ABSTRACT

MIN, JOONG HEE. Toward Flexible Transparent Conductors Using Metallic Nanostructures. (Under the direction of Dr. Chih-Hao Chang).

Recent advances in science and technology have led researchers to develop both flexible and transparent conductors using various nanomaterials including metals, carbon-based materials, and conducting polymers. Those nanomaterials provide unique mechanical, thermal, electrical and optical properties, but are typically restricted to a single physical domain. Only by using a systemic approach different functionalities across multiple domains can be simultaneously achieved and engineered.

In this dissertation, I demonstrate a comprehensive study on design, fabrication, and characterization of transparent flexible nanostructures using metal materials. Such a structure and material-based approach be an attractive solution due to their excellent structural stability as well as superb electrical and thermal conductivity. Firstly, I present an approach fabricate and control novel complex platinum nanostructures with accordion-like profile on silicon substrate using atomic layer deposition (ALD) and interference lithography. A polymer template with one-dimensional periodic grating profile is prepared as a sacrificial layer for thin conformal platinum film on top, and removed by thermal process. During this template removal process, a unique structural transformation of the nanostructure profile is occurred and a geometric model is suggested to anticipate the final profiles of metal layer. Using different duty cycles and aspect ratios of polymer template, I present a wide variety of cross-
sectional profiles from wavy geometry to pipe array patterns, and electrical characterization of those profiles is performed.

Secondly, as an alternative method to have conformal metal film on nanostructured polymer surfaces, I introduce an approach using conventional physical vapor deposition (PVD). To enhance the step coverage of metal PVD, a thin metal oxide interlayer by ALD is presented. The improvement on conformality and morphology of the metal layer is analyzed using scanning electron microscopy, transmission electron microscopy, energy-dispersive x-ray spectroscopy, and electrical conductivity measurement. Gold thermal evaporation on complex polymer templates using different aspect ratios and deposition speeds is mainly tested, and three different metal oxide layers, which are aluminum oxide, zinc oxide, and titanium dioxide, are examined as adhesive interlayers for better conformal metal coating by PVD technique.

Finally, after completing the steps for fabricating metallic nano-accordion structures on silicon substrate by ALD or conformal PVD, a follow-up process to overcome the limited optical transmission of metallic structures and to transfer the nanostructures onto elastomeric substrate are discussed. By a secondary patterning of metal layer, physical openings on metal layer are created and then, the optical transmittance of microstructured metallic nano-accordions is examined. After transfer step of metallic nano-accordions to soft substrate, the stretchability of the novel metallic nano-accordion structures is tested using a tensile module to confirm the mechanical flexibility. The proposed metallic nanostructures can find their applications not only in flexible or stretchable electronics, but also potentially in photonics and nanofluidics.
Toward Flexible Transparent Conductors Using Metallic Nanostructures

by
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BIOGRAPHY

Joong Hee Min is born in March 23, 1981 in Seoul, the capital of South Korea (Republic of Korea). He received B.S. and M.S. degree in mechanical engineering from Yonsei University, Seoul, South Korea in 2006 and 2008, respectively. Then, he came to U.S. and earned another M.S. degree in biological engineering from Purdue University, West Lafayette, Indiana in 2012.

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Outside of work, he enjoys watching and playing sports, such as baseball, basketball, and golf, and likes to spend his free time in the company of family and friends.
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CHAPTER 1

INTRODUCTION

In recent years there has been significant interest in flexible and stretchable electronics not only from academic or industrial researchers, but also from general consumers for next-generation electronics. The fundamental advantages you can obtain by having this mechanical compliance is that the design of electronics can be much less limited by the geometry of the surface. Typically, most electronics, such as televisions, mobile phones, and notebook computers, need flat and rigid substrates to build up their complex structures and circuits inside, which allows for protection from ambient outside conditions. However, those inflexible substrates have restricted the applications of electronic devices, which aim to be smaller and lighter so that they can give more mobility and have more interaction with their users. Surfaces with uneven or complex geometry, such as rounded, edged, and sharped surfaces, are the next targets to be conquered by new electronics, and consumers want to escape from the constraint of where to put their new devices. Therefore, the new generation of electronics should be able to be placed anywhere the users want without too much occupation of physical spaces.

The mechanical compliance means something more in mechanical point of view; it also demands structural durability. A material with excellent flexibility, such as cloth or rubber, can be more resistant to the external force and it is hard to break it into two because of its mechanical compliance. Many high-tech integrated devices are sometimes too sensitive to mechanical shocks and require too much attentions to retain its functions. For example, a
mobile phone must sustain dropping from hand-high position. This is a very natural consequence of multifunctional devices with complex combination of electronic components inside. However, most of this low durability come from their rigid substrates and can be improving compliance.

In the area of electronic devices, the most actively studied and developed application by leading electronics manufacturers is in the flexible display area. As shown in Figure 1-1(a), there are already many prototype products, which will be introduced to the market very soon. The size of those flexible displays varies from very small ones for wrist smart watches to very large ones which can cover the whole one side of wall in your house. This flexible display can actualize the bendable or rollable display, and carrying an electronic newspaper in your pocket is not the story of scientific fiction novels or movies anymore.

Flexible electronics can also be a novel platform to help generate energy. The common solar panels have very rigid supporting bases and need a certain area of flat place to hold their components. However, if the substrate of solar panels has flexibility and lightweight, as an example in Figure 1-1(b), there will be less limitation of space or location to install the solar cell system. They are made of organic/polymer photovoltaic cells and the thickness is only about 200 µm in total. They are fabricated as a module or printed on the desired surfaces, so that the consumers can install them on any shapes of building roofs and any geometries of surfaces, such as rounded pillars, uneven grounds, and edged corners. Also, the wearable solar cells and the embedded solar cells in clothes are another examples of flexible electronics that can generate energy. They can be used for military applications, such as supplying power to
electronic devices while walking in the desert, or for charging smartphones when the users are outside with sunlight.

Figure 1-1. Examples of flexible electronics: (a) flexible display with 18 inch and 55 inch diagonal screens by LG Display, and (b) flexible solar panels by VTT Technical Research Centre.

This mechanical flexibility can be easily miscounted as an excessive function for those electronics. In other words, one can claim that this function is only for certain circumstances or specialized applications, and not needed for general use of these electronics. However, when it comes to the applications for interaction with human bodies, it performs a more fundamental and essential function. Researchers have been trying to develop wearable electronics which
can collect biometric data from human body, such as heart rate, brain wave, and body temperature, or can complement human activity by giving them more information right on their side, for example, smart watch, smart glasses, and smart clothing.

Two examples of recently developed wearable devices are presented in Figure 1-2. The first one is a so-called “smart skin”, which can stick and stretch like a temporary tattoo in Figure 1-2(a) [1]. This skin-mounted electronics can collect biomedical signals, including electroencephalogram (EEG) and Electromyography (EMG), and monitor user’s nerve and muscle activity. The biggest benefits from this electronics are that they are much more comfortable than traditional patch-type electrodes and give to the user the freedom of movement. The second example shown in Figure 1-2(b) is also for healthcare application, which is named imperceptible electronics [2]. They made the ultrathin film-like organic transistor integrated circuits, and they are extremely light, flexible, and durable so that you can attach to any surface without limitation from non-flat geometric profiles.
The common aspects among those many different types of flexible electronics are that they are thin enough to be flexible or stretchable and their base materials are not the ones for conventional rigid electronics. These two important requirements have led the researcher to approach to develop flexible electronics in two major ways that has been enabled by nanoscale materials research: a material-based approach and a geometry-based approach. In following sections, I will explore more in details about those approaches.

1.1 Approaches to Enable Flexible Electronics

1.1.1 Nanomaterial-Based Approach

One strategy to achieve mechanical compliance is to disperse zero-dimensional (0D), 1D, and 2D nanomaterials onto elastomeric substrates such as polydimethylsiloxane (PDMS) or
polymer-based materials [3]–[7]. In particular, nanomaterials with excellent electrical conductivity, such as nanoparticles [8]–[10], carbon nanotubes [11]–[13], and graphene [14]–[18], have been widely studied. This approach allows the combination of electrical conductivity of the nanomaterials and the mechanical compliance of the polymer substrate resulting in a multifunctional material.

Figure 1-3 shows examples of those material-based research works to achieve flexibility on electronic devices. Carbon-based materials are the most popular subjects to be introduced to fabricate flexible conductors due to its superb electrical property. Figure 1-3(a) presents one research work using graphene films to develop transparent, elastic organic light-emitting device (OLED), which can be repeatedly stretched with maximum strain of 106% in horizontal direction, folded and twisted while remaining lit, and the optical transmittance of this device is about 90% at wavelength of 670 nm [14]. Metal based nanowires, nanoparticles and alloys are another widely used materials for flexible devices. As shown in Figure 1-3(b), highly sensitive and wearable sensors were accomplished by applying thin silver nanowires layer onto flexible soft substrate, and found applications in monitoring thumb movement, sensing the strain of the knee joint in patellar reflex, and detecting many other human motions [19].

Also conducting polymers including polyaniline (PANI) [20], [21], polypyrrole (PPy) [22], and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) [23] are widely researched for stretchable electronics. One example in Figure 1-3(c) utilized PANI nanofiber and created electrodes that can have more than 80% of axial strain. In this work, the nanofibers were spray deposited onto pre-strained flexible electrodes, and by controlling voltage applied
to the electrode, it can be expanded and restored with high repeatability and low conductivity drops [21]. However, in these approaches the nanomaterials are hard to control precisely, much more expensive than other conductive materials, potentially harmful for human body, and may delaminate from the substrate over time.

![Figure 1-3](image)

Figure 1-3. Examples of nanomaterial-based approaches to flexible electronics: (a) stretchable OLED devices using graphene [14], (b) metal nanowire based biosensors [19], and (c) PANI nanofiber electrodes [21].

Another effective method to generate nanoscale films with well-known materials, such as metals, oxides, and ceramics, is atomic layer deposition (ALD), which can treat and functionalize surfaces of fabricated nanostructures and nanoscale devices with an ultra-thin material layer [24]–[26]. Typical ALD processes are based on the sequential use of two different chemicals, which called precursors, in gas phase. One cycle of ALD is composed of exposing a target surface with each chemicals separately, and by controlling the number of
cycle, the final thickness of new material can be precisely determined. Using this benefit of ALD, many research groups have fabricated three-dimensional nanostructures including micro/nanolattice structures [27]–[29], photonic crystals [30], and nano-accordions [31]. In these processes, a broad range of materials (TiN, Al₂O₃, ZnO, etc.) were deposited onto sacrificial polymer templates, which are subsequently removed. The resulting final nanostructures consist of non-polymer material, and can have better physical properties when compared with the original polymer template. These advances have led to low-density materials with enhanced stiffness [27]–[29], better photonic response [30], and stretchable transparent conductors [31]. The details of films processing using ALD will be described in more details in section 1.3.

1.1.2 Geometry Based Approach

Beyond nanomaterials, the second approach utilizes nanostructure geometry to increase flexibility of conducting materials [1], [19], [32]. This is analogous to a macroscale spring, which can untwine and unfold to increase stretchability. However, the key is to reduce the feature size of the spring geometry, which will be also facile integration into electronics and displays. Using wavy geometries caused by strain–release–buckling process, the semiconducting or metallic structures can be stretched, compressed, and bent without property degradation.

As shown in Figure 1-4, many different materials from metals to nanomaterials can be used to have this wavy geometries. First, the example in Figure 1-4(a) demonstrated a stretchable form
that consists of thin silicon films structured with wavy geometries in sub-micrometer scale on an elastomeric substrate [33]. By changing the amplitudes and periods of the waves, substantial strains in the silicon itself can be avoided. Using this method a new class of wavy electronic devices, including metal oxide semiconductor field-effect transistors (MOSFETs) and p-n diodes, were successfully demonstrated. In second example of Figure 1-4(b), three-dimensional nanoribbons were created by using elastic deformations of a supporting substrate to induce well-controlled local bucklings [34]. These structured single-crystal silicon and gallium arsenide (GaAs) nanoribbons showed extremely high stretchability, compressibility, and bendability.

Expanding on this approach, nanomaterials discussed in previous section can yield even more flexibility with help of geometric transformation. In Figure 1-4(c), carbon nanotubes (CNT) was prepared on pre-strained PDMS substrates and after releasing the wavy ribbon structures were achieved [35]. Due to the excellent mechanical and electrical properties of CNT, the resistance increased only about 4.1% even after using a substrate with pre-strain of 100%. In this case the connectivity was sustained even when stretched, folded, or twisted to a large extent. However, in most of geometry-based approaches, the wavy or curly structures are typically in the microscale, and it is difficult to control the buckle geometry precisely.

More random structures can also be employed in the same prospect. As in Figure 1-4(d), stretchable and transparent gold nanomesh electrodes on elastomers were fabricated by grain boundary lithography, which utilizes the grains of indium deposited on silicon oxide layer as a physical mask and obtains a gold layer only on their boundaries after lift-off process. The
nanomesh 2D structure exhibited good electrical conductivity as well as transparency since it is composed of fully interconnected metal wires [36]. Although this gold nanomesh showed good stretchability and repeatability from the nature of noble metal, the unsystematic geometry can scatter light randomly and will result in optical haze. Therefore, it is expected that more engineered and ordered geometry will allow more systemic improvement of its flexibility as well as optical transparency.

Figure 1-4. Examples of geometry-based approaches to flexible conductors: (a) stretchable form of single-crystal silicon on rubber substrate [33], (b) semiconductor nanoribbons with controlled buckling [34], (c) wavy ribbons of carbon nanotubes [35], and (d) gold nanomesh electrodes [36].
1.2 Transparent Electronics

Transparent electronics have been studied along with the developing trends of flexible electronics since the enabling technology is also based on the materials and geometry. Recent advances in science and technology have led researchers to develop both flexible and transparent electronics using various nanomaterials including metals, carbon-based materials, and conducting polymers.

Figure 1-5 presented many types of transparent electronics that can be useful and widely applied in various field. For example, if the display is transparent as in Figure 1-5(a), one can expect more interaction between the information on screen and the real world. If it’s installed on the show windows in the department stores, a shopper can not only see the product inside it, but also have the information about the product, such as brand, price, and materials, using transparent displays.

One of the primary drivers for transparent display is augmented reality (AR) and mixed reality (MR) technology, which requires transparent electronics because the interaction between real world and information from device is the most important factor in enabling this technology. As the examples in Figure 1-5(b) and (c), using smart goggle or transparent smartphone, the user can design 3D objects, visualize information beyond the size of the monitor, play video games with holographic images, and even watch 3D movies in real 3D spaces. In near future, these functions can also be possible not by using weighty goggle-type electronics but by using light and soft contact lens electronics.

Transparency also means that the device will not block the view in terms of visibility across
broad wavelength band. As shown in Figure 1-5(e), a transparent solar panel can be installed even on glass windows without defacing or degrading exterior of buildings [37]. This is one example that surpass the placing limitation of a certain electronic device by having optical transparency. This visibly transparent luminescent solar concentrator devices selectively harvest NIR photons based on fluorescent organic salts, and emit another wavelength of infrared light to be guided to the edge of solar cell. The optical transparency of this device was measured over 86% in the visible light spectrum.

In most existing work, the nanomaterials used for fabricating flexible electronics are basically opaque materials. However, the device transparency can be controlled by changing the material concentration or thickness. Carbon-based materials, such as CNT [38]–[42] and graphene [17], [43], [44], can offer high optical transmission by lowering concentrations on substrates, and so do ultra-thin metal-based materials, such as metal NW [45]–[52] and film [8], [53], [54]. Also, conducting polymers can be synthesized to obtain better transparency [55]–[59]. However, in these techniques the device transparency and flexibility are coupled. The question is that whether the mechanical compliance and optical property can be engineered independently.
1.3 Strategy to Enable Flexible and Transparent Electronics

The overarching goal of my research is to achieve both flexibility and transparency by combining material-based and geometry-based approaches. This work will be based on thin metal film using ALD and other physical vapor deposition (PVD) techniques. For applications requiring better electrical and thermal conductivities and less brittleness, metal nanostructures can be an attractive solution. Various studies have shown ALD fabrication of thin conductive layer consisting of gold [60], nickel [61], [62], tungsten [63], [64], or platinum [65]–[70] for electronics, solar cell components, and sensor devices. In these applications, the advantages of
metal ALD including low resistivity, high purity, and excellent conformity can be specifically utilized. Others have also demonstrated freestanding metal nanostructures, including nickel nanotube [71], ruthenium nanowire array [72], and platinum nanobridge [73].

The possibility of my approach to achieve both electrical conductivity and transparency by rendering metal layer can be positively expected from current work in the literature. Leosson et al. utilized an ultra-thin gold film on special optical polymer called BCB (or Cyclotene-3000 polymer by DOW Chemical Co.) with 75% transmittance at 530 nm [53]. Compared to the bare glass (SiO$_2$) substrate, the gold on BCB polymer formed smaller and more densely packed islands, as shown in Figure 1-6, and the sheet resistance was only 86 Ohm/sq with 4.2 nm thickness. However, to have more transparency without any electrical conductivity drop on my nanostructures, the more systemic geometry-based approach using nanolithography will be employed to help the proposed material-based approach.

Figure 1-6. SEM images of gold films on SiO$_2$ (top row) and BCB polymer (bottom row) at different deposition thickness [53].
In previous work of our group, we fabricated multifunctional nano-accordion structures exhibiting a unique combination of conductivity, stretchability, and transparency through a combination of interference lithography and atomic layer deposition [31]. More than 50% stretchability and up to 70% broadband optical transmission were demonstrated. However, the electrical conductivity was relatively low and the stretchability was limited by the brittle nature of oxide materials. While I will change the materials to metals, the geometric strategy using interference lithography for having potentially stretchable and foldable nanostructures will remain the same with additional hierarchical modification. Metal is excellent in electrical properties, however, limited in optical properties due to its high reflective nature. To overcome optical drawback, there will be physical windows in microscale on the metal layer while sustaining its high electrical conductivity.

The primary technique in defining the nano-accordion geometry is interference lithography. The schematic of the Lloyd’s mirror interferometer to lithographically define periodic grating template is shown in Figure 1-7(a) [74], [75]. The period (Λ) of fabricated template can be designed by the principal of interference of two coherent plane waves to form an intensity pattern as follows:

$$\Lambda = \frac{\lambda}{2 \sin \theta}$$

where λ is the wavelength of light source and θ is the incident angle. As shown in Figure 1-7(b), different 1D and 2D periodic patterns can be readily fabricated by controlling expose conditions as well as experimental setup. Compared to the wavy geometry by strain–release–buckling process, the grating geometry by interference lithography can be more systematically
and precisely controlled in nanometer scale. Therefore, the added design freedom can lead to more flexibility from novel metallic nanostructures with combined approach using lithographic patterning and precise metal deposition process.

Figure 1-7. (a) Lloyd’s mirror interferometer, (b) SEM images of 1D and 2D periodic nanostructures fabricated by Lloyd’s mirror interferometer.

1.4 Dissertation Structure

In this dissertation, I will present my research works on design, fabrication, and characterization of transparent flexible metallic nano-accordion structures. In this chapter, I introduced the background of flexible electronics and transparent electronics separately so that I can insist those two different properties cannot be achieved readily without systemic approach. Then I briefly showed my strategy to reach my ultimate research goal, which is to fabricate a better transparent flexible conductor with combination of material-based and geometry-based approaches.
In Chapter 2, I will discuss about the fabrication process of metallic nano-accordion structures using interference lithography (IL) and metal atomic layer deposition (ALD). In this approach, first a sacrificial polymer template will be lithographically fabricated to have an accordion-like surface profile, which will be deposited with a thin metal film. Then, the coated platinum (Pt) layer will be characterized to confirm its metallic nature. The thermal process to remove polymer template and leave metal film only will be studied since the Pt layer undergoes a unique deformation during this process. To control the geometry of final metal nano-accordion structures, the profiles of polymer template will be fabricated along with first-order geometric modelling. The experimental results will be compared with the models. Later, the final profile map of Pt nano-accordion structures by geometric factor will be suggested and electrical characterization of fabricated Pt nanostructures will be discussed.

In Chapter 3, I will demonstrate another method to have conformal metal films without using metal ALD. This approach is based on physical vapor deposition (PVD) and developed to overcome several disadvantages of metal ALD, while retaining advantages of general PVD techniques. The poor step coverage of PVD will be improved through this method, which allows more choices of depositing metal materials to create the final metallic nano-accordion structures. Using different test conditions, my new approach of conformal PVD will be analyzed and various types of microscopic tools will be utilized to show the enhancement by this approach. The detailed electrical characterization on fabricated metal layer by new process will be performed to confirm this process as an alternative way to have conformal film layer.
In Chapter 4, first, I will present the whole fabrication process for transparent and flexible metallic nano-accordion structures. Then, as one part of it, a detailed step for improving the optical transmission of metallic nanostructures by making physical opening will be discussed. The optical characterization of the nanostructures will be performed to verify its increased transparency. After that, a transfer step of the nano-accordions from silicon substrate to elastomeric substrate will be demonstrated. With help of this soft substrate, the mechanical properties of the nanostructure will be characterized and the high stretchability will be finally confirmed.

In Chapter 5, a colloidal lithography, the more complex IL technique for fabricating 3D periodic nanostructure will be demonstrated. The repeated 3D periodic patterns generated by colloidal monolayer will be analyzed using a finite element based simulation tool, and the more freedom of design on 3D periodic structures will be investigated. Based on the simulation design, the actual nanostructures will be experimentally materialized in negative photoresist. Finally the detailed comparison between analytical, numerical, and experimental data will be discussed.
CHAPTER 2

DESIGN AND FABRICATION OF METALLIC NANO-ACCORDION STRUCTURES

In this chapter, I will introduce a process to fabricate and control novel free-standing 3D metal nano-accordion structures using ALD and interference lithography (IL) [76]. In this approach, a lithographically defined periodic grating functions as a geometric template for conformal ALD coating of platinum (Pt). The polymer is subsequently removed using a thermal treatment process, leaving behind a free-standing metal structure with an accordion-like geometry. The profile of the final structure can take many forms and is determined by the polymer template and coating layer. The template feature height and width have dominant influence, and can be readily and systematically controlled by the lithography process. The complex nature of the structure profiles can potentially find applications not only in flexible/stretchable electronics, but also photonics and nanofluidic devices.

2.1 Fabrication Process

The proposed fabrication process is illustrated in Figure 1, with corresponding scanning electron micrograph (SEM) images in the inset. Initially, 90 nm thick antireflection layer (ARC i-CON-7, Brewer Science, Inc.) were spin-coated on a silicon wafer to prevent back-reflection during lithography, and 500 nm of SU-8 (Microchem, Corp.) were spin-coated as a buffer layer. A buffer layer of fully cross-linked SU-8 was used to improve adhesion template structure. On
top of the two layers, the target SU-8 layer was spin-coated and soft-baked at 95 °C. Then, 1D periodic photoresist structure were patterned using a Lloyd’s mirror IL with 325 nm laser (HeCd UV laser, Kimmon Koha Co., Ltd), as shown in Figure 2-1(a) [74], [75]. The structure period, height, and feature width can be controlled by exposure angle, resist thickness, and exposure dose, respectively. For most cases described in this chapter, the SU-8 polymer template was patterned with 1 μm period and the range of exposure dose from 3~6 mJ/cm² was used to control the template feature width. After exposing process, the samples were post-expose-baked at 65 °C, developed with propylene glycol monomethyl ether acetate (PGMEA), and rinsed in Isopropyl Alcohol (IPA). After lithography, a hard bake at 210 ~ 220 °C was performed to fully crosslink the photoresist to improve material stability (For more information on fabrication process recipes see Appendix A).

The polymer structure was then deposited with a conformal Pt layer using ALD, which is the sole structure remaining after a subsequent thermal treatment process, as illustrated in Figure 2-1(b) and (c), respectively. The Pt ALD was performed at 1 Torr and 200 °C using (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe₃) as a precursor and ozone (O₃) as a reactant gas (For more information on ALD recipes see Appendix B).

The cross-sectional SEM images in Figure 2-1 illustrate the Pt nanostructure fabrication results after each processing steps. Here the period of SU-8 grating is 1 μm, and the width and height of the grating are 500 nm, achieving a duty cycle (DC) of 50% and an aspect ratio (AR) of 1. The DC is defined as a fraction of a feature width over one period, and the AR means a fraction of a feature height over its width. A thin alumina interlayer (t ~ 2 nm) can be deposited using
ALD over the resist template to enhance surface reaction and material chemistry [70], [77].

For better film quality and consistent thickness of metal layer, the presence of interlayer is extremely important during metal ALD process. The detailed Pt deposition results with and without alumina interlayer will be demonstrated layer in this chapter. The interlayer is followed by 20 nm of Pt deposition, both using ALD. As shown in the SEM images of Figure 2-1(b), the Pt grating structure on the resist template has high fidelity and good morphology throughout the whole sample with uniform thickness. Here the sample area is limited by the lithography setup, and is around 1 inch by 1 inch in this work. After polymer template removal process using convection oven at 550 °C, a high temperature which can evaporate and remove SU-8 polymer template, a free-standing metal nanostructure resembling an accordion remains on the silicon substrate, as shown in Figure 2-1(c). The overall cross-sectional profile and period of the Pt structure has no significant changes in all aspects, however the structure width was reduced by about 50%, which is obviously happened by evaporating polymer template during thermal process. In this case the SU-8 photoresist functions as a sacrificial template for fabricating and shaping the resulting thin nanostructured films.
2.1.1 SU-8 Negative Photoresist

The negative-tone photoresist SU-8 was selected as the polymer template material due to its high glass transition temperature. This is important since a relatively high process temperature is required for Pt ALD. In most Pt ALD processes, Pt film deposition involves surface combustion and dehydrogenation reactions with the use of (methylcyclopentadienyl)trimethylplatinum(MeCpPtMe$_3$) and molecular oxygen (O$_2$) at elevated temperatures $>$ 300 °C [65], [66], [78], [79]. However, lower reaction temperatures can be realized through the use of plasma-excited species (e.g. H$_2$, O$_2$) or ozone (O$_3$) [67]–[70]. Films produced with these alternative counter-reactants are metallic Pt with minimal contamination, exhibit high electrical conductivity, and may be formed at lower temperatures, making their use ideal for Pt
ALD on temperature-sensitive substrates such as polymers in our case. Based on these benefits, by using O$_3$ as the reactant gas we successfully deposited metallic Pt layer on top of SU-8 template at just 200 °C, which is under its glass transition temperature. The template profile fidelity were verified using electron microscopy.

After the ALD process, a thermal treatment process in a convection oven was used to remove the SU-8 template under platinum layer. A differential scanning calorimetry (DSC) test was performed for planar SU-8 layer on Si substrate with and without the ALD Pt layer on the surface to monitor the polymer removal process. The results indicate efficient removal of SU-8 at around 450 ~ 600 °C [80]. As shown in Figure 2-2, the DSC result showed that a peak at around 500 °C can be observed for both cases, which indicates a phase change of SU-8 to gas. More important the similarities in other peaks indicate that the Pt layer does not affect upon this thermal transition of polymer layer. Accordingly, a thermal process at 550 °C to remove polymer template was used to yield free-standing metallic Pt nano-accordion structures. The thermal stability of Pt nanostructured at higher temperature than 550 °C was also examined and demonstrated in section 2.5.
Figure 2-2. Differential scanning calorimetry (DSC) result of SU-8 layer with and without platinum layer on top of it.

2.1.2 Aluminum Oxide Intermediate Layer

The thin interlayer of aluminum oxide plays a critical role in the quality of the Pt ALD process. The first platinum ALD coating on polymer grating template was processed without employing intermediate Al₂O₃ layer. In these samples the Pt layers had relatively rough surface morphology, as seen in the SEM image of Figure 2-3(a). Such morphology was not observed when the same Pt ALD process was used on bare silicon and silicon oxide substrates. In addition, the thickness was only around 10 ~ 15 nm after 630 cycles of Pt ALD process, while it was expected to be 30 nm with a normal Pt deposition rate of 0.6-0.7 Å per ALD cycle [68]–[70]. The structure profiles also changed dramatically because the platinum nuclei adhere poorly to the polymer template directly. The X-ray photoelectron spectroscopy (XPS)
measurements confirmed that the top layer is not pure Pt, since there is a weak peak for metallic Pt at 71.0 eV but a strong peak for oxygen components, indicating the presence of oxides (PtO\textsubscript{x}) at 529 ~ 530 eV [68], as in Figure 2-3(b).

![Figure 2-3. (a) SEM image of Pt Oxide film after direct Pt ALD coating on polymer template without intermediate layer of Al2O3 (b) XPS result for Pt Oxide film.](image)

While the Pt oxide samples can also yield similar nano-accordion structure, they resulted in poor structure fidelity after template removal. First, they are typically more flexible and forms a round-edged nano-accordion structures, as seen in Figure 2-4(a). For AR > 1, the two sidewalls collapse together and round ceiling result in a perfect circular profile, shown in Figure 2-4(b). However, the structure has significant film discontinuity due to cracking. Second, Pt oxide nano-accordions (t ~ 20 nm) have no absorption in the visible spectrum, a characteristic of metallic films and are mostly transparent. Also, the structure resistivity is significantly higher than Pt film and the calculated resistivity was around 10 Ω·cm, which obviously shows its non-metallic electrical property.
Based on these results, it can be concluded that Pt ALD directly on the polymer template yield poor material film. To promote surface reaction, an intermediate alumina layer (Al₂O₃) between the resist and Pt layers was introduced by ALD (For more information on ALD recipes see Appendix B) in all samples. This resulted in better Pt film morphology, electrical properties, and consistent thickness, as shown in Figure 2-5(a). This is believed to be attributed to good nucleation and film growth of metallic Pt on alumina surfaces. [70] XPS measurement was performed for the new sample to examine the elemental composition of the thin Pt layer as depicted in Figure 2-5(b). A strong binding energy peak of ~ 71.0 eV can be observed, indicating that the film composition is pure metallic Pt [68]. The alumina interlayer was not detected by XPS due to the limited thickness resolution. Small peaks in the measurements indicate other elements such as oxygen and carbon, but are negligible.

To examine the electrical properties, the sheet resistance of Pt nano-accordion structures were characterized by four-point probe system. Four-point probe technique is widely used in measuring sheet resistance of thin flat films, and compared to the radius of probe tip, which is
generally in micrometer scale, the fabricated Pt nano-accordions has much smaller structures and can be regarded with uniform planar metal film with a negligible roughness. The sheet resistances of the 20 nm-thickness Pt nanostructures on polymer template prior to the template removal process is 10.45 Ω/square, yielding a calculated film resistivity of 20.9 μΩ·cm. After the template removal process to remove the underlying SU-8, the resistivity remained about the same and measured 20.7 μΩ·cm. These data were measured with the probes parallel to the structure ridge direction. For comparison, the sheet resistance of planar 10 nm-thick Pt film on SU8 was measured to be 20.0 Ω/square, yielding comparable resistivity of 20.0 μΩ·cm. The measured data are summarized in Table 2-1.

These characterizations verify the material purity and metallic nature of the Pt nanostructure, as well as its uniformity of quality for different template geometries. It also highlights the importance of the alumina interlayer on the material composition of the ALD deposited Pt film. The measured electrical conductivity of our Pt nano-accordion structure is comparable to that of the most recent works on stretchable electronics with existing conductive nanomaterials, such as metal nanowire [47], [51], [81], [82], carbon nanotube [13], [39], [83], [84], and graphene-based [17], [44], [85] electronics.
Figure 2-5. (a) SEM image of Metallic Pt film on polymer template with intermediate layer of Al2O3, (b) Experimental XPS data of thin Pt structure deposited using ALD. A binding energy peak at 71.0 eV indicates pure metallic Pt.

Table 2-1. The sheet resistance and resistivity of platinum planar film and nano-accordions.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Thickness</th>
<th>Sheet Resistance (Ω/square)</th>
<th>Resistivity (μΩ·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar Pt on SU-8</td>
<td>10 nm</td>
<td>19.50</td>
<td>19.50</td>
</tr>
<tr>
<td>Pt Nano-Accordion before Template Removal</td>
<td>20 nm</td>
<td>10.45 ($R_{∥}$)</td>
<td>20.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.82 ($R_{⊥}$)</td>
<td>21.64</td>
</tr>
<tr>
<td>Pt Nano-Accordion after Template Removal</td>
<td>20 nm</td>
<td>10.34 ($R_{∥}$)</td>
<td>20.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.86 ($R_{⊥}$)</td>
<td>21.72</td>
</tr>
</tbody>
</table>
2.2 Geometric Control of Metallic Nano-Accordions

2.2.1 Structural Deformation during Template Removal

The effects of resist template geometry on the final Pt nanostructure were investigated. Two normalized geometric parameters, duty cycle (DC) = width/period and aspect ratio (AR) = height/width, were considered. The DC can be controlled by varying the energy dose. The grating has rounded tops to resemble sinusoidal waves, as observed in Figure 2-6(a) and (b), but changes to flat tops to resemble square waves when the energy dose was increased to obtain a higher DC, as in Figure 2-6(c) and (d). In my experiments when the DC is just over 50%, the rounded top grating was achieved, and when DC is higher than around 60%, the flat top grating was generated due to the nature of negative-tone photoresist when the energy dose is high enough. Therefore at high energy dose essentially the more resist contrast was accomplished, which leads to sharper corners. Such a template structure induced a unique geometric deformation of the metal film during template removal after ALD process.
Figure 2-6. SEM images of polymer templates with (a) DC < 50%, (b) DC = 50%, (c) DC = 60%, and (d) DC = 70%. Round-top templates were formed when DC < 60%, and flat-top templates were formed vice versa.

The fabricated metal nanostructures can have complex profiles after the template removal process. Figure 2-7(a) depicts a SEM image of the resist template with DC = 60% and AR = 0.83 before ALD. Significant changes in the resulting Pt structure profile were found after ALD and template removal processes, as shown in Figure 2-7(b). In this case the grating failed to retain its original shape, unlike the case of round tops in Figure 2-1. Figure 2-7(c) shows a part of the sample after incomplete template removal under the Pt structure, caused by temperature gradient on polymer gratings. The structure deformation and collapse mechanisms can be identified by comparing each grating unit cell. The units on the left have more residual
polymer and are observed to be less wrinkled compared to those on the right, offering a progression of the collapse process as polymers are removed. It can be observed that as the template is removed, the side walls and the ceiling collapse towards the center as the structure becomes wrinkled, creating a unique cross-sectional profile. Based on these results, the template geometry can be designed to control structure collapse and engineer the resulting Pt nanostructure.

Figure 2-7. SEM images (1 μm scale bars) of (a) Pt coating on resist template surface, and (b) Pt nano-accordion after template removal. (c) A region showing incomplete template removal and transition of structure deformation process.
2.2.2 Geometric Model

In order to further study the profile formation process of the metal nano-accordions, we propose a first-order geometric model, as illustrated in Figure 2-4(a). The key deformation mechanisms are the vertical sagging of the top ceiling and lateral collapse of the side walls associated with the template removal process, where the Pt films undergo structural wrinkling caused by the surface tension of evaporating SU-8.

Based upon this mechanism, a uniform structure collapse rate ($v$) for the top and side walls of the grating unit is defined. As depicted in Phase I of Figure 2-8(a), the structure starts to deform as the polymer template is being removed and the shape change occurs on both the top ceiling and the side walls. During the template removal process the wrinkling on ceiling and walls gets more pronounced (Phase II), finally resulting in the complex shape in Phase III, which was experimentally observed in Figure 2-7(b). Based upon the proposed model, the structure profiles of Pt nano-accordions can be predicted by the grating width and height of the initial resist template, as illustrated in Figure 2-8(b).

In the case with AR < 1, the ceiling would collapse before sagging of side walls. When AR > 1, the two side walls merge before the ceiling collapses. In the intermediate regime where AR ~ 1, the ceiling and side walls are expected to collapse together. It is important to note that this model is restricted to flat-top template, and the wavy profile will not experience a significant geometric change for the round-top templates. In these cases, such as those shown in Figure 1, the round curvature is more mechanically stable and is only expected to reduce in width, as illustrated in Figure 2-8(c).
2.3 Variety of Cross-Section Profile

To test the models for both flat-top and round-top templates, samples with height ranging from 300 nm to 1200 nm and width from 100 nm to 750 nm were fabricated, representing AR from 0.4 to 5.0. Figure 2-4 shows comprehensive cross-sectional SEM images of the various metal nano-accordion profiles after template removal. The SEM images of the corresponding resist templates are shown in the inset diagrams. Two different top shapes were generated by controlling the duty cycle of the grating on the resist template. Flat-top templates were fabricated with DC = 60%, and round-tops were created with DC = 50%. The aspect ratios were controlled by varying the thickness of the resist template, exposure dose, or isotropic plasma etching.
2.3.1 Flat-Top Template

For flat-top templates, the AR was controlled by varying the resist thickness from 300 nm to 1200 nm while fixing the template width as 600 nm. The general case of flat top is shown in Figure 2-9(b), where the template used has an intermediate AR = 0.83. The final Pt structure resembles a sprout-like shape, indicating the ceiling sagging and side-wall collapses merged and terminated at around the same time.

For the case of a template with lower AR = 0.5, as shown in Figure 2-9(a), the ceiling completely collapsed prior to the wall and the final profile resemble mushroom-like shape. Also the deformation of the walls was believed to be induced not by the evaporated polymer template, but by the ceiling collapse. In the opposite extreme, a higher AR = 2 resulted in a T-like shape, as shown in Figure 2-9(c), since the side wall collapses occurred prior to the ceiling. These results follow the general trend predicted by our geometric model described in previous section.

It is expected that there will be less deformation or sagging of ceiling part when the AR is much lower than my lower extreme cases because of the limited amount of polymer template and less removal time in that case. In the same manner, if the AR is much higher than 2, which is my higher extreme case, the deformation of wall might not be dramatic as before and less deformation or collapse will be occurred.
Figure 2-9. SEM images of free-standing Pt nano-accordion structures with flat-top templates (DC = 60%). The inset pictures in each image depict the photoresist template before thermal process. The structure aspect ratios (AR) are (a) 0.5, (b) 0.83, and (c) 2.0. Scale bars in main and inset images are 1 and 2 μm, respectively.

2.3.2 Round-Top Template

For round-top templates, the fabricated cross-section profiles were less complex than flat-top cases. This can be attributed to enhance mechanical stability for curved corners, as opposed to the sharp edges for square wave samples. The gradual change of the polymer grating has made by increasing the time of isotropic etching, as depicted in Figure 2-10. Starting with AR = 1, the grating width can be shortened while the keeping height the same using 3 minutes of isotropic oxygen plasma etching (power of 300 W and pressure of 1 Torr) since as the top layer
was being etched the bottom layer was also being etched. Further etching on polymer template has made a neck between grating layer and buffer layer, resulting in AR of around 5. Therefore only the AR can be changed with less height reduction during plasma etching and the rounded top shape can be survived until the neck part is completely removed.

Figure 2-10. Aspect ratio of polymer grating template controlled by isotropic plasma etching. SEM images for each AR cases before template removal. (a) initial sample with AR = 1 was etched to obtain (b) AR ~ 2, and (c) AR ~ 5 with etch time of 3 min and 6 min, respectively. (d) More than 9 min of etch time will remove most of the grating structures.

After template removal, the top ceiling does not sag due to improved mechanical stability of the rounded ceiling and only the side walls collapse, in contrary to the flat-top templates. For low AR = 1, the resulting free-standing Pt structure closely resembles the original template.
profile, with about 50% decrease in structure width, as shown in Figure 2-11(a). For template with AR = 1.25, the sidewall collapse developed further to result in a narrower waist, as shown in Figure 2-11(b). For higher template AR = 5.0, the collapse of the sidewall was more pronounced, resulting in a sealed pipe-like shape with a vertical column, as shown in Figure 2-11(c). The spaces enclosed by the Pt nanostructures are a distinguishable feature only observed on round top templates, and can potential find applications in nanofluidics.

Figure 2-11. SEM images of free-standing Pt nano-accordion structures with round-top templates (DC = 50%). The structure aspect ratios (AR) are (a) 1.0, (b) 1.25, and (c) 5.0. Scale bars in main and inset images are 1 and 2 μm, respectively.
2.3.3 Cross-Section Profile Map

The overall experimental results can be compared to the geometric model in a cross-section profile map defined by template width and height, as shown in Figure 2-12. Lines of constant AR = 0.5, 1, and 2 are drawn to indicate the regimes of low, intermediate, and high AR, respectively. For low AR = 0.5, the final Pt structures are wrinkled and have completely collapsed. This represents the regime when the ceiling sagging is more dominant than the side wall collapse. This effect of immediate ceiling collapse is expected to be even more pronounced at AR < 0.5. For intermediate AR = 1. The ceiling sagging and wall collapse both play equally important roles, as the ceiling and side walls merge in the final structure to yield sprout-like profiles. On the other hand, for relatively high AR = 2, the side wall collapse is dominant and occurs prior to ceiling sagging. These structures generally have enclosed opening at the top of the structures while being sealed at the waist. The same effect is expected for AR greater than 2, where the sidewalls will collapse immediately and the ceiling will experience no geometrical change at all during the template removal process. Using this profile map, the final cross-sectional profiles of thin metal nanostructures can be predicted and designed for various applications.
Figure 2-12. Cross-section profile map of fabricated Pt nano-accordion structures. The resulting structures are plotted as functions of template width and height. The ceiling sag is dominant when AR < 1, and the wall collapse is dominant when AR > 1. For AR ~ 1, both ceiling and wall collapses effects are equally important.

2.4 Electrical Characterization

Given the complex cross-sectional profile and high directionality of the Pt nanostructure, the anisotropy of electrical conductivity was further evaluated. Prior sheet resistances were measured parallel to the structure ridge direction ($R_\parallel$). When the measurement probes are aligned in the perpendicular direction ($R_\perp$), the electrons follow the wavy profile in a more tortuous path and the structure could have higher resistance. The anisotropy ratio ($R_\perp/R_\parallel$) of the fabricated Pt nano-accordions before and after template removal process are shown in
Figure 2-13 (For raw data see Table 2-2). The anisotropy effect in electrical property was small prior to template removal, gradually increasing with AR to yield a maximum of 10% increase for AR = 2. This can be attributed to sharper edges and roughness in higher AR structures. [86] However, the overall effect of AR was small since the structures of thin Pt film do not have significantly different cross-sectional profiles prior to template removal by high temperature in convection oven.

The anisotropy ratio in free-standing Pt structures after template removal, on the other hand, has a stronger dependency on complexity of the structure. For low AR = 0.5 where structure has collapsed ceilings, anisotropy ratio is close to 1 to indicate no directional difference in sheet resistance. For the sprout-like profile structure with AR = 0.83, the complex geometry resulted in $R_\perp$ being about 10% higher than $R_\parallel$. At even higher AR = 2, the anisotropy increased to more than 45% due to more complicated profiles and sharper edges. Complex profiles also lead to more structure collapse during the template removal process, which can result in crack formation along the structure ridge direction and increase anisotropic effects. These characterizations demonstrates that Pt nanostructures with complex cross-sectional profiles can maintain high conductivity in along orthogonal directions parallel and perpendicular to the fold geometry. These structures can potentially be transferred to flexible substrates for stretchable devices, and the dependence of electrical properties on strain is the subject of future studies.
Figure 2-13. Sheet resistance anisotropy ratio \( (R_\perp/R_\parallel) \) vs. aspect ratio for Pt nano-accordion structures before and after template removal. The ratio increases with increasing AR for both cases. The anisotropy is more significant after template removal with the resistance ratio up to 1.45, while it is limited to 1.10 for structures before template removal.

Table 2-2. Sheet resistance and anisotropy ratio of platinum films and nano-accordions before and after template removal for 5 different AR cases.

<table>
<thead>
<tr>
<th>Sheet Resistance (Ω/square)</th>
<th>Before Template Removal</th>
<th>After Template Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R_\parallel )</td>
<td>( R_\perp )</td>
</tr>
<tr>
<td>AR = 0.5</td>
<td>12.36±0.10</td>
<td>12.58±0.33</td>
</tr>
<tr>
<td>AR = 0.83</td>
<td>10.45±0.19</td>
<td>10.82±0.37</td>
</tr>
<tr>
<td>AR = 1.33</td>
<td>12.62±0.26</td>
<td>13.46±1.33</td>
</tr>
<tr>
<td>AR = 1.71</td>
<td>11.39±0.32</td>
<td>12.30±0.27</td>
</tr>
<tr>
<td>AR = 2.0</td>
<td>11.92±1.04</td>
<td>13.17±0.84</td>
</tr>
</tbody>
</table>
2.5 Thermal and Structural Stability Characterization

The thermal and mechanical stability of Pt nanostructures were examined at high temperature test using a convection oven. Even with thermal treatment up to 700 °C, the Pt nano-accordion remained its shape and electrical conductivity once cooled to room temperature. The cross-sectional SEM images of the Pt nanostructures after 700, 800, and 1000 °C are shown in Figure 2-14(a) and (b). However above 800 °C, the structures morphology alters and systematic collapse can be observed. The structures are also no longer conductive, which we believe to be caused by crack formation. This can be attributed to metal oxidation and other chemical reaction at high temperature10 (Figure 2-14(c)). The structure collapse is more dramatic as temperature was increased to 1000 °C, as shown in Figure 2-14(d). In this experiment the initial sprout-like profile was difficult to be distinguished from its cross-sectional view while the periodicity of the nano-accordion barely persisted.

Thermal treatment at 550 °C, however, the fabricated free-standing structure is robust. The structural stability of platinum nano-accordion over large area after template removal can be confirmed by top-view SEM. As shown in Figure 2-15, the Pt nanostructures with two different profiles showed few structure collapses, which is characteristic representation over the whole sample area.
Figure 2-14. Cross-sectional view SEM images of Pt nano-accordions structures (DC = 60%, AR = 0.83) (a) after the normal temperature removal process at 550 °C, and after high temperature thermal tests at (b) 700 °C, (c) 800 °C, and (d) 1000 °C.
2.6 Summary

In this chapter demonstrated Pt nano-accordion structures with complex cross-sectional profiles using a combination of ALD and IL. The cross-sectional profiles of these metal nanostructures can be designed by specifying the template geometry. Pt structures undergo structural transformation during the template removal process, which can be qualitatively predicted using the proposed geometric model base on structure duty cycle and aspect ratio. This model generates a cross-section profile map, where the structure geometry can be designed as functions of template width and height. These free-standing nanostructures exhibit
anisotropic electrical properties, with sheet resistance up to 45% higher in the direction perpendicular to the structure ridge for the most complex profile. Due to their good structural stability and excellent electrical conductivity from the nature of metals, these structures can potentially be stretched, leading to future applications in stretchable electronic and photonic devices.
CHAPTER 3

CONFORMAL METAL COATING USING CONVENTIONAL THERMAL EVAPORATION

In this chapter, I would like to introduce another fabrication method to create conformal metal film on nanostructured surface using conventional physical vapor deposition (PVD). This work will focus on improving the conformality of thermal evaporation, which is one of the most widely used PVD methods to deposit various materials. Even though platinum ALD demonstrated a successful result on fabricating metallic nano-accordion structures, as demonstrated in Chapter 2, the limited choice of depositing materials and expensive precursors for process can obstruct this approach for scale-up mass and cost-effective production. Therefore, a novel approach based on PVD can be an alternative way to fabricate the same nanostructures, and will bring versatility to my strategy to produce flexible metallic conductors.

To overcome poor step coverage and incomplete conformality of PVD, oxide layers by ALD will be introduced as adhesion interlayers before thermal deposition of gold. The quality of gold films will be analyzed using scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS or EDX), and electrical conductivity measurement.

3.1 Conformal Coating of metal materials using PVD

PVD has been one of the most widely used technologies for metallization of surfaces and devices in many area, including integrated circuit (IC) production, MEMS/NEMS research,
and thin film coating, due to its process versatility and material purity. However, it poor step coverage and limited conformality on complex structures with high aspect ratio (AR) has been a long time challenge to overcome.

To illustrate the shadowing effect, Figure 3-1 shows a general result after thermal or electron beam (e-beam) of metal on nanostructured surfaces. The structures in that figure is exactly the same as those I used for platinum nano-accordion structures, demonstrated for Chapter 2, but only for this case, the deposited material was gold. This metal has sat only on trenches and valleys of polymer template, and the uncoated sidewalls revealed the poor step coverage and directionality of anisotropic PVD process.

![Figure 3-1. SEM image of general example for 30 nm gold thermal deposition on polymer template.](image)

To mitigate this problem, several approaches without changing the main concept of PVD, including ionized PVD [87]–[89] and oblique angle PVD [90], [91], have been suggested. Ionized physical vapor deposition (IPVD) utilizes ionized depositing materials and electric fields on the sample substrate, and the conceptual setup of this technique is demonstrated in
Figure 3-2(a). This method was developed from the need to deposit metal layers and barriers into trenches or vias with high aspect ratio structures, which is the reason it is also known as ionized metal plasma (IMP). Metal atoms are ionized in an intense plasma, and directed by electric fields perpendicular to the sample surface. Only the directed flux of metal can reach the bottom of deep trenches and cover the sidewalls of structures. Figure 3-2(b) shows one example of metal deposition using IPVD, and the trench with aspect ratio more than 4 was covered by titanium thin film. However, only the porous and columnar structure of metal film was deposited on 90º sidewalls, and its thickness is much thinner than top or bottom side of trench.

Another advanced PVD technology, called oblique angle physical vapor deposition (OAPVD) uses an obliquely tilted and rotating substrate in the main chamber, as shown in Figure 3-3(a). More surfaces on sidewalls of trenches or valleys will be exposed to the evaporated target
materials and the conformality will be enhanced without any void area which cannot be reached by normal incident flux. Figure 3-3(b) shows some of the experimental results of ruthenium (Ru) film deposition on trench structures with an aspect ratio around 2.0 using OAPVD system. The rotation speed they used was 30 rpm, and the deposition rate of 15 ~ 17 nm/min, and the tilted angles they chose were 0º, 15º, and 30º. Experiment results proved that higher angle lessened the thickness difference on between top (or bottom) and sidewall, therefore overall step coverage improved without void area and overhang structures. However the conformality of OAPVD is very sensitive to the aspect ratio of surface topography, and more dominant for certain PVD techniques which are utilizing high density plasma and ionized materials, such as sputtering and IPVD.

![Figure 3-3. (a) Conceptual setup image of oblique angle physical vapor deposition (OAPVD), (b) deposition results using OAPVD with different deposition time and tilt angle of the system [91].](image)

Though these advanced PVD showed better step coverage and conformality, they still have limitations when deposited on complex nanostructured geometry. More advanced and progressive deposition techniques with perfect conformality are especially critical at the
nanoscale. One such process is a metal atomic layer deposition (ALD) which was described for Pt nano-accordions in Chapter 2, have been introduced to replace the conventional PVD process. However, the limited selection of depositing materials, long reaction time, complex process, and pricy precursor materials are the disadvantages to be considered.

3.2 Approach to Conformal Metal Coating

In most of metal PVD processes, an adhesion layer of another metal is used for better deposition on a delicate substrate, such as silicon and silicon dioxide. For example, a very thin layer (< 5 nm) of titanium (Ti) or chromium (Cr) is widely used for gold evaporation on the glass substrates [92], [93]. By having these adhesive layer, the target material sticks well to a high energy surface, instead of nucleating and forming larger grains on low energy surface. However, these materials help only for promoting better adhesion between the substrate and metal, not for increasing step coverage of target metal on substrate.

Similar occasions frequently happen on metal ALD process for special substrates or surfaces. For instance, an ultra-thin layer of aluminum oxide (Al₂O₃) was used for ALD of platinum on fabric materials. Also mentioned in previous chapter, the same oxide layer with 2 nm thickness was used for metallic platinum ALD on polymer template. These results can be explained by the motion of metal atom on oxide layer and a unique catalytic property of aluminum oxide for platinum deposition. To understand and utilize this mechanism, many research groups have been studied and found that the adhesion of several metals, such as copper, platinum, and gold, is significantly increased by the support of oxide underlayers, and the binding of those metals
depends on the properties of the oxide [94]–[102].

The goal of this work is then to investigate and enhance the quality and conformality of metal PVD on nanostructured template with various interlayer materials. Different oxide layers can be deposited by ALD process on complex templates with high quality and conformality in moderate experimental conditions as opposed to metal ALD (For more information on oxide ALD see Appendix B). Typically, an oxide ALD can be processed in much lower temperature (around 60 ~ 80 °C) than metal ALD and no special treatment is required on the target surfaces. Like the preparation step of an adhesive layer by PVD, such as Ti and Cr, an oxide interlayer can be deposited by simple ALD process before the main metal PVD step. This ALD-assisted PVD is my approach to enable conformal metal coating, and the quality of the deposited metal film will be discussed with various characterization results.

Based on others research works mentioned above and my own experiences on Pt ALD layer quality, the PVD of gold on aluminum oxide ALD layer was first examined and the experimental results are shown in Figure 3-4. The polymer template was prepared using laser interference lithography described in Chapter 2. The thickness of target SU-8 layer was 250 nm, the same as the buffer SU-8 layer, and the period of nanostructure was 1 µm. Then the 10 nm of aluminum oxide layer was deposited on top of polymer template, and the thermal deposition of gold was conducted for 30 nm using thermal evaporation system (Kurt J. Lesker Company).

Initial results are promising. Compared to Figure 3-1, the cross-sectional image in Figure 3-4(a) indicates better conformality and step coverages on lithographically prepared polymer
nanostructures. Also the tilted view SEM in Figure 3-4(b) shows the quality of depositing gold on sidewalls, and no remarkable differences between valleys and sidewalls in terms of uniformity were observed. This is the first evidence that the metal oxide layer, which can be fabricated readily by ALD, can help the adhesion of metal overlayer deposited by PVD even with complex geography. One effective breakthroughs to acquire film conformality, process versatility, as well as economic feasibility can be achieved by this approach. More detailed examination on metal layer over ALD-oxide-interlayer will be conducted with different experimental conditions in following sections to prove its superiority.

3.2.1 Experiment Design

The first successful PVD of conformal gold on polymer template was fabricated under three special conditions. First one is the presence of aluminum oxide layer by ALD process and its
thickness was around 10 nm. Gold film was deposited better on aluminum oxide layer than on polymer template because oxide layer has higher surface energy. Second condition is the low aspect ratio (AR = 0.5) of the polymer template. Shorter nanostructures must be easier to be covered by evaporated metals since there will be only a weak shadow effect. The last one is the slower evaporation rate, which was around 0.4 Å/s. In most of microfabrication process, 1.0 ~ 2.0 Å/s of evaporation rate is used for good quality of depositing materials, and slower deposition time can give the material more time for diffusion and spreading over the target surfaces.

To demonstrate the effectiveness of metal oxide layer as interlayer, those conditions were broken down and examined separately. Different thickness of aluminum oxide layer, different aspect ratios, and different evaporation rates were tested to validate the conformality which the oxide layer can induce and show the limit of this approach. Electron microscopy will be utilized to investigate the effect of the interlayer. The quality of the coating can also be quantified by measuring the electrical conductivity of the fabricated films. This approach gives a global evaluation of the film deposition based on various experimental parameters.

### 3.2.2 Deposition Results

Deposition results with different conditions will be demonstrated and the quality of deposited gold film on polymer template observed from each SEM images is discussed in this section. Like the case of Pt ALD with thin aluminum oxide interlayer, the improvement can be primarily observed by electron microscopy.
First of all, the thickness of aluminum oxide layer was examined. Three different thickness of the oxide layer, 5, 10, and 15 nm, were prepared for 30 nm of gold evaporation, and the results are shown in Figure 3-5. No big difference in quality of gold overlayer was observed, and this agrees with the general understanding that even only an ultra-thin layer of oxide can cause the conformal coating of gold over the interlayer. Typically 5–10 nm of Ti or Cr is deposited for better coating of gold or aluminum on delicate surfaces, and the same thickness of oxide significantly changed the morphology and improved the conformality of gold film on the surface of polymer template. Reducing the thickness can be made down to 2 nm, as the case of Pt ALD in Chapter 2, however the following tests on aspect ratio and evaporation speed were conducted with oxide thickness of 5 nm, which were verified by this test.
Secondly, the effect of the aspect ratio of polymer structures were examined. Four different height of nanostructures, $h = 400, 600, 900, \text{ and } 1200 \text{ nm}$, were fabricated with the same width, $w = 600 \text{nm}$, and the corresponding aspect ratios of each samples are 0.67, 1.0, 1.5, \text{ and } 2.0, respectively. From the cross-sectional SEM images of those samples shown in Figure 3-6, the uniformity and good morphology of valleys and trenches can be readily observed. This is a significant improvement on samples fabricated without the interlayer. However, the sidewalls which will be the indicator of conformality of this approach can be hardly observed from cross-sectional view. Only the side view SEM images in Figure 3-7 show the different deposition thickness of gold through the sidewall when AR is 1.0 or higher, however this needs to be
examined in more rigorous ways. This will be discussed in Section 3.3.

Figure 3-6. Gold deposition results on different aspect ratio of polymer nanostructures. (a) AR = 0.67, (b) AR = 1.0, (c) AR = 1.5, and (d) AR = 2.0 (scale bars indicate 1 µm).

Figure 3-7. Side view SEM of gold film on polymer nanostructures with (a) AR = 1.0, and (b) AR = 1.5.
Lastly, different deposition rate was compared as slow evaporation rate is believed to be better for more uniform deposition. For this test, the results from 0.2 Å/s and 1.0 Å/s deposition rates will be mainly compared. From SEM images in Figure 3-8(a), it is hard to tell if the slow process dominates fast process or not, especially on low AR case. However, a slight difference of film quality on sidewalls between two different deposition rates can be visually observed from the sample with highest AR of 2.0 in Figure 3-8(b). The gold film on sidewalls with the fast rate has more definite color change from bright to dark than the one in Figure 3-6(d), which indicates that the gold film coverage is less than the slow rate case. This characterization, also, will be more reasonable and practical with more data in Section 3.3.

3.2.3 Effects of Different Metal Oxide Layers

Other oxide films than aluminum oxide were examined to demonstrate the improvement on introducing oxide interlayer for conformal metal coating. Zinc oxide (ZnO) and titanium
dioxide (TiO$_2$) were prepared by ALD process as expected to induce high surface energy, and the thickness of both oxide films were 5 nm, as same as aluminum oxide. Both ALD processes were conducted at around 1.8 Torr and 90°C, and as precursors, titanium (IV) chloride (TiCl$_4$) for TiO$_2$ and di-ethyl zinc (DEZ) were used for TiO$_2$ and ZnO ALD, respectively (For more information on each ALD process, see Appendix B). This experiment will examine the role of the metal oxide species and shed light on the mechanism in which the interlayer is assisting conformal coating.

The deposition results exhibited good quality and morphology of gold film similar to the aluminum oxide cases, as shown in Figure 3-9. The periodic nanostructures with valleys and trenched with aspect ratio of 1.0 were conformally coated, and even sidewalls covered well with no big visual differences from SEM images. Only difference that can be found in SEM images is that the thickness of sidewalls in TiO$_2$ cases looks thicker than ZnO cases. However, the quality of the deposited metal films cannot be evaluated only by SEM, and more detailed comparison between different oxide interlayers will be discussed by using EDS mapping data and electrical resistance values.
Figure 3-9. Deposition results of gold film on polymer template using (a) ZnO interlayer and (b) TiO$_2$ interlayer.

### 3.3 Characterization of Conformal Metal Layer

#### 3.3.1 EDS Mapping

Energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique and widely used for materials analysis and characterization of a sample. A detector for EDS can be attached to many different electron based microscopy such as SEM and TEM (Transmission Electron Microscopy), and the resolution of it depends on the resolution of the microscopy. Therefore, high-resolution EDS mapping data can be acquired by STEM (Scanning Transmission Electron Microscopy) which resolution is approximately 0.07 nm (FEI Titan 80-300).
Figure 3-10 is a general example of STEM and EDS mapping images. The same sample used for Figure 3-1 to show the poor step coverage of PVD with no surface treatment or adhesion layer was tested for this measurement. As expected, much thinner or no gold film was covered sidewalls of nanostructures and the thickest part was still less than 5 nm. EDS mapping data for gold component in Figure 3-10(b) is fairly identical to the STEM image in Figure 3-10(a), which shows that only gold was deposited on the structures. Another important thing in these images is that the roughness of gold film. Since the metal deposition on polymer template cannot be done readily, there are a lot of deviation on thickness of gold even on valleys and trenches. This is another disadvantage of PVD when it is compared with ALD-coated metal film such as Pt film in previous chapters.
Then, the sample with gold deposition by thermal evaporation on aluminum oxide layer was inspected with STEM and EDS. This has structures with an aspect ratio \(~ 0.8\) (i.e. height \(= 500\) nm, width \(= 600\) nm) and period of \(1 \mu\text{m}\). The aluminum oxide layer was prepared by ALD on top of polymer template and its thickness is \(5\) nm, the thinnest thickness tested in previous section. The deposited gold is \(30\) nm in thickness and the deposited rate used for this sample was \(0.2\) \(\text{Å/s}\). As shown in Figure 3-11(a), the conductive gold film covers the structure completely with introduced oxide layer, and the component of film is confirmed by Figure 3-11(b). Aluminum oxide layer was prepared by ALD and the conformality shown in Figure 3-
11(c) is better than evaporated gold film as expected. And more importantly, this oxide layer mitigate the roughness of deposited gold which is observed in Figure 3-10. It looks like the oxide layer helps depositing metal to be spread out and dispersed through the shape of nanostructures. The roughness of deposited material is dominant in determining the electrical, optical and mechanical properties of the film, and therefore the improved morphology and uniformity of the film can cause a favorable effect on every applications which use PVD process.

Figure 3-11. (a) STEM image of gold film on polymer template with aluminum oxide interlayer and corresponding EDS mapping images of (b) gold, (c) aluminum, and (d) oxygen components.
Taller structure with aspect ratio of around 1.5 were also characterized in the same way, as shown in Figure 3-12. It is conspicuous that less coverage of gold film on sidewalls than the lower AR case was observed from STEM image in Figure 3-12(a). The EDS mapping data of gold component in Figure 3-12(b) confirms that only an ultra-thin layer of gold film was detected on the sidewalls. The thickness of gold on the valleys was measured 30 nm as designed, and decreases gradually through the sidewall profile. As it gets closer to trench, the thickness of gold gets thicker and is measured 30 nm again on most of structure base side. Therefore the thinnest part of gold film is around the center part of sidewalls, while the Al₂O₃ interlayer by ALD was detected with uniform thickness and perfectly conformal feature through whole nanostructure profile as in Figure 3-12(c) and Figure 3-12(d). These results indicate that while the interlayer improves conformal coating using PVD, ALD is still significantly better in terms of step coverage. For more STEM images and EDS mapping images on more fabricated samples see Appendix D.
3.3.2 Electrical Characterization

To compare the quality of each depositing results in more quantitative way, the electrical characterization of gold film was conducted using 4 point probe system. All sheet resistances in this section was measured perpendicular to the structure ridge direction. In Chapter 2, the
electrical resistance data of ALD platinum film on polymer template showed that there was only up to 10% increment even for aspect ratio of 2.0 case due to its uniform thickness. This demonstrated the effect of structure profile is not dominant or significant in deciding the electrical property of metal film. However, the gold film deposited by conventional thermal evaporation exhibits more rough morphology as well as less constant thickness. And it is expected that there will be more increasing on electrical resistance properties in this PVD case. Most of experimental results which were discussed in previous section will be compared in this manner.

First of all, the effect of oxide film as an interlayer and gold depositing speed were examined as shown in Figure 3-13. It is confirmed that the presence of oxide layer helps the migration of metal atoms onto the structured surface even in the lowest AR case (AR = 0.5). The sheet resistance measured for lowest AR samples without any interlayer was about 10 times higher than samples with aluminum oxide layer (For raw data, see Table 3-1). This trend can be better observed in higher AR cases: the resistance values with oxide layer (red and pink lines) were increased gradually as AR gets higher, while those without interlayer (black and blue line) rose extremely when AR = 1.5. This big jump at AR = 1.5 specifies the limitation of conventional PVD techniques for coating materials on surfaces with high valleys and deep trenches. Also, the slow and steady rise on oxide layer cases shows the possibility of this approach as an alternative way to have conformal deposition using only conventional PVD techniques. Even though the thickness of sidewalls are thinner than valleys or trenches, as seen in STEM and EDS images, the electrically conductive layers can be created by using this approach.
The effect of depositing speed on the quality of gold film was also investigated by comparing two different rates, 0.2 Å/sec and 1.0 Å/sec. Though the increasing trend of two deposition speeds in either oxide layer cases or no interlayer cases looks identical, it is clear that slow deposition results in lower resistance values. The difference in sheet resistance values was more noticeable for the samples with AR under or equal to 1.0, and the slow deposition led to approximately 50% less resistance than fast deposition. It is assumed that there will be more time for gold film to disperse on depositing surface when the depositing occurs slowly. Therefore, it is recommended to use slow deposition rate for creating more conformal and uniform film by PVD since it takes only about 25 minutes even with 0.2 Å/sec of deposition speed, which is still much faster than the advanced deposition techniques such as ALD.
Sheet resistance of gold film with different oxide interlayers, Al₂O₃, ZnO, and TiO₂, was also investigated as shown in Figure 3-14, and the detailed values are listed in Table 3-1. Compared to aluminum oxide case, zinc oxide layer resulted in very similar trend as AR increased, meaning that zinc oxide acts in the same way as aluminum oxide does as a adhesion interlayer. However, titanium dioxide showed most beneficial effects on helping the migration of gold film on structured surfaces (blue dots and line in Figure 3-14). The changes in sheet resistance of gold film on TiO₂ was less dramatic than any other oxide layer cases. Its sheet resistance at
AR = 1.5 was measured only about 100 Ω/square, which can be regarded as a flat film made of other less conductive materials than gold, silver, or copper. Compared to the case with no interlayer, the TiO$_2$ interlayer improved about 14 times better at this point. Also it is interesting that the sheet resistance of gold on TiO$_2$ interlayers is always about 10 times smaller than the one with no interlayer. Thus, a titanium dioxide layer by ALD can be a good choice as an interlayer for depositing gold film on structures with high AR, and a zinc oxide layer can also be used for better step coverage of gold deposition.

![Graph showing sheet resistance vs. aspect ratio for different interlayers](image)

**Figure 3-14.** Sheet resistance vs. aspect ratio graph of 30nm gold film on polymer template with 3 different oxide interlayer (Al$_2$O$_3$, ZnO, and TiO$_2$) and no adhesion interlayer. The deposition rate of 0.2 Å/sec was used for this test.
Table 3-1. Sheet resistance data of 30nm gold films with four different surface treatments and two different depositing rates.

<table>
<thead>
<tr>
<th>Sheet Resistance (Ω/square)</th>
<th>1.0 Å/sec</th>
<th>0.2 Å/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No Layer</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Flat Film</td>
<td>1.834</td>
<td>1.830</td>
</tr>
<tr>
<td>AR = 0.5</td>
<td>25.17</td>
<td>2.050</td>
</tr>
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<td>AR = 0.67</td>
<td>641.80</td>
<td>174.56</td>
</tr>
<tr>
<td>AR = 1.0</td>
<td>852.16</td>
<td>296.47</td>
</tr>
<tr>
<td>AR = 1.5</td>
<td>2304.50</td>
<td>412.67</td>
</tr>
</tbody>
</table>

3.4 Summary

As an alternative approach to fabricate conformal metal layer on complex nanostructures, the conventional thermal evaporation process was examined. To enhance the step coverage and conformality of PVD, a metal oxide layer were prepared by simple ALD process. Gold films created with different thickness of oxide layer, different aspect ratio of nanostructures, and different depositing speed were compared and analyzed using SEM, EDS, and electrical conductivity measurement. For all the cases of AR, from 0.5 to 1.5, gold films with oxide layers of at least 5 nm thickness showed better quality and step coverage with slow deposition speed. Also, three different oxide layers, aluminum oxide, zinc oxide, and titanium dioxide, were tested as adhesive interlayers and all of those resulted in better conformal coating of gold films on nanostructured polymer templates. The ALD process for these oxide layers only needs comparably low temperature and short process time, so this approach can be used for any
surfaces and materials without any significant constraints. Also, due to the variety on materials selection of PVD techniques, various types of metallic nano-accordions can be fabricated with this cost-effective process. Actual metallic nanostructures made with this approach will be presented in the following chapter.
CHAPTER 4

FUNCTIONALIZATION OF METALLIC NANO-ACCORDION STRUCTURES

In previous chapters, I have demonstrated a method to fabricate novel nano-accordion structures using interference lithography and thin metal deposition techniques, achieving precise control of the geometry and size of the flexible conductors. Owing to the metallic nature, excellent electrical conductivity and robust structural stability were achieved and demonstrated. However limited optical transmission is one major drawback and roadblock in becoming an alternative method to create transparent flexible conductors. In this chapter, I demonstrate a novel approach to fabricate both transparent and flexible conductors using nano-accordion structures with lithographically patterned microstructured window opening. A selective etching process on metal film to improve optical transmission and a transferring step of metallic nanostructures to soft substrate, such as polydimethylsiloxane (PDMS), were developed and added to the fabrication process for free-standing metal nano-accordion structures, described in Chapter 2. Optical transmission and mechanical tests on the microstructured nanostructures will be performed to confirm the superiority as both transparent and flexible conductors.
4.1 Fabrication Process

A detailed fabrication process is proposed in Figure 4-1, which begins with spin-coating of thin poly(styrenesulfonate) (PSS) layer and first photoresist layer on silicon substrate. PSS is prepared by thermal annealing with 200 °C for 5 minutes, and will be used during transferring step to separate the structured part from silicon substrate. Then using ALD or conformal thermal evaporation developed in the previous chapters, metal films will be created on the patterned photoresist. These steps follow the same process reported for free-standing platinum nano-accordion structures.

The fabricated nano-accordions have low optical transmission, typically in the visible light range for more than 10 nm thick film. To enhance optical transparency, the second photoresist layer is spin-coated and planarizes the metal accordion layer for another lithography step. Using conventional contact lithography, 1D physical periodic openings parallel to the first accordion fold direction were patterned, as shown in Figure 4-1(c). Through these micro-windows, metal layer exposed is removed using an acid-based wet etching, leaving only the parts covered by patterned second photoresist, as shown in Figure 4-1(d). Two different photoresists, a negative-tone photoresist for first patterning before ALD and a positive-tone PR for second patterning after ALD, were used for this two-step patterning process. Subsequently, the residual second photoresist is washed away, and the microstructured metal layer is bonded to the pre-cured transparent soft substrate, such as PDMS. Finally, by dissolving PSS layer with water and removing the first photoresist layer with oxygen plasma,
only a group of free-standing nano-accordion structures is left on the soft substrate, as depicted in Figure 4-1(f).

Figure 4-1. Fabrication process for transparent flexible nano-accordion structures including (a) interference lithography (IL) of first PR layer, (b) deposition (ALD or PVD) of metal, (c) patterning of second PR layer, (d) selective metal wet etching, (e) transferring to soft substrate, and (f) final microstructured metallic nano-accordion structures on soft substrate.

Figure 4-2 illustrated the fabricated structures right after metal deposition process, having thin PSS layer with thickness of around 200 nm. The structured first photoresist was patterned by interference lithography (IL) with period of 1 µm and aspect ratio of 0.5, which will make the shortest structures among my flexible metallic conductors. Then, 30 nm of gold film was deposited using thermal evaporator on top of aluminum oxide layer by ALD, as proposed in previous chapter. The additional PSS layer had no harmful effect on SU-8 template, and a conformal gold layer on nanostructures was achieved as shown in Figure 4-2(b). This PSS
layer enables another method to remove SU-8 polymer template beyond thermal treatment using furnace or oven. Since the high temperature during thermal treatment can damage soft materials, such as PDMS, it is not a suitable process after transferring the metallic nanostructure from silicon substrate (For more information on fabrication process recipes see Appendix A).

Figure 4-2. Cross-sectional SEM images of gold film deposited on lithographically structured first PR and PSS layer with silicon substrate.

The second patterning step using positive photoresist (PFI-88, Sumitomo Chemicals Co., Ltd.) as a second photoresist layer was also examined. Conventional photolithography using a chrome mask (MA6, Karl Suss) was implemented to make photoresist line pattern in perpendicular direction of first PR’s ridge direction, as shown in Figure 4-3(a). To selectively etch metals on the uncovered parts by patterned second photoresist, aqua regia (nitro-hydrochloric acid), a mixture of nitric acid and hydrochloric acid in a molar ratio of 1:3, was used. The acid-based solution can etch noble metals, such as gold and platinum, as well as other common metals like tungsten and aluminum. An example of the sample right after metal
wet etching step is presented in Figure 4-3(b) with colored microscopic image, and showing the patterned gold nano-accordion structures and the exposed first photoresist templates. Some undercutting and line edge roughness can be observed, the characteristics of wet etching processes. In this case, the opening ratio of 70% (in other words, 30% of gold part was remained) was employed by line patterns with period of 10 µm and width of 3 µm.

![Figure 4-3. (a) SEM image of the sample after second PR patterning using conventional photolithography, (b) photographic image of the sample after selective wet etching of gold film.](image)

The surface of gold layer is treated with oxygen plasma to activate the surface with hydroxyl groups and bonded with pre-cured PDMS. Then the whole sample is soaked to deionized (DI) water, the prepared PSS layer is dissolved quickly and the silicon substrate can be readily removed from the sample. Then, by flipping the sample’s upside down, the metallic layer placed directly on PDMS side, and the first photoresist template patterned using IL will be exposed as the top layer without any protection. As the trimming process in polymer template geometry control step, described in Chapter 2, an oxygen (O₂) plasma etching process can effectively remove the first PR layer in this stage. However, due to its periodic geometry with
trenches, the etching time by only O2 plasma might be increased up to more than 1 hour with slow etching rate. Therefore, reactive ion etching (RIE) using O2 and sulfur hexafluoride (SF6) gas with ratio of 20 to 1 was used, which can reduce the processing time to 2 minutes with faster etching rate. A direct comparison of three different dry etching recipes is depicted in Figure 4-4, where around 90 nm/min for O2 plasma ashing, 185 nm/min for O2 RIE, and 1.1 µm/min for O2 and SF6 RIE (For more detailed etching recipes, see Appendix A).

Figure 4-5 shows the gold nano-accordion structures on PDMS after RIE etching with O2 and SF6. No residual PR layer was observed in any location on the whole sample. The accordion-like nanostructures was well preserved and transferred to PDMS side without any structural deformation. Now, the optical characterization of metallic nanostructures is operable due to the transparent nature of PDMS substrate, and discussed in the following section.
Figure 4-4. Etching rates for SU-8 template with O₂ plasma ashing, O₂ RIE etching, and O₂/SF₆ RIE etching.

Figure 4-5. SEM image of gold nano-accordion structures after transferring to PDMS and removing polymer template. The structures (a) at free edge and (b) at broken part confirms that only single metallic layer has been left on substrate.
4.2 Mechanical Characterization of Stretchability

The pattern transfer described in the previous sections allows the use of flexible soft substrate, which enables mechanical testing. The stretchability test of metallic nano-accordions in fold direction can be performed, and initial test was conducted using solid gold nano-accordion structures. As shown in Figure 4-6(a), a mechanical test module with two clamp sides was installed within a SEM chamber for *in situ* imaging of the stretched nanostructures. Other than this manual stretching module, an automatic tensile module which is specially designed for dynamic *in situ* mechanical testing, as in Figure 4-6(b), can also be used for real-time imaging of the nanostructures while they are being stretched.

![Figure 4-6. Photographic image of (a) a manual mechanical test stage with two clamps and (b) an automatic tensile module for *in situ* SEM imaging.](image)

The initial stretch test results with gold nano-accordion structures with period of 1 µm, width of 600 nm, and height of 300 nm on PDMS substrate are shown in Figure 4-7. The strain percentage was approximately by direct measurement of 10 period of the structures, and with
0% indicates that it is in the initial stage of the test without any tensile force. Here it can be observed that the length of 10 periods is 10 µm, as expected. Then, the following 5 images are showing 18%, 26%, 30%, 34%, and 41% stretched gold nano-accordions by pulling one free side of PDMS substrate against the fixed side on the test module. Here it can be observed that the structure maintain the fold geometry without degradation. The initial test, then, has been stopped simply because the PDMS substrate was torn after around 45% of strain. However, it is expected that the gold nano-accordions can be survived beyond 45% of strain because there was no significant sign of crack or breakage until 41% of strain on metal film side. This is a very promising result compared to other advanced techniques and nanomaterials for flexible electronics since it is achieved only with AR of 0.5, which is the lowest fabricated in this process.

Figure 4-7. SEM images for initial stretchability test of gold nano-accordions with AR = 0.5 on PDMS substrate from 0% to 41% strain.
Based on our geometry of nano-accordion structures, the maximum strain can be calculated by the equation as follows [31]:

$$\varepsilon_{\text{max}} = \frac{4\sigma_{FS}}{3E_{NA}Ar} \left( \frac{h^3}{t} \right)$$

where $\sigma_{FS}$: failure stress, $E_{NA}$: Young’s modulus of metal

$r$: radius of curvature of ceiling part

$A$: period, $h$: height, $t$: thickness

Among these parameters, the failure stress is an experimental value which can be achieved by a tensile test on the material with specific thickness, the Young’s modulus is a theoretical value of the material, while the radius, period, height, and thickness of structures can be measured from actual samples. As described by this equation, nano-accordion structures with higher AR and thinner thickness will have more stretchability. For example, if the height is increased by 2 times, the maximum stretchability of the structure will be 8 times higher than the original structure. Therefore, it is expected that the metallic nano-accordion structures with higher AR is expected to show much a stretchability of more than the 100%, given the fracture strain of gold is around 120%. More flexible substrates, such as Ecoflex (Smooth-On, Inc.), will be needed for further mechanical characterizations even though the PDMS with lower ratio of curing agent to silicone elastomer base can have more flexibility. It is also expected that after higher strain test, the gold nano-accordion structures can experience inelastic tensile force, which results in less repeatable electrical measurements for high cycles, and permanent deformation on gold film can be occurred.
4.3 Optical Characterization

A solid metallic nano-accordion structure with a certain thickness greater than a few nanometers fundamentally cannot pass the visual range of light due to its metallic nature and high absorption. Figure 4-8 shows an example of optical transmission test on two different thickness of platinum by ALD on glass slides. The background letters on paper can be seen through the 5 nm thickness sample with dimmed brightness by grayish color of thin platinum film. However, the letters are not visible for 30 nm thickness sample simply because the light barely transmit through much darker black colored metal film on glass. The optical characteristics of the fabricated samples will be examined by broadband spectrometry to demonstrate the transparency of the proposed structures.

Figure 4-8. Photographic image of platinum coating on glass slides by ALD with two different thickness: 5 nm (left) and 30 nm (right).
This low transparency can be improved with patterning step of metallic layer described in the fabrication process. Two different ratios of open and closed areas on gold nano-accordion structures, 70% (7 and 3 μm for open and closed areas, respectively) and 95% (20 and 1 μm for open and closed areas, respectively) openings, were fabricated and tested to measure the optical transmittance. Initial optical test was performed using a green diode-pumped solid-state laser (λ = 532 nm, P = 20mW, Melles Griot) to measure the transmission in visible light range. First, the solid gold nano-accordion structures without patterning was transferred to PDMS (left one in Figure 4-9) and tested, which is resulting in only 20% of transmission. This compares to more than 90% transmission for bare PDMS substrate. Then the microstructured gold nano-accordions with 70% opening window was examined and showed 65% of optical transmission. Finally, the one with 95% opening window (right one in Figure 4-9) demonstrated 80% of optical transmission, which can be comparable to the other transparent and flexible electronics mentioned in Chapter 1. It is expected that even higher optical transmission can be acquired with more portion of micro-windows on metal films, and its excellent electrical conductivity can be maintained due to the superior nature of metal materials as conductors. The SEM images of gold nano-accordion structures on PDMS with 70% opening windows are shown in Figure 4-10, and it is confirmed that the accordion structures were well maintained through wet etching and transfer processes.
Figure 4-9. Photographic image of a solid gold nano-accordion structures (left) and microstructured ones with 95% opening window (right) on PDMS.

Figure 4-10. SEM images of microstructured gold nano-accordion structures with 70% opening window on PDMS.
The broadband transmittance test using spectrophotometer (Cary 5000 UV-Vis-NIR, Agilent Technologies) was also performed to examine the improved optical transparency of the microstructured nano-accordions. As shown in Figure 4-11, the solid metallic nano-accordions exhibited very low optical transmittance through the wavelength from 300 nm to 1600 nm, represented UV to NIR ranges (green line in Figure 4-11). However, the nano-accordions with 70% micro-windows showed more than 60% in most of the UV-NIR wavelength ranges (red line), and the ones with 95% micro-windows presented more than 80% in the same ranges (blue line). This results agreed with the initial transmission test by green laser, and proved that the disadvantage of metal as a transparent conductor can be overcome by having physical openings within the film. More optical transmittance can also be achieved by transferring the microstructured nano-accordions onto other flexible substrates with better transparency since the optical property of the final structures must be limited by the optical property of its substrate, as in this case, PDMS transmitted the incoming light only around 90% in most wavelength cases (black line).
Figure 4-11. Broadband optical transmittance test on solid gold nano-accordions, microstructured gold nano-accordions with 70% and 95% openings, and only PDMS substrate.

The changes in optical transmittance of microstructured gold nano-accordions when they are stretched by tensile force are also measured. As shown in Figure 4-12, both gold nano-accordions with 70% and 95% micro-windows were stretched with 40% strain, and showed slightly more optical transmittance than the initial status. The improvement for each cases was around 5~8% through the wavelength from 300 nm to 1600 nm. This can be attributed to the tensile force on the gold nanostructures in one direction caused the compressive force in perpendicular direction. The metal area can be smaller and the micro-window area can be larger by this compressive force, therefore the optical transparency of microstructured gold
nano-accordions can be improved during they are being stretched. However it is expected that this improvement will be limited by the mechanical property of nano-accordion materials, and observed only before the failure or breakage of the structures.

![Graph showing transmittance](image)

Figure 4-12. Broadband optical transmittance test with strain on microstructured gold nano-accordions with 70% and 95% openings.

### 4.4 Summary

In this chapter, I demonstrated a novel approach to functionalize the metallic nano-accordion structures to be both transparent and flexible by using two important steps. First new step is to pattern the metal layer so that the nano-accordion has a physical opening windows. A
photolithography on second PR layer and a following wet etching enabled to create the microstructured nano-accordions, and the ratio of opening windows can be readily controlled by the simple change on photomask design. Second step is to transfer the nano-accordion from silicon substrate to soft substrate, and PSS layer was used for this process. After adding these two steps, the transferred microstructured metallic nano-accordion structures was optically tested for transparency, and mechanically for stretchability. The optical test results showed that the new structures with 95% of micro-windows can have more than 80% light transmission in UV-NIR range, and more than 40% of stretchability with aspect ratio of 0.5. This stretchability is expected to be improved readily by having thinner and higher AR nano-accordion nanostructures.
CHAPTER 5

DESIGN OF UNIT CELL IN THREE-DIMENSIONAL PERIODIC NANOSTRUCTURES USING COLLOIDAL LITHOGRAPHY

In previous chapters, I presented a comprehensive study of designing, fabricating, and characterizing of metallic nano-accordion structures for transparent flexible conductors. In this chapter, I will present another research area on three-dimensional (3D) nanolithography using colloidal phase shift lithography. This approach is based on the illumination of a two-dimensional (2D) ordered array of self-assembled colloidal nanospheres [103], and it is an effective method for the fabrication of periodic three-dimensional (3D) nanostructures. I investigated the design and control of the unit-cell geometry by examining the relative ratio of the illumination wavelength and colloidal nanosphere diameter. Using analytical and finite-difference time-domain (FDTD) modeling, I examined the effect of the wavelength-diameter ratio on intensity pattern, lattice constants, and unit-cell geometry. These models were validated by experimental fabrication for various combination of wavelength and colloid diameter. The developed models and fabrication tools can facilitate the design and engineering of 3D periodic nanostructure for photonic crystals, volumetric electrodes, and porous materials.

5.1 Three-Dimensional Periodic Nanostructures

Three-dimensional (3D) periodic nanostructures have many interesting applications in photonic materials, microbatteries, fluidic filters, and metamaterials [104]–[112]. One
effective method to fabricate 3D nanostructure is phase-shift lithography, where an optical phase element diffracts normal incident light and generates a 3D intensity distribution in close proximity. The optical pattern is governed by the Talbot effect, and can be recorded by photoresist [112]–[119]. Such method has been employed by various groups, where a conformal polydimethylsiloxane (PDMS) mask is used to pattern periodic 3D nanostructures. However, in these processes it is important that a high-quality mold is used for the PDMS mask, which typically requires use of expensive and time-consuming fabrication processes such as deep-ultraviolet, electron-beam, and atomic force lithography followed by plasma dry etching.

Another method to implement phase-shift lithography is using a 2D colloidal nanosphere array, which replaces the PDMS mask as the optical diffractive element [120]. In this scheme, the colloidal sphere arrays act as a periodic phase element to generate periodic Talbot patterns, eliminating the need for physical masks. The nanospheres can be also be assembled into a regular pattern [121] directly on the photoresist, reducing fabrication complexity and other close-contact issue involved in masks. It is also possible to control the lattice parameters in all three directions by controlling sphere diameter and illuminating wavelength. This approach provides a low-cost method for the scalable fabrication of 3D periodic nanostructures. The use of colloids can also enable other complex geometry, including nano-volcano arrays [122], [123], 3D hierarchical nanostructures [124], and other colloidal-assisted lithography [30], [125]–[127].

In this work, I investigate the design of feature geometries within a 3D nanostructure unit cell in colloidal phase lithography. This is accomplished by examining the illumination wavelength
normalized by the wavelength, which leads to a unit-less parameter. Using analytical modeling, the Talbot distance and sub-image planes of the periodic intensity patterns can be examined. This is then compared to a numerical model using finite-different time-domain (FDTD) methods, which will provide a design map on the influence of the wavelength-diameter ratio on the unit-cell geometry. The analytical and numerical models are confirmed by experimental fabrication, and the error will be studied.

5.2 Colloidal Lithography and Talbot Effect

Colloidal phase lithography is based on the well-known Talbot effect, which occurs in the near field when a periodic pattern is illuminated with normal incidence light [128]–[130]. A schematic of this system is illustrated in Figure 5-1, where an array of monolayer particles are assembled on thick photoresist and illuminated with normal incident light [120].
Figure 5-1. (a) Schematic of colloidal lithography system and (b) 3D intensity pattern after 2D colloidal nanosphere array is recorded on photoresist layer [120].

To demonstrate the details of 3D intensity distribution after 2D colloidal nanosphere array, an example of the cross-section particle array and its simulated intensity in the underlying resist layer using FDTD is presented in Figure 5-2. Orthogonal cross sections in both $x$ and $y$ directions are examined to investigate the 3D intensity distribution. In this example, the wavelength and sphere diameters are set to 105 nm and 500 nm, respectively, which generate primary images, secondary phase-reversed images, and other complex frequency-multiplied images.
Figure 5-2. The simulated intensity cross-sections by FDTD along with (a) x-direction and (b) y-direction of colloidal nanosphere hexagonal array.

The Talbot distance \( z_t \), or one period of the periodic Talbot pattern in the axial direction as noted, can be calculated by the equation below,

\[
z_t = \frac{\lambda}{\frac{n}{n_d}} \frac{1}{1 - \sqrt{1 - \left(\frac{\lambda}{n_d}\right)^2}}
\]  

(1)
where $\lambda$ is the wavelength of incident light, $n$ is the refractive index of propagating medium, and $D$ is the diameter of colloidal particle in this equation. Note that the lateral period, $\Lambda = D\sqrt{3}/2$ because the colloidal spheres form a hexagonal array [131]–[133]. The Talbot distance can be normalized by the lateral period, and defining the unit-less parameter $\gamma = \lambda/n\Lambda$ yields,

$$\frac{z_t}{\Lambda} = \frac{\gamma}{1-\sqrt{1-\gamma^2}} \quad (2)$$

Note the normalized Talbot distance is governed only by $\gamma$, therefore it is the sole factor in defining and controlling the longitudinal lattice constant of the generated 3D periodic nanostructure [120]. Beyond the lattice constant, the $\gamma$ parameter also determines the diffraction order allowed to propagate in the photoresist. Higher $\gamma > 1/\sqrt{3}$ allows only 0th and 1st diffraction orders ($m = 1$), resulting in simpler periodic patterns, while lower $\gamma < 1/\sqrt{7}$ makes more complex Talbot patterns with higher diffraction orders ($m > 2$), yielding multiple sub-image planes [120]. The existence of the sub-images results in higher spatial frequency features within a unit cell then specified by the lattice parameter. Therefore, a variety 3D periodic nanostructure with different geometry can be generated simply by varying $\gamma$ parameter through different combinations of wavelengths and colloidal particle diameters. This approach enabled the design and control of feature geometry within a single unit cell.

Using FDTD method [134], the periodic optical intensity profile can be studied to optimize the 3D exposure parameters. Simulation results of $\gamma = 0.1$ to 0.9 with a step of 0.05 are shown in Figure 5-2. The index and diameter of the sphere were kept constant at $n = 1.67$ and 500 nm, respectively, and the gamma values were obtained by varying wavelengths. It can be observed
that higher $\gamma$ results in simpler intensity patterns, while lower $\gamma < 1/\sqrt{7}$ shows well-defined Talbot sub-images, such as a primary image at $z_t$, a phase-reversed image at roughly $z_t/2$, and multiple frequency-multiplied images within one Talbot period. Below $\gamma = 1/\sqrt{3}$, various sub-images were observed and defined readily due to multiple diffraction orders ($m > 1$). However when $\gamma > 1/\sqrt{3}$, only primary and secondary phase-reversed images can be observed and they repeat in the axial direction, as predicted by the Talbot effect.

To analyze the features in more details, the corresponding unit cells from each intensity pattern were extracted, normalized in the axial direction, and compared in lower side of Figure 5-3. For $\gamma < 0.2$, the unit cells contain complex features with higher spatial frequencies due to multiple sub-image planes. The Talbot distance also increases significantly to several multiples of the longitudinal lattice spacing, making the unit cell highly elongated in the axial direction. On the other hand, the intensity profiles in higher range of $\gamma > 0.6$ showed simpler periodic patterns. Simple unit-cell geometries in this regime will lead to facile control over height and width of constituent elements by choosing proper sphere size and wavelength. In this regime the structures have uniform pore sizes and can find applications in photonics and nanostructured materials. In the intermediate range where $0.2 < \gamma < 0.6$, the unit cells have complex intensity profile but presented fewer sub-images that are dominant. In this case fabrication of the structure is more feasible.
Figure 5-3. Numerical FDTD simulation of Talbot intensity pattern for colloidal phase shift lithography under normal illumination. The $\gamma$ parameter is varied from 0.1 to 0.9, resulting in different unit-cell geometries. Lower $\gamma$ parameter results show various Talbot sub-images including frequency-doubled and -tripled fractional images. Only primary and secondary images can be observed at higher $\gamma$ parameter.

5.3 Fabrication Process

The optical simulations described in the previous section can be validated using experiments. The fabrication process for colloidal phase-shift lithography using assembled nanospheres is illustrated in Figure 5-4. For all experiments, anti-reflection coating (ARC i-CON-7, Brewer Science, Inc.) was spin-coated on a silicon wafer to prevent reflection during lithography. SU-8 (Microchem, Corp.), a negative photoresist was selected for its relatively low optical absorption to enable thick structures. To promote adhesion between ARC and SU-8, an SU-8 buffer layer of 500 nm was used. The buffer layer was flood-exposure (200 mJ/cm2) and hard-baked at 220 °C for 5 minutes. Then, a target layer of SU-8 with controlled thickness (5~7 µm) was spin-coated on top of the buffer layer and soft-baked at 95 °C. A monolayer of 2D
polystyrene nanosphere array with various ranges of sphere diameter ($D = 350$~$1000$ nm, Polyscience Polybead Microspheres in 2.5% aqueous solution) was assembled on top of the photoresist layer, as shown is a cross-sectional SEM image in Figure 5-4(a). The exposure process was performed with 3 different light sources, a HeCd laser ($\lambda = 325$ nm), a mercury lamp with bandpass filter (centered at $\lambda = 365$ nm), and a laser diode module ($\lambda = 405$ nm). The exposure dose differs for the light sources due to the difference in light absorption coefficient of SU-8 at different wavelength. The dose was about 4~8 mJ/cm$^2$ for $\lambda = 325$ nm, and 50~100 mJ/cm$^2$ for $\lambda = 365$ and 405 nm. A photo-initiator cyclopentadienyl(fluorene) iron(II) hexafluoro-phosphate (Sigma-Aldrich) was added to SU-8 for $\lambda = 405$ nm exposure to increase resist sensitivity.

After exposure, the colloidal spheres were removed using ultrasonication system, and the post-exposure bake step was conducted at around 70 $^\circ$C for 5 minutes. The resulting structure is shown in Figure 5-4(b), and some material shrinkage due to polymer crosslinking can be observed. The sample was then developed with propylene glycol monomethyl ether acetate (PGMEA) and the rinsed in isopropyl alcohol (IPA). The final 3D periodic nanostructure is shown in Figure 5-4(c), which has multiple periods of Talbot patterns within about 5~6 µm of thickness. The fabrication parameters, especially exposure dose, post-exposure bake temperature and time were optimized experimentally to confirm well-organized and durable 3D periodic nanostructures.
5.4 Experimental Results

Based on the analytical and numerical models, different combinations of incident light wavelengths and sphere sizes can be utilized to control the $\gamma$ parameter and demonstrate various types of 3D nanostructures. According to Eq. (2), longer wavelength and smaller diameter of sphere results in higher $\gamma$ parameter, and vice versa. 3D nanostructures with $\gamma = 0.23$ to 0.65 were experimentally fabricated, as shown in Figure 5-5. The FDTD simulation data for the corresponding $\gamma$ parameter are also shown, and agrees well with experimental results. From the analysis in the previous section, the most complex 3D patterns were achieved.
at low $\gamma < 1/\sqrt{7}$, which results higher diffraction order was allowed in this case. Note that a thin layer on top of every structures was generated while the oxygen plasma surface treatment step for assembling colloidal nanospheres on SU-8. In the fabricated structure with $\gamma = 0.31$, the frequency-doubled sub-image plane can be observed at 992 nm and the feature period is around 360 nm, which is less than half of the sphere period. The $\gamma = 0.23$ case was expected to generate more complex fabricated 3D structures, however the finer features by the frequency-multiplied sub-images did not develop. This can be attributed to lower exposure contrast in those areas, and resulted in fully crosslinked layer. The first frequency-multiplied sub-image plane, on the other hand, can still be observed and has feature period of about 500 nm. When $\gamma$ parameter is higher than $1/\sqrt{7}$, the fabricated nanostructures showed simpler unit cell and more robust structures because the primary images were repeated with much shorter period while the sub-images do not exist. The most durable structures were achieved at $\gamma = 0.58$, where the thickness of its column and plane were almost the same everywhere inside the structure.
Figure 5-5. Comparison of FDTD simulations and experimental results with various $\gamma$ parameters. Lower $\gamma$ (0.23 and 0.31) shows complex patterns, and higher $\gamma$ (0.58 and 0.65) results in simple patterns. Scale bars in every SEM images indicate 1 $\mu$m.

Some structural collapse and breakage can be observed for structures fabricated using a mercury lamp with a 365 nm bandpass filter. I believe this is due to the finite bandpass bandwidth, which is about 10 nm. As a result the Talbot image is blurred, reducing exposure contrast and leading to collapse during development. This shows that while not required, single-wavelength laser sources are preferred when fabricating robust 3D nanostructures. In addition, the exposure using 405 nm laser diode module ($\gamma = 0.57$) showed many partial collapses or breaks than other fabrication results. This can be due to the chemistry incompatibility of the photo-initiator to enhance sensitivity. The process optimization of the ratio of photo-initiator to SU-8 solution is currently underway to avoid these defects due to the incomplete cross-linking.
Another limitation of our work came from the nature of SU-8, which requires a post-exposure bake step to crosslink the polymer and swells during development [135]. Although the baking process was optimized experimentally to obtain structures with high quality, the swelling issue cannot be resolved thoroughly and resulted in mechanical instability of 3D nanostructure. This occasionally leads structural failure during aqueous rinsing and drying step due to the surface tension. However this limitation can be mitigated by using critical point drying (or supercritical drying). Structures with finer features and physical defects are much vulnerable to this issue, and I believe this explains why the lower γ nanostructure was more difficult to obtain experimentally because they typically contain multiple frequency-multiplied sub-images.

Lastly, the dependency of the normalized Talbot distance, \( z_t/\Lambda \) on γ parameter for the fabricated nanostructures are compared with analytical and FDTD models, as depicted in Figure 5-6. The different diffraction regimes are also identified, where \( m = 1 \), \( m = 2 \), and \( m > 2 \) results in Talbot patterns with secondary phase-reversed image, single sub-image plane, and multiple sub-image planes, respectively. In general, both the analytical and FDTD models agree well with the experimental data and less than 5% of error was observed in most range of γ. However for \( \gamma < 0.3 \), the analytical and FDTD models diverge slightly, and the experimental data shows better agreement to the analytical model. The possible reason is that the interface between nanosphere array and photoresist layer on FDTD model caused noisy patterns on following Talbot intensity profile, which made difficult to measure the exact Talbot distance from the following repeated patterns. Also, the higher errors among experimental data were mainly from the samples with a bandpass filter, which is explainable again by the dispersed wavelength after the bandpass filter. Other than that, the experimental data showed
good agreement, and this demonstrates the unit cell in our 3D nanostructure is designable and controllable by selecting a proper $\gamma$ parameter. The detailed comparison between analytical, numerical, and experimental data is shown in Table 5-1.

Figure 5-6. Comparison of analytical, numerical (FDTD), and experimental values of normalized Talbot distance between $\gamma = 0.2$ and 0.9. The colored area shows the regions which $m$ diffraction orders are allowed. The boundary values are $\gamma=1/\sqrt{3}$ and $\gamma=1/\sqrt{7}$. 

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Table 5-1. Analytical, numerical and experimental Talbot distance data with corresponding $\gamma$ parameter.

<table>
<thead>
<tr>
<th>$\gamma$ Parameter</th>
<th>Experimental (nm)</th>
<th>Analytical (nm)</th>
<th>Error (%)</th>
<th>Numerical (nm)</th>
<th>Error (%)</th>
</tr>
</thead>
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<tr>
<td>0.65</td>
<td>901</td>
<td>908</td>
<td>0.8</td>
<td>908</td>
<td>0.8</td>
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<tr>
<td>0.58</td>
<td>1048</td>
<td>1053</td>
<td>0.5</td>
<td>1053</td>
<td>0.5</td>
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<tr>
<td>0.57</td>
<td>1254</td>
<td>1397</td>
<td>10.2</td>
<td>1350</td>
<td>7.1</td>
</tr>
<tr>
<td>0.51</td>
<td>1454</td>
<td>1581</td>
<td>8.0</td>
<td>1545</td>
<td>5.9</td>
</tr>
<tr>
<td>0.46</td>
<td>1764</td>
<td>1804</td>
<td>2.2</td>
<td>1683</td>
<td>-4.8</td>
</tr>
<tr>
<td>0.34</td>
<td>3547 (Primary) 885 (Doubled)</td>
<td>3709</td>
<td>4.4</td>
<td>3350 834</td>
<td>-5.9 -6.1</td>
</tr>
<tr>
<td>0.31</td>
<td>3926 (Primary) 992 (Doubled)</td>
<td>4193</td>
<td>6.4</td>
<td>3656 914</td>
<td>-7.4 -8.6</td>
</tr>
<tr>
<td>0.23</td>
<td>3630 (Secondary) 1850 (Doubled)</td>
<td>3767</td>
<td>3.6</td>
<td>3358 1679</td>
<td>-8.1 -10.1</td>
</tr>
</tbody>
</table>

5.5 Summary

In this work I have demonstrated a method exploiting the Talbot effect generated by colloidal phase mask to design unit cell geometries for periodic 3D nanostructures. First, I analytically calculated Talbot distance and numerically simulated Talbot intensity patterns for a wide range of unit-less parameter, $\gamma$. Then, using a 2D self-assembled polystyrene nanosphere array as a phase shift mask, 3D nanostructures were successfully fabricated within a thick negative-tone photoresist. The $\gamma$ parameter was the sole factor to control the lattice parameters, unit-cell feature sizes, and complexity of intermediate sub layers, and different nanostructures were
achieved experimentally by various combinations of incident light wavelengths and nanosphere sizes. The experimental results were compared with analytical and numerical models, and it showed a good agreement with less than 5% error in most of cases. Both complex unit cell with lower $\gamma$ and simple unit cell with higher $\gamma$ are expected to be useful in practical applications, such as photonic crystals, microfluidics, and ordered cellular materials.
CHAPTER 6

CONCLUSIONS

In this thesis, I presented an approach to the design and fabrication of transparent and flexible metallic nano-accordion structures by advanced lithography and thin metal film deposition techniques. This was a combined approach using both geometry-based and material-based approaches, which are two common strategies to achieve flexible electronics by many researchers and engineers. To reach the final goal, I first demonstrated the fabrication process for a free-standing metallic nano-accordions on silicon (Si) substrate. In this stage, I used Lloyd’s mirror interference lithography (IL) to make a 1D periodic grating structure on photoresist as a sacrificial polymer template, and then employed platinum (Pt) atomic layer deposition (ALD) technique to create a thin conformal metal film on the nanostructures. After thermal process, the metallic Pt film with accordion-like geometry has been left only on top of Si substrate, and the resistivity of the film remained about 20 µΩ·cm as same as before thermal process, showing the excellent electrical property of a conductive material. The final cross-sectional profiles of Pt films was controlled by changing geometric parameters, such as duty cycle (DC) and aspect ratio (AR), of sacrificial polymer template. Mainly two different top shapes, a round top and a flat top, can be fabricated on periodic gratings of polymer template by IL, then after thermal process, wave-like, and pipe-like Pt nano-accordions were made from the round top templates while sprout-like, mushroom-like, and tree-like Pt nano-accordions.
were made from the flat top templates. The superb structural and thermal stability of this metallic nanostructures were also verified.

Then I demonstrated another thin conformal metal film deposition techniques based on physical vapor deposition (PVD) to overcome several disadvantages of ALD techniques and retain advantages of PVD techniques. The poor step coverage and low conformality of gold (Au) film by thermal deposition were improved by introducing aluminum oxide (Al₂O₃) interlayer on polymer template before metal deposition, and the uniformity of the metal film was also promoted. The better quality of metal layer was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) first, and electrical conductivity test helped its quantitative measurement to confirm the enhancement. Other metal oxide interlayers, zinc oxide (ZnO) and titanium dioxide (TiO₂), were also tested and showed their merit as a seed layer for depositing metal layer on it. Using this another approach, I could have more choices of materials for the final nano-accordion structures and benefits on reducing process time and cost.

Later, having my own material and geometry based approaches, the overall fabrication process was confirmed and presented with additional steps for better optical transparency. Metal film itself has a very reflective nature against incoming light, I made a physical opening on the film by secondary patterning. Through this micro-windows the optical transmission could be improved and broadband transmission test was performed with different micro-window ratios. Then, to test the stretchability of metallic nano-accordion structures, a transfer step from Si substrate to soft substrate, such as PDMS and Ecoflex, was developed. By applying tensile
force on soft substrate, the flexibility of my metallic nanostructures could be examined and visualized using electron microscopy.

In the last chapter, the design and fabrication of 3D periodic nanostructures using colloidal lithography was presented. In this work I have demonstrated a method using Talbot effect generated by colloidal phase mask to design unit cell geometries for periodic 3D nanostructures. A unit-less parameter, \( \gamma \), a combination of wavelength of incident light and size of colloidal sphere, was introduced to analytically calculate Talbot distance and numerically simulate Talbot intensity patterns. Different types of 3D nanostructures by wide range of \( \gamma \) were successfully fabricated within a thick negative-tone photoresist. Then, experimental results were compared with analytical and numerical models, and it showed a good agreement in most of cases. The applications of various types of 3D periodic nanostructures, such as photonic crystals, microfluidics, and ordered cellular materials, are subject of future study. Large-area and continuous fabrication process using roll-to-roll system is also under investigation for fast and low cost production.
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A.1 Fabrication of polymer template for platinum ALD

First, 90 nm thick antireflection coating (ARC i-CON-7, Brewer Science, Inc.) and 500 nm of SU-8 (Microchem, Corp.) were spin-coated on a silicon wafer to prevent back-reflection during lithography and create a buffer layer, respectively. SU-8 was spin-coated on top of the buffer layer and soft-baked at 95 °C. An interference lithography setup with HeCd laser (wavelength of 325 nm) was used to pattern the template grating with 1 μm period. A range of exposure dose from 3–6 mJ cm⁻² was used to control the template feature width. After exposing process, the samples were post-expose-baked at 65 °C, developed with propylene glycol monomethyl ether acetate (PGMEA), and rinsed in Isopropyl Alcohol (IPA) followed by hard-bake at 220 °C.

A.2 Removal of polymer template by thermal process

The SU-8 template removal process was performed using convection oven at 550 °C. Slow temperature ramping of 0.5–1.0 °C per minute was used to avoid structure collapse attributed to sudden temperature changes. The samples were then treated with oxygen plasma to clean organic contaminants and other residuals.
A.3 Removal of polymer template by dry etching process

I used three different recipes to remove SU-8 template by dry etching. First one is O$_2$ plasma etching (March PM 600) with RF power of 300 W at 600 mTorr. Etch rate of this recipe was about 90 ~ 100 nm/min, and I usually use 12 minutes of etching time for a polymer template with 1 μm thickness. Second one is reactive ion etching (RIE, Oxford NGP 80) with 80 sccm of O$_2$ at 250 W and 150 mTorr, and etch rate is around 175 ~ 185 nm/min. The last one is RIE with 80 sccm of O$_2$ and 4 sccm of SF$_6$ at 250W and 150 mTorr, and etch rate is about 1100 ~ 1200 nm/min. These etch rate was measured by the actual results with my polymer template with periodic trench structures, and can be changed with other results on different geometric shapes.
APPENDIX B

RECIPES FOR ATOMIC LAYER DEPOSITION OF MATERIALS

Courtesy of J. Zachary Mundy, Paul Lemaire, Dennis T. Lee, Dr. Christopher Oldham and Prof. Gregory Parsons, Department Of Chemical And Biomolecular Engineering, NCSU

B.1 Aluminum Oxide (Al₂O₃)

An aluminum oxide (Al₂O₃) layer was coated on the polymer template using ALD in a lab-made hot-wall viscous-flow vacuum reactor (1 Torr at 200 °C). A metal precursor, trimethylaluminum (TMA, 98% pure, Strem Chemicals) is first dosed for 0.5 seconds, followed by nitrogen (filter-dried by Entegris GateKeeper, 99.999% pure) purge for 30 seconds, and then a co-reactant, UV-deionized water, is dosed into the chamber for 0.5 seconds, followed by another nitrogen purge for 30 seconds. The growth rate is about 1.3 Å per cycle, and 40 cycles were conducted to deposit around 5 nm of Al₂O₃. Clean wafer silicon wafers were placed up- and downstream of the samples, verifying a uniform ALD coating.

B.2 Titanium Dioxide (TiO₂)

The atomic layer deposition of titanium dioxide (TiO₂) were conducted at ~1.8 Torr and 90°C. In TiO₂ ALD cycle, titanium (IV) chloride (TiCl₄, 99%, STREM Chemical) was first dosed to the reactor chamber for 1 second, followed by 40 seconds of N₂ (99.999%, Airgas, further purified with an Entergris GateKeeper) purge. After the dose and purge steps, deionized water
was dosed to the chamber for 1 second, followed with 60 seconds of N\textsubscript{2} purge. The growth rate is about 0.4 Å per cycle, and 130 cycles were conducted to deposit around 5 nm of TiO\textsubscript{2}.

**B.3 Zinc Oxide (ZnO)**

The pressure and temperature used for ALD of ZnO is the same as in TiO\textsubscript{2} ALD process (~1.8 Torr and 90°C). In ZnO ALD cycle, the substrates were exposed to 2 seconds of di-ethyl zinc (DEZ, 95%, STREM Chemicals) and 2 seconds of deionized water alternatively, with 60 seconds of N\textsubscript{2} (99.999%, Airgas, purified with an Entergris GateKeeper) purge between dose steps. The growth rate is about 0.7 Å per cycle, and 70 cycles were conducted to deposit around 5 nm of ZnO.

**B.4 Platinum (Pt)**

A platinum layer was coated at 1 Torr and 200 °C using (methylcyclopentadienyl) trimethylplatinum (MeCpPtMe\textsubscript{3}) as the precursor and ozone as the reactant gas. The typical dosing scheme is composed of 4 second for Pt precursor dose, 5 seconds of Pt precursor hold, 30 seconds of nitrogen purge, and then 4 second for ozone dose, 5 seconds of ozone hold, 30 seconds of nitrogen purging. The hold steps were included to effectively increase precursor and reactant exposure to the target substrate. The Pt precursor, MeCpPtMe\textsubscript{3} (99% pure, Strem Chemicals) was prepared at 60 °C in a stainless steel vessel and the ozone was generated from research-grade oxygen (99.999% pure, Machine & Welding Supply Company) with
concentration set to 11 wt%. The platinum growth rate is about 0.45 Å per cycle, and 420 cycles were repeated to deposit around 20 nm of metallic Pt.

**B.5 Tungsten (W)**

The tungsten ALD was performed at 1 Torr and 220 °C using argon (Ar) gas (99.999%, Machine & Welding Supply Company) as the process carrier gas. A tungsten film was achieved by alternately pulsing SiH$_4$ (Custom Gas Solutions, Durham, NC) and WF$_6$ (Sigma-Aldrich) with inert gas purge steps following each exposure. SiH$_4$ with dilute mixture (2% in Ar) was for our silane dose. The W ALD process used a pulse sequence of 60 seconds of SiH$_4$ dose, 45 seconds of Ar purge, 1 second of WF$_6$ dose, and 60 seconds of Ar purge. The tungsten growth rate was about 5.0 Å per cycle at this pressure and temperature.
APPENDIX C

SEM IMAGE DATA

C.1 Platinum Nano-Accordion by ALD

C.1.1 More Examples of “Sprout-like” Cross-Sectional Profiles
C.1.2 More Examples of “Pipe-like” Cross-Sectional Profiles

C.1.3 More Examples of “Mushroom-like” Cross-Sectional Profiles

C.1.4 Thicker Pt ALD ($t = 30$ nm)
C.1.5 Results after 10 Minutes Oxygen Plasma Etch Trimming

- Before ALD Process

- After ALD and Thermal Process

C.1.6 2D Periodic Hall Array

- Before ALD Process
• After ALD and Thermal Process
C.2 Tungsten (W) Nano-Accordion by ALD

C.2.1 W ALD on Polymer Template with AR = 0.67 (h = 400 nm, w = 600 nm)

C.2.2 W ALD on Polymer Template with AR = 1.0 (h = 600 nm, w = 600 nm)

C.2.3 W Nano-Accordion on PDMS after RIE
C.2.3 W ALD on Stretch Test (up to 30%)
C.3 Gold (Au) Nano-Accordion by PVD

C.3.1 Au Film (30 nm) on ZnO Interlayer (5 nm)

C.3.2 Au Film (30 nm) on TiO$_2$ Interlayer (5 nm)

C.3.3 Gold Nano-Accordion on PDMS before BOE Cleaning
C.3.3 Gold Nano-Accordion on PDMS after BOE Cleaning
C.4 Aluminum (Al) PVD on Al₂O₃ Interlayer over 2D Polymer Pillar Array
APPENDIX D

STEM IMAGE AND EDS MAPPING DATA

D.1 Gold (Au) PVD without Oxide Interlayer

- Au 30 nm on SU-8 template with AR = 0.67 (h = 400 nm, w = 600 nm)

- STEM image

- EDS mapping data
D.2 Gold PVD on Aluminum Oxide (Al₂O₃) Interlayer

D.2.1 SU-8 Template with AR = 0.5 (h = 300 nm, w = 600 nm)

- Au 30 nm on Al₂O₃ 5nm
- STEM image
- EDS mapping Data
D.2.2 SU-8 Template with AR = 0.67

- Au 30 nm on Al₂O₃ 5nm

- STEM image

- EDS mapping data
D.2.3 SU-8 Template with AR = 1.0 (h = 600 nm, w = 600 nm)

- Au 30 nm on Al₂O₃ 5nm
- STEM image
- EDS mapping data
D.3 Gold PVD on Zinc Oxide (ZnO) Interlayer

- Au 30 nm on ZnO 5 nm over SU-8 template with AR = 1.0 (h = 600 nm, w = 600 nm)
- STEM image
- EDS mapping image
D.4 Gold PVD on Titanium Dioxide (TiO$_2$) Interlayer

- Au 30 nm on TiO$_2$ 5 nm over SU-8 template with AR = 1.0

- STEM image

- EDS mapping image
D.5 Tungsten ALD on Aluminum Oxide (Al₂O₃) Interlayer

- W 20 nm on Al₂O₃ 2 nm over SU-8 template with AR = 1.0
- STEM image
- EDS mapping image