept provides a general route for template synthesis of tubular structures. In our template, the solid conducting polymer nanoribbons were obtained which indicate the weak interaction between the electrochemically grown polymer and growth channel wall.

![Figure 4-5: Optical image of five 2.2 µm wide, 55 nm high template channels partially filled polyaniline grown electrochemically inside.](image-url)
The polyaniline nanofibril eventually emerges out of the channels into the access regions, as seen in Figure 4-7 and Figure 4-8 for 4.5 μm wide and 150 nm wide channels, respectively, with longer polymerization times when the cathode is positioned in the access regions. However, it is also possible to fill in the channel partially, and where desired, by halting the electropolymerization earlier as may be discerned from Figure 4-5 and Figure 4-6. As when grown polyaniline emerges out of the nanochannels, the control of geometry of deposited polymer outside the nanochannels is no longer valid.

**4.3.3 Electropolymerized polyaniline emergence out of the channels**

Figure 4-6: Fluorescent image of five 2.2 μm wide, 55 nm high template channels partially filled polyaniline grown electrochemically inside.
Figure 4-7: Optical image of five 4.5 μm wide, 55 nm high channels with polyaniline grown electrochemically inside and extending into the access region.

Figure 4-8: Optical image of five 150 nm wide, 55 nm high channels with polyaniline grown electrochemically inside and extending into the access region.
4.3.4 Current-Time behavior during potentiostatic electropolymerization in channels

The current was monitored simultaneously during electropolymerization of aniline at certain potential. The growing conducting polyaniline in the channels decreases the resistance between the cathode and anode with time, so the electropolymerization current gradually increases with time at fixed applied potential +0.45 V in five 150 nm wide, 55 nm high, and 40 µm long channels as shown in red rectangle in Figure 4-9. The channels were created on insulating SiO₂ layer with insulating Si₃N₄ capping layer, and the floor of the fluidic access region was also the insulating SiO₂ layer, so the current only passed through the solution between electrodes, not through substrate or anywhere else. Figure 4-9 further shows the current-time relationship for different potentials during potentiostatic electropolymerization of polyaniline. The current at noise level does not increase with time with potentials lower than +0.40 V which are shown in blue and green because the potential is not high enough to trigger the electropolymerization of aniline. The electropolymerization starts from the potential +0.45 V which is shown in red rectangle in Figure 4-9. For this potential, the current increases with polymerization time. We report here results for +0.45 V since that potential gave effective electropolymerization of aniline and avoided over-oxidation which causes irreversible loss of conductivity.
4.3.5 Conductivity measurement

After polymerization, conductivity measurements for our polyaniline nanoribbons were undertaken on a probe station using an HP 4145 semiconductor parameter analyzer at room temperature. For this characterization polyaniline nanoribbons residing in the growth-channels and encapsulated with Si₃N₄ capping/SiO₂ floor were directly electrically measured by using the built-in electrodes in two-point and four-point configurations at room temperature. We used the built-in contacts to independently assess the electrical properties of the polyaniline nanoribbons and of the polyaniline/platinum contacts.

Figure 4-9: Current-time behavior during potentiostatic electropolymerization of polyaniline in five 150 nm wide, 55 nm high, 40 µm long channels. Polymerization starts at a potential of +0.45V.
4.3.5.1 Two-point measurement

The two-point measurements were carried out by using two built-in platinum electrodes to measure current while sweeping voltage on the same electrodes. The contact resistance is included in the measured resistance in the two-point measurement configuration. Figure 4-10 shows the resulting current–voltage (I–V) characteristics of the two-point measurement of five polyaniline nanoribbons with dimensions of 55 nm high, 150 nm wide, and 3 µm long. The latter quantity is determined by the spacing between two applied built-in electrodes. The I-V curve is seen to be linear and goes through the origin, and the results are repeatable which indicates the conducting polyaniline nanoribbons did not degrade during measurement. The slopes of the I-V curves are identical at positive and negative voltage which indicates no directional conductivity along the polyaniline nanoribbons. The average conductivity obtained by this direct two-point measurement of five parallel individual polyaniline nanoribbons is 48 S/cm.

Figure 4-10: I–V characteristics of five 150 nm wide, 55 nm high polyaniline nanoribbons measured by an HP4145 in the two-point measurement configuration.
4.3.5.2 Four-point measurement

Four-point measurements were done using four adjacent built-in platinum electrodes contacting the given nanoribbons. These electrodes were all equally spaced 3 µm apart. In this case the current was applied to the outer two electrodes and the resulting voltage difference between the inner two electrodes was measured. The four-point measurement eliminates all concerns about voltage drops at the contacts and allows undisputable determination of the true conductivity of the polyaniline nanoribbons. Figure 4-11 shows the resulting I-V data obtained with the four-point measurement. It is seen to be linear, to pass through the origin, and to yield a four-point conductivity value of 50 S/cm.

![I-V characteristic of four-point measurement](image)

Figure 4-11: I–V characteristics of five 150 nm wide, 55 nm high polyaniline nanoribbons measured by an HP4145 in the four-point measurement configuration.
4.3.5.3 Comparison of two-point and four-point measurement results

Since this four-point conductivity value is essentially the same as that of two-point measurement, this establishes that our metal/polymer contacts are ohmic (negligible series contact resistance) and not Schottky barrier-like. Both the two-point and four-point current-voltage characteristics were found to be unaffected by voltage sweeping rate or sweeping direction, which indicates that ionic conductivity is not an issue.

We note that previously reported electrical conductivity data for conducting polymer nanostructures were mostly obtained using two-contact measurements,[9, 11, 28-29] all of which are subject to contact effects. Most typically these measurements have been done by metallization of the two opposite faces of a template membrane, measuring the I-V behavior, and then calculating the resistance by the number of nanostructures encompassed and their diameters. Another kind of two-contact measurements have also been done using scanning probe microscope techniques which have additional problems coming from variations in contacting force.[30] The other kind of two-contact measurements that have been done use permanent but open templates in an open channel defined in SiO₂, but the I-V curve does not go through the origin for this data.[19] There are two four-point conductivity measurements, which exclude contact effects, known to us for polymer nanostructures. One measures conductivity for films prepared from stacking conducting nanostructures and not for individual nanostructures.[9, 11, 28] However, this approach may result in conductivities even lower than those monitored with the two-point measurement across the template membrane due to the inclusion of voids between nanostructures in the film.[11] The other
is a direct four-point measurement done on polyaniline nanostructures by fabricating Pt microelectrodes by focused ion beam (FIB) deposition. [31] Single polyaniline nanotubule conductivity measurements were performed by Long et al. employing this technique. They established the conductivity of template-free synthesized polyaniline nanotubules of 180/140 nm outer/inner diameter as 31 S/cm. Post-polymerization processing, however, opens the door to possible property changes due to the processing itself. In our approach all contact-forming processing is done before polymer growth. As a result, there is no possibility that the polyaniline properties are modified by processing effects. We also note that the microfluidic-assisted alignment method [32-33] only provides the control of the orientation and location for nanoribbons or nanotubules. In this technique, the dimensions of the microchannels are much larger than that of the pre-grown nanoribbons or tubules, and generally, bundles rather than a single nanoribbon or nanotubule remain after the solvent evaporation. Consequently, electrical characterization of a single nanoribbon or nanotubule becomes difficult with this approach.

4.3.6 The relationship between conductivity and channel width

Using our conductivity assessment methodology, we found the relationship between the conductivity and the channel width for widths from 50 nm to 4.5 µm for the same channel height of 55 nm. These data are shown in Figure 4-12. The polyaniline conductivity is found to be enhanced with decreasing nanoribbon width possibly due to the better alignment of the polymer chains with decreasing cross-section. This
conductivity enhancement trend was also observed for polyaniline nanotubules synthesized (both chemically and electrochemically) in porous membranes. For instance, Delvaux et al., by measuring the bulk resistance across a polyaniline filled membrane with two probes, showed a systematic increase of the conductivity from a few S/cm to \(-90\) S/cm as the average pore diameter was reduced from 220 to 20 nm.\[29\] Martin et al., on the other hand, conducted four-point probe measurements on compressed films of nanotubules extracted from membranes.\[9, 11, 28\] Similarly, they observed a conductivity increase from 9 to 50 S/cm as the average pore diameter was varied from 400 to 100 nm.\[11, 28\] Their 100 nm diameter pores and our 55 nm height by 150 nm width nanochannels are close in cross sectional area, and they both yield polyaniline with a conductivity of 50 S/cm. The conductivity values reported by Delvaux et al. lie around 5-40 S/cm for pore diameters ranging between 150-50 nm. Although lower, these conductivities show reasonable agreement with ours for the same pore/nanochannel cross sectional dimensions, especially when one notes our polyaniline is in the form of nanoribbons and not nanotubules.
We also explored chemical polymerization in our template structures. Figure 4-13 shows the fluorescent image of a template with five 200 nm wide, 55 nm high channels after chemical polymerization of aniline done by introducing 0.8 M aniline in 1 M HCl from left fluid access region, and 0.8 M (NH₄)₂S₂O₈ in 1 M HCl from right access region at 15 °C. The polymerization time was 25 minutes, and the sample was rinsed by DI water after polymerization. Polyaniline was grown chemically when the two solutions met in the channel and is seen in Figure 4-13 to be located near the monomer introduction side (left access region). The polyaniline is seen to have filled the left part of the channel.

4.4 Chemical polymerization of polyaniline in nanochannels template

Figure 4-12: The relationship between conductivity and channel width obtained by four-point measurements.
since the fluorescein is excluded from that region. As we saw for the electrochemical polymerization case, the polyaniline forms solid nanoribbons, not hollow nanotubes, in the channels in chemical polymerization in our templates. Figure 4-13 shows that the polyaniline-filled part of the channel is hindering reactant solution diffusion and thus retarding complete polymer growth throughout the channel. In terms of the efficiency of filling the channels, electropolymerization is superior to chemical polymerization of aniline in our nanochannel templates because in electropolymerization there is no necessity for reactant diffusion through the length of the already grown polymer.

Figure 4-13: Fluorescent image of five 200 nm wide, 55 nm high template channels with polyaniline grown chemically.
4.5 Electrochemical polymerization of polypyrrole in nanochannels template

Polypyrrole is another frequently used conducting polymer in commercial applications, and it can also be formed by the electropolymerization. We used our nanochannels with built-in electrode as the growth template to electrochemically polymerize pyrrole in the same manner as we did with aniline.

Pyrrole monomer was purified by distillation prior to use and all solutions were made up with Milli-Q grade water. An aqueous solution containing 0.1 M pyrrole in 0.2 M H₂SO₄ was introduced into channels from the fluid access regions. Electrochemical polymerization was accomplished potentiostatically at +0.45 V through using built-in electrode at room temperature. A platinum probe placed in the solution in the fluid access region was served as the cathode for the figures of this thesis. After polymerization, the sample was rinsed with DI water and dried in air. The whole experimental setup and electropolymerization mechanism for polypyrrole are the same as those for polyaniline electropolymerization discussed in Section 4.3.

The electrical potential was applied on electrode 1 in Figure 4-14. The polypyrrole was formed on the electrode as the dark shadow near the electrode 1. However, unlike polyaniline, the polypyrrole growth stopped after depositing very thin layer on anode even after very long reaction time or changing different potential, or electrolyte.
This initial growth with subsequent stopping probably results from the polypyrrole overoxidation. Overoxidation is the irreversible, electrochemical oxidative degradation of a conducting polymer. During overoxidation, almost all the beneficial features of a conducting polymer are destroyed. The overoxidation can be ascribed to the formation of oxygen-containing group in the polymer. The carbonyl group (C=O) shown in Figure 4-15 suggesting that the overoxidation rapidly reduces the conjugation of the polymer, leading to a loss of conductivity. The polypyrrole can be reversibly switched between the first three states shown in Figure 4-15 at the electrochemical potential, but the highest oxidation state which is referred to as overoxidized is not reversible. As the
polymer on the electrode is not conducting any more, the electrochemical polymerization process automatically terminates because the electrical current stops.

Since the amount of the pyrrole in the channels is limited by the channel volume and the diffusion of neutral pyrrole to the cathode is not fast enough to consume the electrons provided during electropolymerization, the pyrrole tends to increase the oxidation state. When the growing polypyrrole goes to the irreversible overoxidation state, the polypyrrole becomes the insulating polymer and thus the electropolymerization stops. The oxidation rate for pyrrole is much faster than aniline for electrochemical polymerization, that is why we can have successful electrochemical polymerization of aniline in the channel but not the pyrrole even though they have the same growth mechanism.

Figure 4-15: Oxidation states of polypyrrole.
4.6 Conclusion

We have shown the use of permanent, horizontal, encapsulated, nanochannel growth templates for electrochemically producing arrays of individual polymer nanoribbons with fully controlled dimensions, position, alignment, encapsulation, and electrical contacting. During polymer growth in these templates, the built-in electrodes are used to drive the electropolymerization in pre-selected regions of the growth-template. After growth, our nanochannel templates with their built-in contacts serve as the permanent encapsulation, contact/interconnect structures of the array. We used this “grow-in-place” electrochemical polymerization to specifically produce polyaniline nanoribbons. We explored the polyaniline growth during the electro-polymerization and determined that the growth produced fibrils and not tubes. The fibril growth did not initiate at the template walls but, instead, began in the central region of the growth-channel template cross-section, as the fibril propagated from the anode. In addition we used the built-in contacts of our templates to independently assess the electrical properties of the polyaniline nanoribbons and of the polyaniline/platinum contacts. The resulting electrical characterization, done by both two-point and four-point configurations, gave an undisputable polyaniline conductivity value and also showed that the contact structure we developed is truly ohmic for polyaniline. Using this electrical characterization approach, the polyaniline conductivity was studied as a function of nanoribbon width and found to increase with decreasing width for a given height. This suggests better alignment of the polymer chains with decreasing growth-channel cross-section. We found that electrochemical polymerization in the grow-in-place approach is
superior to chemical polymerization, at least for polyaniline, in terms of efficiency of the filling the nanochannels and process control. In particular, electrochemical polymerization does not suffer from diffusion-limited growth and allows precise placement of the nanoribbons in the growth-channel. We also found that, unlike polyaniline, polypyrrole could not be synthesized in our templates even for very long reaction times. It is believed this is due to polypyrrole’s tending to overoxidize in the channel during electropolymerization.
References


Chapter 5

Summary and future work

5.1 Summary

The objective of this research is to develop a fabrication procedure for producing nanowires and nanoribbons in arrays and circuits without the need for any pick-and-then-place processing. The approach developed uses nanodimensional channels as permanent templates for the formation of nanomaterial arrays with precise dimensional, positional, and orientational control as well as with built-in electrical access, when appropriate. Two versions of these nanochannel templates for the nanomaterial growth were fabricated in this research, and the growth of different nanomaterials in these nanochannels was demonstrated. The approach gives us precise control over nanowire geometry, orientation, and location, and the nanowires can be organic, conducting, insulating, or semiconducting materials, and even the combinations. The procedure is general, allowing the synthesis of different materials inside the nanochannels, and opens the door to “grow-in-place” manufacturing.

In this thesis, we initially demonstrate the feasibility of the fabrication of the first version of our templates, open nanochannel templates which perform nanowire growth, alignment, precise positioning, and geometrical confinement. The detailed process flow of this nanochannel template is described. Field emission scanning electron microscopy
(FESEM) is used for cross-section verification, and fluorescent microscopy for the top view verification of the open nanochannels. The dimensions of the nanochannels can be as small as 20 nm high, 20 nm wide and 200 µm long. We then use these templates to produce polymer and carbon nanowires. In the case of the polymer demonstration, we synthesized Poly(methyl methacrylate) (PMMA) by radical polymerization and polythiophene (PT) by photopolymerization. FESEM pictures of the polymer nanoribbons after polymerization and after removing the capping layer showed the nanochannel templates were open all the way, and can precisely define the dimensions and location of polymer nanoribbons. It was also shown that the polymer nanofilaments can even be released without breaking. The oxygen plasma etching and atomic force microscope tip cutting were used to verify the polymer material. A nanobridge structure was also done by modifying the process flow to make the nanochannel forming material into the nanobridge by proper patterning and etching.

In the case of the carbon nanofiber demonstration, we developed a version of the first nanochannel template structure which has a catalyst segment in the middle. Selecting the sacrificial metal to be the same material needed for catalyst action allows locating the catalyst inside the nanochannels by partially etching. Carbon nanofibers were shown to grow in this nanochannel template with nickel catalyst inside the nanochannels in chemical vapor deposition (CVD) system at 700 °C with mixture feed gas acetylene and carrier gas helium. The composition of the material inside the nanochannels after CVD growth was verified as carbon nanofibers by Raman spectroscopy. The Raman spectroscopy of the capping layer region showed no sign of carbon composition, which proves that what we detected was not the residual amorphous carbon all over the surface,
but the material inside the nanochannels. Energy dispersive x-ray spectroscopy (EDS) was also used to verify the presence of carbon in the carbon nanofiber region. Carbon nanofibers can grow inside and even grow out of the nanochannels. The dimensions, location and orientation of carbon nanofibers followed the pre-designed nanochannels which establish the nanochannel is an effective growth template for carbon nanofibers.

We then developed a second version of nanochannel templates. This version has built-in electrodes and channel access regions. The use of these permanent, horizontal, encapsulated, nanochannel growth templates to electrochemically produce arrays of individual polyaniline nanoribbons with fully controlled dimensions, position, alignment, encapsulation, and electrical contacting was demonstrated. The structure was first verified by an ionic solution to ensure good contacts between the built-in electrodes and the solution inside the nanochannel thereby permitting effective oxidation by current flow. The structure was then used for “grow-in-place” electrochemical synthesis and direct characterization of the produced conducting polyaniline. We found the polyaniline fibril growth in the nanochannel templates did not initiate at the template walls but, instead, began in the central region of the template cross-section, as the fibril propagated from the anode. We also used the built-in contacts of our templates to independently assess the electrical properties of the polyaniline nanoribbons and of the polyaniline/platinum contacts. The resulting electrical characterization, done by both two-point and four-point configurations, gave an undisputable polyaniline conductivity value and also showed that the contact structure we developed is truly ohmic for polyaniline. Using this electrical characterization approach, we found the polyaniline conductivity increases with decreasing width for a given height. The electrochemical polymerization in the “grow-in-
place” approach was shown to be superior to chemical polymerization in terms of efficiency of the filling the nanochannels and process control because electrochemical polymerization does not suffer from diffusion-limited growth and allows precise placement of the nanoribbons in the growth-channel. We also found that polypyrrole, unlike polyaniline, can not be synthesized in our templates because polypyrrole tends to overoxidize in the channel during electropolymerization.

5.2 Future work

The work we have done so far opens up the possibility for exploring useful nanomaterial growth, nanoeletronic devices, and other breakthroughs. Future work can focus on:

(1). Developing more electronic or sensor devices using the conducting polymers or other materials using our nanochannel templates with built-in electrodes.

(2). More applications for the “grow-in-place” architecture and methodology for synthesis of different materials.

(3). Exploring the use of nanochannel templates in producing extruded nanowires with designed dimensions and orientation for the assemblies and integration for devices and circuits.

(4). Developing biological probe, (electro)chemical probe, and nanoelectronics devices of lateral aligned carbon nanofibers.
Appendix

Nontechnical abstract

Nanotechnology is an emerging field of the scientific and engineering research that has roots that have been developing for decades. It offers the promise of letting us fabricate an entire new generation of products that are cleaner, stronger, lighter, and more precise by using nanoscale fundamental building blocks. A promising approach where nanotechnology can lead the way is in the fabrication of nanowires and their assembly into nanoelectronic devices by nanotechnology. Devices based on the nanowires, may find use in applications ranging from molecular electronics to chemical sensors. Over the past few years, nanowires of different materials have attracted much attention, and considerable progress has already been made in their synthesis and their application in devices. However, a significant obstacle in the application of these nanostructures has been the difficulty in handling, maneuvering, and integrating them to form a complete system. The challenge still has to be faced due to the lack of post-synthesis process suitable for the hierarchical organization of these nanoscale building-blocks into functional assemblies and, ultimately, useful systems. If nanowires could be easily aligned, arranged into patterns, and contacts and interconnects set-up, the impact would be tremendous in many areas. Among the most frequently used nanowire synthesis methods used to gain some control of creating nanostructures is the approach to forming nanoscale structures in commercially available porous membranes as the growth
templates which define the diameter and length of the nanowires. Once the membrane is removed and the nanowires liberated from the membrane, one must employ some pick-and-then-place techniques to capture the nanostructures and to position them at the point of use. Such manipulation can be very time-consuming and arduous. There is an urgent need for an engineered approach for better control of manufacturing and assembling of oriented nanomaterials in order to advance to the next stage of nanoscience and nanotechnology.

In this research we developed a fabrication procedure for producing nanowires in arrays and circuits without the need for any pick-and-then-place processing. The approach developed uses nanodimensional channels as permanent templates for the formation of nanomaterial arrays with precise dimensional, positional, and orientational control as well as with built-in electrical access, when appropriate. These nanochannel templates were fabricated by the combined use of top-down process and the sacrificial material approaches. The dimensions of the nanochannels can be as small as 20 nm high, 20 nm wide and several hundreds µm long. Two versions of these nanochannel templates for the nanomaterial growth were fabricated in this research, and the growth of different nanomaterials in these nanochannels was demonstrated.

In the first version of nanochannel templates, we synthesized Poly(methyl methacrylate) (PMMA) by radical polymerization, and polythiophene (PT) by photopolymerization. We also showed the carbon nanofibers grew inside and grow out of this nanochannel template with nickel catalyst in the nanochannels in chemical vapor deposition (CVD) system. Then our second version of nanochannel templates, this version with built-in electrodes and channel access region, was developed. The use of
permanent, horizontal, encapsulated, nanochannel growth templates to electrochemically produce arrays of individual polyaniline nanoribbons with fully controlled dimensions, position, alignment, encapsulation, and electrical contacting was demonstrated. The structure was used for “grow-in-place” electrochemical synthesis and direct characterization of the produced conducting polyaniline. We used the built-in contacts of our templates to independently assess the electrical properties of the polyaniline nanoribbons and of the polyaniline/platinum contacts. The resulting electrical characterizations were done by both two-point and four-point configurations.

The approach we developed in this thesis gives us precise control over nanowire geometry, orientation, and location, and the nanowires can be organic, conducting, insulating, or semiconducting materials, and even the combinations. The procedure is general, allowing the synthesis of different materials inside the nanochannels, and opens the door to “grow-in-place” manufacturing.
VITA

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Chih-Yi Peng was born in Taiwan, on March 21, 1974. She received the B.S.E.E and M.S.E.E. (with honors) from the Department of Electrical Engineering at National Tsing-Hua University, Hsinchu, Taiwan, in 1996 and 1998, respectively. During the period 1998-2001, she worked as a Research and Development Engineer at United Manufacturing Corporation, Taiwan. Chih-Yi Peng began her graduate studies in the Department of Engineering Science and Mechanics, the Pennsylvania State University, University Park, Pennsylvania, USA, in 2001. She has authored or co-authored several papers in nanochannel fabrication, nanomaterial growth in the nanochannel templates.

Chih-Yi Peng’s research interests are nano- and micro-fabrication and processing of devices and materials.