To my loving parents, without their support, I would not have the achievements I have
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This dissertation basically contains two different research topics. The first topic is covered in Chapter 1 to Chapter 3, describing how to generate periodic nanostructures in large scale on different substrates by assembling nanoparticles via a spin-coating technique. For the second topic, Chapter 4 and Chapter 5 describe how to make single graphene sheets and then use them as nanofillers for making polymer nanocomposites.

Antireflection coatings (ARCs) have been widely utilized to reduce the unwanted reflective losses of incident light from crystalline silicon surface. More than 30% of incident light is reflected back from the surface of crystalline silicon because of its high refractive index. Quarter-wavelength silicon nitride (SiNx) films deposited by plasma-enhanced chemical vapor deposition (PECVD) are the industrial standard for ARCs on crystalline silicon substrates. However, the PECVD-deposited SiNx films are expensive to fabricate. Additionally, commercial SiNx ARCs are typically designed to suppress reflection efficiently at wavelengths around 600 nm. The reflective loss is rapidly increased for near-infrared and other visible wavelengths, which contain a large portion of the incident solar energy.
In order to resolve the throughput and scalability issue of generating nanometer features, we have recently developed a versatile spin-coating technique that enables wafer-scale assembly of submicrometer-sized particles into non-close-packed structures. This technique provides a scalable templating fabrication platform to produce a majority of nanostructured materials with submicrometer-scale periodicity. My research mainly focuses on developing subwavelength-structured “moth-eye” antireflection coatings on silicon substrates by our spin-coating technique to improve the light collection efficiencies of crystalline silicon solar cells. The templated subwavelength silicon nipple arrays exhibit excellent broadband antireflective and superhydrophobic properties. Besides, “moth-eye” antireflection coatings can also be generated on GaSb substrates by spin-coating technique and on glass substrates via soft lithography successfully. To greatly extend the capability of the spin-coating technique in creating periodic nanostructures with resolution beyond the optical diffraction limit, I also demonstrate the scalable production of periodic sub-100 nm features with more than one order of magnitude higher number density than our previous approaches by assembling 70 nm diameter silica particles.

The second topic in this dissertation covers the fabrication of single graphene sheets and graphene – chitosan nanocomposites. Graphene – a single layer of carbon atoms bonded together in a hexagonal lattice – has stimulated a vast amount of research in recent years. Its remarkable properties including high values of Young’s modulus (~1100 GPa), thermal conductivity (~5000 Wm⁻¹K⁻¹) and specific surface area (~2630 m²g⁻¹) make it an excellent carbon-based nanofiller material for polymer-based nanocomposites. Nanocomposites have great potential to exceed the performance of
conventional composites due to its nanoscale fillers at low loading. However, maximal mechanical enhancement can only be achieved when the nanofiller is homogeneously dispersed in the polymer matrix and the external tensile load is efficiently transferred via a strong interaction at the interface between the filler and the matrix.

Chitosan, a natural-biopolymer with unique structure features, possesses the primary amine at the C-2 position of the glucosamine residues and is soluble in aqueous acidic media at pH < 6.5. It is commonly used to disperse nanomaterials and immobilize enzymes for constructing biosensors due to its excellent capability for film formation, nontoxicity, biocompatibility, mechanical strength, and good water permeability. My research is to disperse strong, highly stiff graphene sheets in a chitosan biopolymer matrix with self-assembling layered structures by using a simple evaporation method for developing high-performance lightweight composites in different applications. The photograph and the cross-sectional SEM images of the final composite film show that graphene sheets are uniformly dispersed in the polymer matrix and aligned parallel to the surface of the film, indicating external tensile loads can be successfully transmitted to the strong graphene nanofiller across the graphene–chitosan interface via interfacial interactions. Based on my results, a 90% increase in tensile strength can be achieved at a very low filler content (~4.76 wt%).
1.1 Introduction

Spin coating is a well-established technique in microfabrication to form highly uniform thin films with adjustable thickness over large area.\(^1\) It has already been utilized in making colloidal crystals, such as colloidal masks for nanosphere lithography.\(^2\) However, traditional spin-coating methods utilize volatile solvents (e.g. water and alcohol) to disperse colloidal particles. The rapid evaporation of solvents during spin-coating processes leads to polycrystalline samples with poor qualities.\(^3\) By eliminating solvent evaporation, particles would have sufficient time to be organized into energetically favorable states during spin coating. After colloidal self-assembly, the dispersing solvents need to be removed to release aligned colloidal crystals. The removal process should be gentle enough that does not affect the ordering of the colloidal arrays. Dry etching is a good candidate as it does not involve any wet processing that might torture the colloidal crystals by strong capillary forces. To satisfy the vacuum requirements of drying etching processes, the solvents need to be solidified before etching. Considering all these requirements, non-volatile monomers stand out from other possible solvents as they can be easily polymerized to trap the assembled colloidal arrays, and can subsequently be removed by standard plasma etching to release the colloidal crystals.

1.2 Spin-Coating Process

A volume fraction of ca. 20% silica colloids with diameters from ~ 30 nm to ~ 2 μm are dispersed in ethoxylated trimethylolpropane triacrylate (ETPTA) monomer to form transparent and stable suspensions. In a typical spin-coating experiment, the colloidal
suspension is dispensed on a substrate and then spin-coated on a standard spin coater. The substrate is accelerated in 2 seconds to 200 rpm and kept at this speed for 2-3 minutes, then accelerated to a desired speed at a typical acceleration rate of 200rpm/s and continues to spin for a specific time to achieve a target thickness. The substrate is then transferred to a high intensity UV lamp to polymerize the monomer.

The self-assembled silica colloidal crystal-polymer nanocomposite films exhibit bright monochromatic six-arm diffraction (Figure 1-1), indicating the formation of hexagonally packed spheres parallel to the wafer surface. The long-range hexagonal ordering is confirmed by the top-view scanning electron microscope (SEM) images of two samples consisting of 325 nm (Figure 1-1B and C) and 1320 nm (Figure 1-1D) silica spheres. The ordering perpendicular to the substrate surface is apparent in the cross sectional images shown in Figure 1-2. Most interestingly, the spin-coated colloidal crystals exhibit unusual non-close-packed (ncp) structures as revealed by magnified SEM images (Figure 1-2C and D). This is more apparent after the polymer matrix been selectively removed by oxygen plasma etching (Figures 1-3A and C). For multilayer samples, spheres of the top layer only fill in the triangularly arranged crevices made by the non-touching spheres of the second layer (Figure 1-3C). The center-to-center separation between adjacent spheres for all samples assembled using different-size particles and with different thickness is determined to be ~ 1.41D, where D is the diameter of silica spheres, by the first peak of the pair correlation function (PCF, (Figure 1-3 B)) calculated from SEM images similar to Figure 1-3A and C.

The spin-coated nanocomposite films exhibit excellent thickness uniformity with variation within a four-inch-diameter wafer of less than 4%. The film thickness can be
controlled easily by changing the spin speed and time. It is inversely proportional to the final spin speed and the square root of the final spin time. Figure 1-2 shows cross-sectional images of four crystals of monolayer, 2 layers, 5 layers, and 41 layers made at different spin-coating conditions. Even thicker samples can be assembled by multiple coatings. New colloidal multilayer is spin-coated on the top of the original ones and the process can be repeated many times with the thickness increasing linearly after each coating. The modulated top surface of the bottom layers (Figure 1-2C) functions as templates in aligning the crystalline orientation of the subsequent multilayer. As discussed above, the polymer matrix need to be removed to release the embedded silica colloidal crystals that can be used as templates in creating inverted photonic crystals with high refractive index contrast. Standard oxygen plasma etching is a better method than calcination in removing ETPTA polymer matrix, as it hardly affects the silica spheres and no defects, such as cracks, are introduced. Figures 1-3A, C and D show top- and side-view SEM images of monolayer and multilayer colloidal crystals after polymer matrix removal. The preservation of the hexagonal long-range ordering and the center-to-center separation of the original nanocomposites throughout the plasma etching process are clearly evident. We notice a significant difference in the resulting crystalline quality between monolayer and multilayer colloidal crystals prepared by the same spin-coating process. The typical domain size of monolayer samples is only several hundred microns, much smaller than that of multilayer samples (~cm).

When the spin-coating speed is low (6000 rpm), we only observe six-arm diffraction patterns with exact 60° angles between neighboring arms, indicating the
formation of hexagonally ordered colloidal crystals. Unexpected results occur when the spin speed is higher than 6000 rpm. We observe the alternate formation of hexagonal and square diffraction patterns when the thickness of the colloidal crystals is gradually reduced during spin coating. The spin-coating process is stopped once a strong four-arm diffraction pattern is formed on the wafer surface and the ETPTA monomers are then photopolymerized by exposure to UV radiation. The solidified ETPTA matrix can finally be removed by oxygen plasma etching to release the embedded colloidal arrays.

Figure 1-4A shows a photograph of a 4 in. diameter colloidal monolayer sample made from 380 nm silica spheres and spin coated at 8000 rpm for 150 s. The sample exhibits a distinctive four-arm diffraction pattern under white light illumination, and the angles between the neighboring diffraction arms are 90°. This pattern is a characteristic of long range square ordering. This is confirmed by the SEM image in Figure 1-4B and is further evidenced by the squarely arranged peaks in the Fourier transform of a low-magnification SEM image, as shown in the inset of Figure 1-4B. Further SEM characterization shows that the squarely arranged arrays cover the whole wafer surface, and the crystals are polycrystalline with typical domain size of several tens of micrometers. To obtain colloidal monolayer with larger single crystalline domains, the layer-by-layer thinning technology can be employed to gradually reduce the thickness of the spin-coated multilayer crystals, which usually exhibit better ordering than shear-aligned monolayer arrays.

Finally, Figure 1-5 shows a clear side-view SEM image of monolayer colloidal crystals on the silicon wafer. How this colloidal template can be used for generating nanostructures is discussed in the following chapters.
Figure 1-1. Spin-coated silica-polymer nanocomposites with long-range ordering. A) Photograph of a 4 in. sample consisting of 325nm silica spheres illuminated with white light. B) Top-view SEM image and its Fourier transform (insert) of the sample in A. C) Magnified SEM image of B. D) A sample made from 1320nm silica spheres.

Figure 1-2. Well control over the nanocomposite thickness by spin coating. A) Monolayer, B) 2-layer, C) 5-layers and D) 41-layer.

Figure 1-4. Spin-coated monolayer, non-close-packed colloidal crystal with metastable square lattice. A) Photograph of a 4 in. sample illuminated with white light. B) SEM image of the sample in A.
Figure 1-5. Side-view SEM image of monolayer colloidal crystals on the silicon wafer generated via spin-coating technique for templating nanostructures.
CHAPTER 2
BIOINSPIRED SELF-CLEANING ANTIREFLECTION COATINGS

2.1 Introduction

Fabrication of structures with minimum dimensions of approximately 0.1 to 100 nm can be generally called as nanopatterning. The ability to pattern materials at this scale is of great significance to the microelectronics industry where the reduction of feature sizes has led to increased device performance and lower production costs. Recently large-scale fabrication of sub-100 nm periodic nanostructures attracts a lot of interest for the development of new materials with potential applications in areas such as high-density data storage,6,7 biosensing and bioseparation,8-11 and optoelectronics.12,13 An important example is the creation of subwavelength-structured moth-eye antireflection coatings (ARCs) for developing high-performance solar cells and optoelectronic devices.14,15 These coatings are inspired by biological systems that produce unique functionalities.16-18 For instance, moths use hexagonal arrays of non-close-packed (ncp) nipples as ARCs to reduce reflectivity from their compound eyes.16,18,32 The outer surface of the corneal lenses of moths consists of ncp arrays of conical protuberances, termed corneal nipples, typically of sub-300nm height and spacing.32 As the periodicity of these nipple arrays is small compared to the wavelength of light, they generate a graded transition of refractive index, leading to minimized reflection over a broad range of wavelengths and angles of incidence.20 Similar periodic arrays of ncp pillars have also been observed on the wings of cicada to render superhydrophobic surfaces for self-cleaning functionality.17

Antireflective nanostructures have distinct advantages compared to layers of thin dielectric films.21 Thin film coatings suffer from mechanical stability problems like layer
ablation and tensile stress if optical devices are used over a broad thermal range.\textsuperscript{21,22} Also, appropriate epitaxial materials with proper refractive indices scarcely exist. Common single- and multilayer configurations are therefore applicable within a small wavelength range and normal incidence of light. In contrast, materials with antireflective nanostructures show a broadband, angle-dependent reflectance. Polymer thin film coatings\textsuperscript{23,24} with a nanostructured surface were developed to generate broadband ARCs; however, polymer materials suffer from strong absorbance and radiation damage if they are used with ultraviolet light.

\textbf{2.2 Statements of Problems}

ARCs have been widely utilized to reduce the unwanted reflective losses of incident light from crystalline silicon surface, which is the most important material for solar cells. More than 30\% of incident light is reflected back from the surface of crystalline silicon because of its high refractive index.\textsuperscript{25} Quarter-wavelength silicon nitride (SiNx) films deposited by plasma-enhanced chemical vapor deposition (PECVD) are the industrial standard for ARCs on crystalline silicon substrates.\textsuperscript{26} However, the PECVD-deposited SiNx films are expensive to fabricate. Additionally, commercial SiNx ARCs are typically designed to suppress reflection efficiently at wavelengths around 600 nm.\textsuperscript{25} The reflective loss is rapidly increased for near-infrared and other visible wavelengths, which contain a large portion of the incident solar energy. Different techniques such as electron-beam lithography, mask lithography, and interference lithography have been applied to generate ARCs. To avoid scattering from the optical interface, the structural dimension on the surface has to be smaller than the wavelength of the incoming light.\textsuperscript{27} For ultraviolet and deep-ultraviolet applications, very small feature sizes below 200 nm are necessary. In this size range, conventional fabrication
techniques mentioned before are time-consuming, expensive and restricted to small areas and low throughput.

2.3 Templated Antireflection Coatings on Silicon Substrates

2.3.1 Self-Cleaning Pillar Arrays Antireflection Coatings

In order to resolve the throughput and scalability issue of generating nanometer features, our lab has recently developed a versatile spin-coating technique that enables wafer-scale assembly of submicrometer-sized particles into non-close-packed structures. The outline of the templating procedures for patterning subwavelength pillar arrays on silicon substrates is shown in Figure 2-1. The spin-coating technique is firstly used to generate ncp colloidal monolayers of hexagonally ordered silica particles on (100) silicon wafers (Fig. 2-1A). These particles are then used as etching mask during a chlorine-RIE process (5 mTorr pressure (1 Torr = 1.333 × 10^2 Pa)), 20 SCCM chlorine flow rate, and 80 W). As the etching rate of silica is much lower than that of silicon under above RIE conditions, silica particles protect silicon immediately underneath them from being etched, resulting in the formation of pillar arrays directly on silicon surface (Fig. 2-1B). Once the silicon pillars are deep enough, the templating silica spheres can be removed by dissolving in a 2% hydrofluoric acid aqueous solution. Interestingly, we observe arrays of “micro-candles” consisting of silicon columns as candle bodies and polymer dots as candle wicks (Fig. 2-1C). The polymer dots are unetched residue of the thin polymer wetting layer (~100nm thick) between the spin-coated colloidal monolayer and the silicon substrate. These dots can be easily removed by brief oxygen RIE to generate clean silicon pillar arrays (Fig. 2-1D).

The residual polymer dots play a crucial role in determining the shape and aspect ratio of the templated silicon pillar arrays. This accounts for the poor reproducibility and
low aspect ratio of pillars generated by the SF$_6$ RIE process (40 mTorr pressure, 26 SCCM SF$_6$, 5 SCCM O$_2$, 25 W). In SF$_6$ RIE, reactive oxygen is also an active component that gradually attacks the polymer dots underneath the templating silica particles. When the dots are too narrow to support the silica spheres, they fall down before the silicon pillars reach enough depth. Once particle array collapses, isotropic etching of the exposed silicon pillars further reduces the aspect ratio. In contrast, during the current chlorine RIE process, reactive chlorine ions do not affect the polymer dots. This leads to the formation of silicon pillars with high aspect ratio, which benefits both antireflective and superhydrophobic properties.

The current templating technique can be easily utilized to generate wafer-scale silicon pillar arrays. Figure 2-2A shows a photograph of a 4 in. silicon wafer with the right half covered by subwavelength pillars and the left half unetched. The intact left side is mirror-like and highly reflective, while the right side with moth-eye microstructures exhibits much lower reflection. This is confirmed by the appearance of the overhead lamp used to illuminate the wafer on the left side, while no reflection image is visible on the right side. Figure 2-2B and C show scanning electron microscope (SEM) images of silicon pillar arrays etched for 10 and 50 min, respectively. It is apparent that the templated nipples are hexagonally ordered. The 10 min-etched pillars have vertical sidewalls, while the 50 min-etched pillars are tapered. This is caused by the gradual shrinkage of the templating silica spheres during the RIE process. The templated pillar depths at different RIE durations are measured by cross-sectional SEM images and are shown in Figure 2-2D. Pillars with depth of ca. 2.2 $\mu$m and aspect ratio of ca. 10 can be reached. Longer etching results in damaged pillars.
due to the significant shrinkage of the templating silica spheres which are too small to protect the underneath silicon from being etched.

The specular optical reflectivity of the templated silicon pillar arrays are evaluated using visible-near-IR reflection measurement at normal incidence. The solid lines in Figure 3 show the measured reflection from a bare silicon wafer and a 60 min-etched silicon pillar array. The wafer exhibits >30% reflectivity for all above wavelengths, consistent with previous measurements. The templated subwavelength grating exhibits much lower reflection (<2.5%) over the whole spectrum, indicating broadband antireflection. For pillars with lower aspect ratio, the reflection increases but is always below the value of a flat silicon wafer.

The experimental reflection measurements are complemented by theoretical calculations using a rigorous coupled-wave analysis (RCWA) model. We assume the template pillars as shown in Figure 2-2D have shape like inverted circular paraboloid with base radius \( r \) and height \( h \). We firstly divide the whole inverted circular paraboloid into 100 horizontal circular layers. The z-coordinate \( z^* \) and the radius \( r^* \) of each layer satisfy \( r^* = r \sqrt{1 - \left(\frac{z^*}{h}\right)^2} \), where \( 0 \leq z^* \leq h \). The internipple distance is defined as \( \sqrt{2}D \), where \( D \) is the diameter of templating silica spheres. We can then calculate the fraction of silicon in each layer as \( f(z^*) = \frac{\pi r^*}{\sqrt{3}D} \). The effective refractive index \( n(z^*) \) of the layer at height \( z^* \) can be approximated by \( n(z^*) = [f(z^*)n_{Si}^q + (1 - f(z^*))n_{air}^q]^{1/q} \) where \( q = 2/3 \). The complex refractive index of silicon is used to calculate the reflectance. We finally calculate the reflectance of the whole system by solving the Maxwell equation to express the electromagnetic (EM) field in each layer.
and then matching EM boundary conditions between neighboring layers for the
determination of the reflectance of the system.

The dotted lines in Figure 2-3 show the simulated specular reflection from a flat
silicon wafer and a hexagonal array of silicon pillars with 2200 nm height templated from
380 nm silica spheres. It is apparent that the calculated reflection from the silicon wafer
is very close to the measured spectrum. The simulated reflection from the templated
pillar array also agrees reasonably well with the experimental spectrum, though the
matching is not as good as the flat wafer. This is due to the limitation of the RCWA
model which assumes a uniform refractive index instead of periodic modulation within
each sliced layer.

The templated silicon subwavelength pillar arrays with high aspect ratio can also
significantly enhance the hydrophobicity of the substrate surface due to the high fraction
of air trapped in the trough area between pillars. The hydrophobicity of silicon pillars can
be further improved by functionalizing them with fluorosilane through the well-
established silane coupling reaction. Figure 2-4 show water drop profiles on
fluorosilane-modified silicon pillar arrays. The coatings are super-hydrophobic and the
measured apparent water contact angle (CA) is ca. 172°, significantly enhanced from
c. 108° on fluorinated flat silicon substrates. Figure 2-5 shows the dependence of the
measured water CA on RIE duration. It is apparent that longer etching duration leads to
more hydrophobic surface. This agrees well with previous studies on microstructure-
induced dewetting.

Experimental procedures. Preparation of NCP Monolayer Colloidal Crystal
Templates by Spin Coating: Monodispersed silica colloids with ca. 380nm diameter are
synthesized by the Stober method. The silica colloids are purified in 200-proof ethanol (Pharmaco Products) and then redispersed in ethoxylated trimethylolpropane triacrylate monomer (ETPTA, SR 454, Sartomer). Darocur 1173 (1 wt %) (2-hydroxy-2-methyl-1-phenyl-1-propanone, Ciba-Geigy) is added as the photoinitiator. The final particle volume fraction is adjusted to ca. 19.8%. The colloidal suspension is then dispersed on a silicon wafer (test grade, n type, Wafernet). The wafer is spun at 8000 rpm for 360 s on a standard spin coater (WS-400B-6NPP-Lite Spin Processor, Laurell). The ETPTA monomer is then photopolymerized for 4 s using a Pulsed UV Curing System (RC 742, Xenon).

Reactive Ion Etching: Both oxygen and chlorine RIE are performed on a Unaxis Shuttlelock RIE/ICP reactive-ion etcher. To remove the polymer matrix to release the embedded silica particles, oxygen RIE operating at 40 mTorr pressure, 40 SCCM flow rate, and 100W is carried out for 120 s. The release silica particles can then be used as etching mask during the following chlorine-RIE process operating at 5 mTorr pressure, 20 SCCM chlorine flow rate, and 80W to generate silicon pillars. The templating silica particles are dissolved in 2% v/v hydrofluoric acid aqueous solution for 2 min. The residual polymer dots can finally be removed by the same oxygen RIE process as described above.

Optical Reflection Measurement: An HR4000 High Resolution Fiber Optic UV–vis spectrometer and an NIR-512 spectrometer (both from Ocean Optics) with reflection probes are used for reflectance measurements. A calibrated halogen light source is used to illuminate the sample and the spectrometers can scan wavelengths from 350 to 1650 nm. Absolute reflectivity is obtained as ratio of the sample spectrum and the
reference spectrum. The reference spectrum is the optical density obtained from an aluminum-sputtered (1000nm thickness) silicon wafer. Final value of absolute reflectivity is the average of several measurements obtained from different spots on the sample surface. The resulting reflectivity is calibrated using an Ocean Optics STAN-SSL low-reflectivity specular reflectance standard for templated pillar arrays and glass slides and an STAN-SSH Highreflectivity specular reflectance standard for flat silicon wafers.

Surface Modification and CA Measurement: Both silicon and glass pillar arrays are chemically modified by reacting with a $4.4 \times 10^{-3}$ M solution of (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trichlorosilane (Gelest) in hexane/CCl$_4$ (v/v 70:30) for 2 h at room temperature. The resulting surfaces are rinsed with dichloromethane and ethanol and then dried under air. The apparent water CA is measured using a goniometer (NRL C.A. Goniometer, Rame´-Hart, Inc.) with autopipetting and imaging systems.

SEM: SEM is carried out on a JEOL 6335F FEG-SEM. A thin layer of gold is sputtered onto the samples prior to imaging.

2.3.2 Inverted Pyramid Arrays Antireflection Coatings

A schematic illustration of the fabrication procedures for making wafer-scale subwavelength inverted pyramid gratings on single-crystalline silicon wafers is shown in Fig. 2-6. We start to generate nonclose-packed colloidal monolayers on a (100) silicon wafer (test grade, $n$ type, Montco Silicon Technologies) by the spin-coating technology. The nonclose-packed silica particles function as shadow masks during an electron-beam evaporation process for depositing a 30 nm thick chromium layer. After lifting off the templating silica particles, a periodic array of nanoholes whose diameter is determined by the size of templating silica spheres can be formed. These circular
nanoholes can then be used as etching masks during a KOH anisotropic etching process to create wafer-scale inverted pyramid arrays in silicon substrates.

We are able to control the pyramid size by simply adjusting the anisotropic etching conditions. Figure 2-7 shows scanning electron microscope (SEM) images of two inverted pyramid arrays templated from the same spin-coated silica monolayer sample (320 nm particle diameter). The samples are etched in the same solution containing 62.5 g KOH, 50 ml anhydrous 2-propanol, and 200 ml ultrapure water at 60 °C for 90 and 210 s, respectively. It is apparent that longer etching leads to larger pyramids with well-defined square bases, while the less etched samples have rounded corners. The size of the pyramids can be larger than that of the templating silica spheres due to the undercutting of silicon substrates underneath chromium nanoholes. The longrange hexagonal ordering of the templated pyramidal pits is evident from the SEM images. The orthogonal crosses at the centers of the pits confirm the inverted pyramidal structures.37

The specular optical reflectivity of the replicated pyramid arrays is evaluated using visible-near-IR reflectivity measurement at normal incidence.35 The solid lines in Fig. 2-8 show the measured normal-incidence specular reflection from a polished (100) silicon wafer and the sample, shown in Fig. 2-7B, with 360 nm pyramidal pits. The flat silicon substrate exhibits high reflection (>35%) for visible and nearinfrared wavelengths, while the subwavelength-structured gratings show reduced reflection of ~10% for long wavelengths (>600 nm). The reflection is further reduced to ~2% for wavelengths around 400 nm. For smaller pyramids, the reflection progressively increases with decreased pyramidal pits.
The templated silicon subwavelength gratings exhibit lower reflection than colloid-based antireflection coatings on crystalline silicon solar cells.\textsuperscript{38} Though the normal-incidence reflection from the templated pyramid gratings is higher than other subwavelength-structured ARCs made by lithographic techniques with typical reflection of \textasciitilde 2\% – 10\%,\textsuperscript{32,39-41} the cost benefit of this nonlithographic methodology is a major advantage. Additionally, optimization of the template structures will facilitate further improvement of the antireflection performance. The state-of-the-art silicon nitride ARCs on crystalline silicon solar cells exhibit minimal (<2\%) reflection around 600 nm, but the reflection increases to more than 10\% for near-IR (>800 nm) and visible (<500 nm) wavelengths, which account for a significant portion of the solar spectrum.\textsuperscript{38,42} By contrast, the template pyramid arrays show relatively low reflection at short wavelengths (Fig. 2-8).

A multilayer rigorous coupled wave analysis (RCWA) model\textsuperscript{30} has also been developed to complement the optical measurement. Firstly, we divide the inverted pyramid array into 100 horizontal layers with equal thickness. Since the KOH-etched silicon pyramids have characteristic of 54.7° sidewalls, the depth of the anisotropic V-shape pitches is determined by the base length of the pits. Based on the effective medium theory,\textsuperscript{33} the effective refractive index \( n(z^*) \) of the layer at level \( z^* \) can be approximated by
\[
 n(z^*) = \left[ f(z^*) \bar{N}_{Si}^q + (1 - f(z^*)) n_{air}^q \right]^{1/q},
\]
where \( f(z^*) \) is the fraction of silicon contained in the layer, \( \bar{N}_{Si} = n + ik \) is the complex refractive index of silicon (\( n \) and \( k \) are optical constants), \( n_{air} = 1 \), and \( q = 2/3 \).\textsuperscript{33} The optical constants of silicon which are functions of wavelengths are obtained from literature.\textsuperscript{43} Secondly, we calculate the reflectance of the whole system by solving the Maxwell equation to
express the electromagnetic (EM) field in each layer and then match EM boundary conditions between neighboring layers for the determination of the reflectance of the system.

The RCWA-simulated reflection for a bare silicon substrate and an inverted pyramid array in silicon with 360 nm base length are shown by the dotted lines in Fig. 2-8. It is apparent that the theoretical prediction for single-crystalline silicon is close to the experimental spectrum, while for the subwavelength-structured pyramid gratings, the modeling results only match with experimental data when the wavelength is large. The difference tends to be large when the wavelength becomes small. This is due to the limitation of the modeling where each layer is assumed to have a uniform refractive index, which is, in fact, a two-dimensional periodic function at each layer. Meanwhile, the effective refractive index formula is only accurate when the wavelength of light is larger than the period of the pyramid arrays.

To understand the improved antireflection performance for subwavelength-structured pyramid arrays, we plot the calculated real part of the complex refractive index at $\lambda = 600$ nm versus the depth of pyramids with 60 nm (blue circles) and 360 nm (red circles) base lengths in Fig. 2-9. For 60 nm size pyramids, the refractive index changes sharply at the interface between air and the structured silicon surface. The graded index, which is desirable for suppressing the optical reflection, is observed for 360 nm pyramids—the refractive index changes from 1.0 to ~1.7 at the air/silicon interface and then gradually changes to the bulk index of silicon. We further calculate the normal-incidence reflection at $\lambda = 600$ nm for pyramid array samples with different
sizes and the results are shown in Fig. 2-10. It is apparent that larger pyramids lead to lower reflection, matching our experimental observation.

2.4 Templated Antireflection Coatings on Gallium Antimonide Substrates

Thermophotovoltaic (TPV) cells convert radiation from high-temperature materials to electrical charges that are utilized to power an external circuit.44-46 Gallium antimonide (GaSb) is one of the most appropriate materials for TPV generation due to the excellent match between the radiation spectrum and the spectral response of GaSb cells.47 Unfortunately, approximately 40% of the incident radiation is reflected back from the cell surface due to the high refractive index (RI) of GaSb.45 Vacuum deposited multilayer dielectric films (e.g., ZnS/MgF2) have been utilized as antireflection coatings (ARCs) for reducing the unwanted reflective losses.48 However, these multilayer coatings are expensive to fabricate and they can only suppress reflection over a narrow range of wavelengths. Additionally, the thermal stability of the multilayer ARCs is poor due to the mismatch of the thermal expansion coefficient between the substrate and the coatings.

One promising way to fabricate broadband ARCs is to pattern subwavelength-structured gratings directly on GaSb substrates.48 This is inspired by the grainy microstructures on the corneas of moths, which consist of a non-close-packed (NCP), hexagonal array of subwavelength conical nipples.32,49 These nipples can greatly reduce reflection by creating a RI gradient across the interface between air and cornea. Besides broadband antireflection, the moth-eye gratings are also intrinsically more stable and durable than multilayer ARCs since no foreign material is involved.51,52 However, current production of moth-eye ARCs is greatly impeded by the expensive top-down fabrication technologies. For instance, e-beam lithography (EBL) has been
utilized to create tapered gratings on GaSb substrates that decrease the reflection to 5%–10%.\textsuperscript{48} Unfortunately, EBL is expensive and the low throughput is a major concern. We have recently developed a simple yet scalable templating technology for patterning moth-eye gratings on single-crystal silicon substrates.\textsuperscript{53,54} Hexagonal monolayers of silica colloids prepared by an inexpensive spin-coating technique are used as etching masks during conventional reactive ion etching (RIE).\textsuperscript{54} Here, we demonstrate the fabrication of broadband ARCs on GaSb wafers that exhibit superior antireflection properties and thermal stability than conventional multilayer and EBL-patterned ARCs by using the colloidal templating approach. The effect of the nipple shape and size on the antireflection properties of moth-eye ARCs has also been systematically investigated.

The well-established spin-coating technique\textsuperscript{28,29} is used to generate NCP colloidal monolayers of hexagonally ordered silica particles embedded in a polymer matrix on a single-crystal GaSb wafer [(100) \textit{n}-type, Galaxy Compound Semiconductors]. The polymer matrix is partially removed by oxygen plasma etching (40 mTorr, 40 SCCM (SCCM denotes cubic centimeter per minute at STP) \textit{O}_2, 100 W for 2 min). The released colloidal array can then be used as etching mask during a chlorine-RIE process (5.3 mTorr, 8 SCCM \textit{Cl}_2, 4 SCCM \textit{Ar}) operating on a Unaxis Shuttlelock reactive ion etcher to pattern subwavelength nipple arrays. The templating silica particles can finally be removed by dissolving in a 2\% (v/v) hydrofluoric acid aqueous solution. The top- and tilted-view scanning electron microscope (SEM) images in Fig. 2-11 illustrate the resulting microstructures etched at 150 W for 3 min (Figs. 2-11A and
11B), and 200 W for 2.5 min (Figs. 2-11C and 11D). It is evident that different etching conditions lead to different nipple geometries.

We find that the polymer wetting layer between the spincoated colloidal monolayer and the wafer surface plays an important role in the RIE patterning process. During the oxygen plasma etching, the NCP silica particles protect the underneath polymer to form cylindrical polymer posts as indicated by the bright top posts in Fig. 2-11B and the red arrows in Fig. 2-11D. When the chlorine-RIE power is low (150 W), silica particles protect the GaSb surface immediately under the particles from being etched, resulting in the formation of the unusual candle-stand-shaped patterns as shown in Fig. 2-11B. When the etching power is high (200 W), the isotropic etching of the GaSb substrate leads to the formation of nipples with sharp tips as shown in Fig. 2-11D. Furthermore, the bottom of the polymer posts is damaged when the etching power is high as illustrated by the broken polymer posts in Fig. 2-11C. These polymer posts can be easily removed by a brief oxygen plasma etching at 100 W for 2 min.

The specular optical reflectivity of the template GaSb nipple arrays are evaluated using visible-near-IR reflectivity measurement at normal incidence. A HR4000 UV-visible spectrometer and a NIR-512 spectrometer (both from Ocean Optics) are used to measure the reflectance from 400 to 1700 nm. The solid lines in Fig. 2-12 show the measured reflection from a bare GaSb wafer and nipple arrays etched at 200 W for 1.5 and 2.5 min, respectively. The wafer exhibits >35% reflectivity for all above wavelengths, consistent with previous optical measurements. The 1.5 min etched sample shows lower reflection (5%–15%) and the reflectivity is wavelength dependent. Much lower reflection (<2%) is obtained when the etch duration is longer than 2.5 min.
Most importantly, the resulting subwavelength ARCs are broadband, exhibiting consistent low reflection over both visible and near-IR wavelengths.

The experimental measurements are complemented by theoretical calculations using a rigorous coupled-wave analysis (RCWA) model. Half-ellipsoid-shaped profile is used to simulate the templated nipples as shown in Fig. 2-11D. We divide the half-ellipsoid into 100 horizontal circular layers. The internipple distance is defined as $\sqrt{2}D$, where $D$ is the diameter of templating silica spheres. We can calculate the fraction of GaSb in each layer as $f(z^*) = \frac{\pi r^2}{\sqrt{3}D^2}$, where $z^*$ and $r^*$ are the z coordinate and the radius of the layer, respectively. Based on the effective medium theory, the effective RI $n(z^*)$ of the layer at height $z^*$ can be approximated by $n(z^*) = [f(z^*)n_{GaSb}^q + (1 - f(z^*))n_{air}^q]^{1/q}$, where $q = 2/3$. The complex RI of GaSb is used to calculate the reflectance.

The dotted lines in Fig. 2-12 show the simulated specular reflection from a bare GaSb wafer and a hexagonal array of nipples with 1000 nm height templated from 310 nm silica spheres. It is apparent that the calculated reflection from a GaSb wafer is very close to the measured spectrum. The simulated reflection from the templated nipple array also reasonably agrees well with the experimental spectrum. The excellent broadband antireflection properties of the template subwavelength gratings can be easily explained by mapping the calculated effective RI at $\lambda = 620$ nm across the height of 1000 nm nipples (Fig. 2-13). For bare wafer, the RI changes sharply from air (RI=1.0) to bulk GaSb (RI=5.239), while for templated nipples, the RI changes gradually from 1.0 to ~4.76 and then to 5.239. This RI gradient leads to very low reflection over a wide range of wavelengths.
We also investigated the effect of the nipple shape and size on the antireflection properties of subwavelength ARCs using the RCWA model. Figure 2-14 compares the simulated normal-incidence specular reflection from nipple arrays with three types of shape—half-ellipsoid, paraboloid, and pyramid. It is evident that the paraboloid and pyramid-shaped nipples show lower reflection than half-ellipsoid nipples. We also calculate the reflectance from nipple arrays template from different-size silica particles (100, 200, 300, 400, and 500 nm). The results show that the specular reflection is independent on the templated nipple size. This can be understood by considering the above formulas of \( r^* \) and \( f(z^*) \) which lead to 

\[
f(z^*) = \frac{\pi[1-(z^*/h)^2]r^2}{\sqrt{3}D^2},
\]

where \( h \) is the nipple height. Since \( r = \sqrt{2}/2D \) is always proportional to \( D \) so that \( r/D \) is a constant, \( f(z^*) \) and the RI are then independent of the particle size.

Since the surface temperature of TPV cells is higher than that of a conventional solar cell, the thermal stability of the templated subwavelength ARCs needs to be evaluated. We compare the normal-incidence specular reflection of the 2.5 min etched sample as shown in Fig. 2-12 prior to and after annealing at 200 °C for 6 h. The results in Fig. 2-15 show that the change of the reflection is very small, indicating excellent thermal stability of the templated gratings. This is in sharp contrast with the conventional multilayer ARCs which exhibit significant antireflection degradation even at temperature as low as 100°C.48

2.5 Templated Antireflection Coatings on Glass Substrates

Glass is another important optical substrate. Although the reflective loss from glass is not as severe as that from silicon, a ca. 4% optical reflection from each air/glass interface could still degrade the performance of optical devices especially when multiple...
components are involved.\textsuperscript{56,57} To generate efficient ARCs on glass substrates, various bottom-up self-assembly techniques have been extensively exploited.\textsuperscript{58-60} For instance, layer-by-layer assembly of polyelectrolyte or polyelectrolyte–colloid multilayers has been demonstrated as an efficient means in creating ARCs on glass.\textsuperscript{56,58-60}

Unfortunately, traditional bottom-up techniques suffer from low throughput and incompatibility with standard microfabrication, limiting the mass production of practical coatings. Furthermore, only limited, close-packed crystal structures are available through conventional colloidal self-assemblies, whereas ncp structures are needed to mimic the microstructures on natural moth eyes and cicada wings.\textsuperscript{32}

The templated silicon pillars with high aspect ratio can be used as second-generation templates to replicate polymer or glass moth-eye ARCs on transparent substrates. The PDMS (Sylgard 184, Dow Corning) precursors are mixed and degassed and then poured over the templated silicon pillar array. After curing at 80 °C for 30 min, the solidified PDMS mold is peeled off the silicon array. A thin layer (ca. 900nm thick) of sol–gel glass precursor (512B, Honeywell Electronic Materials) is spin-coated at 800 rpm for 60 s on a glass slide before putting on the PDMS mold. After baking at 120 °C for 5 min and peeling off PDMS, glass pillar arrays with high aspect ratio can be formed on the glass slide. Figure 2-16 shows top- and side-view SEM images of the resulting glass pillars template from a 30 min etched silicon pillar array. It is evident that the long-range hexagonal ordering and the interpillar distance are retained throughout the templating process. The size and depth of the glass pillars are reduced by ca. 10% than those of silicon pillars due to the volume shrinkage during the solidification of sol–gel precursor. The templated glass pillar arrays with high aspect ratio exhibit excellent
antireflective properties over the whole visible spectrum (Fig. 2-17). The featureless glass substrate shows ca. 4% reflection for the visible spectrum, while the subwavelength glass pillar-covered substrate exhibits much reduced reflection (<0.5%). The simulated spectra agree reasonably well with the optical measurements for both flat glass substrate and the glass pillar array.

The templated glass subwavelength pillar arrays with high aspect ratio can also significantly enhance the hydrophobicity of the substrate surface due to the high fraction of air trapped in the trough area between pillars. The hydrophobicity of glass pillars can be further improved by functionalizing them with fluorosilane through the well-established silane coupling reaction. Figure 2-18A and B show water drop profiles on fluorosilane-modified silicon and glass pillar arrays. The coatings are super-hydrophobic and the measured apparent water contact angle (CA) is ca. 160°, significantly enhanced from ca. 105° on fluorinated flat glass substrates. Figure 2-18C shows the dependence of the measured water CA on RIE duration. It is apparent that longer etching duration leads to more hydrophobic surface. This agrees well with previous studies on microstructure-induced dewetting. The volume shrinkage during the sol–gel glass solidification process could explain the reduced CA for glass pillar arrays than the corresponding silicon arrays.
Figure 2-1. Outline of the templating procedures for fabricating antireflective silicon pillar arrays by using ncp colloidal monolayer as template.

Figure 2-2. Templated silicon pillar arrays. A) Photograph of a 4 in. silicon wafer with the right half covered by subwavelength pillars and the left half unetched. The sample is illuminated with white light. B) Silicon pillars after 10 min RIE. C) Silicon pillars after 50 min RIE. D) Pillar depth dependence on RIE duration.
Figure 2-3. Experimental (solid) and RCWA-simulated (dotted) specular reflection at normal incidence from a flat silicon wafer and a 60-min etched silicon pillar array.

Figure 2-4. Water drop profile on a fluorosilane-modified silicon pillar array (60 min RIE).
Figure 2-5. Apparent water Contact Angle of templated silicon pillar arrays etched at different RIE durations.

Figure 2-6. Schematic illustration of the templating procedures for fabricating subwavelength-structured antireflection pyramids grating on single-crystalline silicon.
Figure 2-7. Replicated inverted pyramids arrays in silicon. A) The 300nm size pyramids etched at 60°C for 90s. B) The 360nm size pyramids etched at 60°C for 210s. the 320nm diameter silica spheres are used as templates.

Figure 2-8. Experimental (solid) and RCWA modeled (dotted) specular optical reflectivity at normal incidence. Black: bare (100) silicon wafer. Red: 360nm size pyramids template from 320nm silica spheres.
Figure 2-9. Comparison of the change of calculated effective refractive index at $\lambda=600$ nm from the wafer surface (depth=0) to the vertex plane of inverted pyramids between a 360 nm pyramid array (red circles) and a 60 nm pyramid array (blue circles). The diameter of templating silica spheres is 320 nm.

Figure 2-10. RCWA-simulated normal-incidence optical reflection at $\lambda=600$ nm vs inverted pyramid size. The 320 nm silica spheres are used as templates.
Figure 2-11. SEM images of templated GaSb nipple arrays etched at different RIE conditions. [(A) and (B)] Top and tilted view of nipple arrays etched at 150 W for 3 min. [(C) and (D)] Top and tilted view of nipple arrays etched at 200 W for 2.5 min, 310 nm silica spheres are used as templates.

Figure 2-12. Experimental (solid) and RCWA-simulated (dotted) specular optical reflection at normal incidence. Black: bare (100) GaSb wafer. Blue: templated nipple arrays etched at 200 W for 1.5 min, Red: templated nipple arrays etched at 200 W for 2.5 min.
Figure 2-13. Change of the calculated effective RI at $\lambda=620$ nm from the wafer surface (depth=0) to the bottom of templated GaSb nipples with 1000 nm depth. The dotted line indicates the RI of bulk GaSb at 620 nm wavelength.

Figure 2-14. Comparison of the normal-incidence specular reflection among three types of nipples—half-ellipsoid, paraboloid, and pyramid.
Figure 2-15. Comparison of the normal-incidence specular reflection between an as-fabricated GaSb grating (same as the 2.5 min etched sample in Figure 7) and the same sample after annealing at 200 °C for 6 h.

Figure 2-16. Sol–gel glass pillar array templated from a silicon pillar array(30 min RIE). A) Top-view SEM image. B) Tilted-view (45°) SEM image.
Figure 2-17. Experimental (solid) and RCWA simulated (dotted) specular reflection at normal incidence from a flat glass substrate and a spin-on glass (SOG) pillar array as shown in Figure 2-16.

Figure 2-18. Superhydrophobic coatings achieved on both templated silicon and sol–gel glass pillar arrays. A) Water drop profile on a fluorosilane-modified silicon pillar array (60 min RIE). B) Water drop profile on a fluorosilane-modified glass pillar array templated from the sample in (A). C) Apparent water CA of templated silicon and glass pillar arrays etched at different RIE durations.
CHAPTER 3
LARGE-SCALE FABRICATION OF SUB-100 NM PERIODIC NANOSTRUCTURES

3.1 Introduction

In recent years, several methods had been created to generate sub-100 nm features. Molding and imprinting methods, which have been promising advances in research, are simple, inexpensive and capable of patterning high-resolution sub-100 nm features in parallel over large areas.\textsuperscript{50,61-64} These advantageous properties, especially the prospects for low-cost manufacturing, have engendered significant interest in these techniques as potential alternatives to optical projection lithography in manufacturing processes for microchips with feature sizes at and below the 45nm node.\textsuperscript{61,65} The basic processes of molding and imprinting involve using a topographically patterned rigid (e.g. silicon, quartz, or metals)\textsuperscript{66-68} or soft (e.g. elastomers such as poly(dimethylsiloxane) (PDMS))\textsuperscript{69-71} mold to form an inverse pattern in a polymer through intimate contact. Nanoimprint lithography (NIL) is one of the famous molding and imprinting methods. A thermoplastic polymer film on a substrate is heated above the glass transition temperature (Tg) to a viscoelastic state. The patterned mold is then pressed into the polymer, and the viscous polymer is displaced and fills the voids in the patterned mold. The assembly is then cooled below the Tg of the polymer, and the patterned mold is removed.\textsuperscript{72,73} This technique is also referred to as thermal NIL, or hot embossing, because it uses heat to assist in the transfer of a pattern from a mold to a polymeric material. During this process, a residual polymer scum layer connecting the features is also formed. This undesirable feature is formed because of the polymer being trapped under the raised features of a mold during imprinting. The continuous pattern can then be broken into separate features on the substrate though a following etching step. The
molded polymer is often used as a mask for spatially controlling modifications of the underlying. 74-77 This is accomplished by first removing the thin, residual polymer film (scum layer) remaining between the molded features in the polymer by reactive ion etching (RIE). The substrate is then modified by deposition or etching. These steps have been used to generate the templates required to pattern surfaces with biomolecules, 78,79 conducting polymers, 77 and metals 76 for applications in sensing, photonics, and microelectronics. 80

Besides, Replica Molding (REM) is also an important technique that has found wide-spread applications in nanometer-sized features. This technique is composed of three simple processes. First, PDMS is cast and cured against a patterned template. The PDMS mold, in turn, acts as a template for a second UV-curable or thermally curable prepolymer. The final product is a near replica of the original template. The deformability of PDMS can be used to create novel molds that can cast polymers and ceramic precursors into non-planar fixed geometries with sub-micrometer control. 81 However, no matter what kind of molding and imprinting methods, these molds are generally made either directly (hard molds) 82-85 or indirectly (soft molds) 86,87 using conventional lithographic techniques, which is an expensive and/or slow processing step even if each resulting mold can be used many times for generating patterns relatively quickly and inexpensively.

Dip-pen nanolithography (DPN) is one of the scanning probe nanolithographic techniques that has received considerable attention in recent years. 88,89 DPN uses an inked atomic-force microscope (AFM) tip as a pen for direct, serial writing of nanoscale patterns on surfaces. The tip is inked by dipping the tip in a solution of ink – most
commonly the adsorbates used to form SAMs – such as the thiols used to form thiolate SAMs on Au. DPN allows the user to both form and subsequently image nanostructures. This offers the prospect of generating nanostructures made of different materials with near-perfect alignment. SAMs of different molecules have been patterned with separations as small as 5 nm using DPN. The idea of generating multiple patterns in registry by DPN is related to analogous strategies for generating multicomponent structures through alignment marks by e-beam lithography. DPN, however, has potential added advantages in that it does not use resists and it uses a scanning probe to both generate and locate the alignment marks. This latter point is important because it is less destructive than e-beam lithography for locating the alignment marks, particularly with soft materials. DPN offers high enough resolution that arrays of dots with diameters of \(~45\text{nm}\) and nanogaps as small as \(12–100\ \text{nm}\) can be fabricated when it is used in conjunction with wet-chemical etching. Even higher resolution with DPN may be possible through the use of high-aspect-ratio tips made of CNTs. While DPN can easily obtain sub-100 nm features with high resolution, writing nanoscale patterns with single or multi tips is still a slow process, especially over large areas.

Nanosphere lithography (NSL) also has the advantages that it is a low-cost, parallel, and substrate-independent technique for producing well-ordered sub-100 nm array structures with nanometer precision. Latex or silica spheres are typically used to form a sacrificial 2D self-assembled hexagonal close-packed (hcp) monolayer. This structure has triangular void spaces that are enclosed by three neighboring particles, which act as a mask for producing nanostructures with a triangular in-plane shape and array symmetry. In the case of multiple layers, different stacking arrangements are
possible with the FCC structure being more thermodynamically stable than the HCP structure.\textsuperscript{97} In contrast to the single-layer nanosphere masks, double-layer nanosphere masks allow for a different structure and corresponding pattern of smaller hexagonal nanoparticles that have a larger periodic spacing. The attractive feature of NSL is that the lateral dimensions of resulting structures are approximately one seventh the diameter of the spheres used. However, it does suffer from the limited areas that can be applied and the restriction to close-packed structures.

Besides, block copolymers provide rich capacities for generating controlled structures on the nanometer scale that in turn can be used to template secondary forms of nanoscale patterning. The simplest forms of block copolymers consist of two chemically distinct polymer chains (or blocks, A and B) joined through a covalent bond. Due to the chemical connectivity and the incompatibility that typically characterizes binary mixtures of high polymers, these systems spontaneously phase-separate at mesoscopic-length scales at equilibrium into ordered nanometer-sized domains.\textsuperscript{98-101} These polymeric mesophases exhibit a rich, and segment-length dependent structural behavior that can be exploited in thin-film form as a means to self-assemble uniform, nanometer-sized polymer features over wafer-scale areas. The dense, periodic patterns of diblock copolymer thin films have been used as masks to transfer patterns into silicon nitride, silicon, and germanium with feature sizes less than 30nm and a density of $\sim 10^{11}$ cm$^{-2}$.\textsuperscript{102,103} Even though these advances are significant and encouraging, patterning capabilities for long-ranged ordering and high aspect ratio features remain necessary to be improved. For antireflection applications, self-organization of block copolymers has been used to generate antireflection coatings.\textsuperscript{104-106} The selectivity between acrylic and
aromatic polymer components is used to influence the surface topography. Structure depths between 8 and 30 nm have been reported in silicon, which is too thin to obtain a substantial antireflective effect.

3.2 Large-Scale Assembly of Sub-100 nm Colloidal Nanoparticles

Self-assembled monolayer or multilayer colloidal crystals have been widely utilized as sacrificial masks to pattern periodic microstructures and nanostructures for a large variety of applications ranging from biosensors and high-density magnetic storage to field-emission displays and miniaturized plasmonic devices.\textsuperscript{107-111} However, most of the current colloidal self-assembly techniques suffer from low throughput and incompatibility with standard microfabrication, impeding mass production and on-chip integration of practical devices. It usually takes hours to days to create a centimeter-sized colloidal crystal template by current assemblies.\textsuperscript{112,113} In addition, conventional colloidal templating technology employs submicrometer- to micrometer-scale colloidal particles. Though sub-100 nm features can be fabricated,\textsuperscript{108} the number density of the templated nanostructures is limited by the relatively large separation between the neighboring particles. Moreover, only close-packed colloidal crystals are available through traditional self-assembly, whereas non-close-packed crystals are preferred for many applications, such as in creating moth-eye ARCs with non-close-packed structures.\textsuperscript{32}

To resolve the scalability issue of current colloidal assemblies, we have recently developed a versatile spincoating technique that enables wafer-scale assembly of submicrometer-sized particles (usually 300 nm in diameter) into unusual non-close-packed structures.\textsuperscript{28,29} The technique also provides a scalable templating fabrication platform for producing a large variety of microstructured materials with submicrometer-scale periodicity, such as polymer microvial arrays, two-dimensional (2D) magnetic
dots, and metal hole arrays.\textsuperscript{114,116} Although this templating platform has significant cost
benefit over traditional topdown techniques, many of the templated microstructures can
be fabricated by optical lithography, such as interference lithography.\textsuperscript{117} To greatly
extend the capability of the spin-coating technique in creating periodic nanostructures
with resolution beyond the optical diffraction limit, here we demonstrate the scalable
production of periodic sub-100 nm features with more than one order of magnitude
higher number density than our previous approaches. We also show that both multilayer
and monolayer non-close-packed colloidal crystals consisting of 70 nm diameter silica
particles can be assembled by shear-induced ordering, and the rheological response
during the shear-alignment process is investigated.

\subsection{3.2.1 Preparation of Colloidal Suspensions via Microemulsion}

The well-established microemulsion method was used to synthesize
monodispersed silica nanoparticles with \( \sim 70 \) nm diameter.\textsuperscript{118,119} A microemulsion may
be defined as a transparent, isotropic and thermodynamically stable solution of two
immiscible liquids (e.g., water and oil) consisting of microdomains of one liquid
stabilized by an interfacial film of surfactant. The surfactant molecules optimize their
interactions by residing at the oil/water interface, thereby considerably reducing the
interfacial tension and allowing a stable emulsion to form. A co-surfactant such as a
short chain alcohol is often added to further stabilize the microemulsion system as it
bridges the oil and water interface. In water-in-oil microemulsions, the aqueous phase is
dispersed as microdroplets (typically 10–25 nm in size) surrounded by a monolayer of
surfactant molecules in the continuous hydrocarbon phase. The aqueous cores of
microemulsion systems can serve as compartmentalized media for chemical reactions,
for example as microreactors for the synthesis of nanoparticles. Recently, silica
nanoparticles have been prepared by using the microemulsion water pools as microreactors for the Stober synthesis. This preparation method produces much higher particle yields than the typical microemulsion synthesis, while maintaining the relative size uniformity characteristic of the Stober synthesis. Particle size variation and dispersity have been extensively studied as a function of some synthesis variables (surfactant nature, water-to-surfactant molar ratio ($w_0$) and ammonium concentration) and seem to have a complex dependence on these parameters.\textsuperscript{119} Figure 3-1 shows a typical transmission electron microscope (TEM) image of the as-made nanoparticles. The diameter of the spheres was determined to be $72 \pm 6$ nm by averaging over 100 particles using the image analysis software Scion Image.

The synthesis of uniform silica nanoparticles with $\sim 70$ nm diameter was performed according to ref. 118. In a typical synthesis, a microemulsion was prepared by rapidly stirring 750 ml of cyclohexane, 30 ml of $n$-hexanol, 95 ml of Triton X-100 surfactant, 35 ml of water, and 8.5 ml of 29.3% aqueous ammonia. 50 ml of freshly distilled TEOS was rapidly added to the above microemulsion and the final solution was stirred at ambient temperature for 2 days.

3.2.2 Spin-Coating of Colloidal Suspensions and Photopolymerization

The nanoparticles were purified in 200-proof ethanol by multiple centrifugation–ultrasonication cycles and then dispersed in non-volatile ethoxylated trimethylolpropane triacrylate (ETPTA, SR 454, Sartomer) monomers to make a final particle volume fraction of $\sim 20\%$.\textsuperscript{28} 1% (by weight) Darocur 1173 (Ciba-Geigy) was added as the photoinitiator. The suspension was disposed on a 3-acyloxypropyl trichlorosilane-primed silicon wafer and then the wafer was tilted and rotated to spread the solution to achieve full wafer coverage. The wafer was gradually accelerated to 10,000 rpm and
kept at this speed for various durations, using a standard spin coater (WS-400B-6NPPLite spin processor, Laurell). The recipe for spin-coating a monolayer of silica nanoparticles was 200 rpm for 1 min, 300 rpm for 1 min, 1000 rpm for 30 s, 3000 rpm for 10 s, 6000 rpm for 10 s, 8000 rpm for 10 s, and 10 000 rpm for 26 min. For preparing multilayer colloidal crystals, the spin-coating conditions were the same, except for a shorter spin time in the last step at 10 000 rpm. The gradual increase of the spin speed was crucial for obtaining uniform coatings over large area; otherwise, patchy samples resulted. The monomer was rapidly polymerized by exposure to ultraviolet radiation using a pulsed UV curing system (RC 742, Xenon) to form ordered colloidal crystal–polymer nanocomposites. More details of the spin-coating process can be found in section 2. Contrary to the distinctive six-arm Bragg diffraction formed on spin-coated crystals consisting of submicrometer-sized particles,28 the resulting nanocomposites were transparent and colorless due to the index match between the silica nanoparticles and the polymer matrix, as well as negligible scattering and diffraction of visible light by subwavelength nanoparticle arrays.

The polymer matrix could be selectively removed by a brief oxygen plasma etch operating at 3 mTorr pressure, 20 SCCM oxygen flow rate, and 50 W for 3 min to release the embedded silica colloidal crystals. Figure 3-2A shows a top-view scanning electron microscope (SEM) image of a multilayer crystal prepared by spin-coating at 10 000 rpm for 10 min. The long-range hexagonal ordering of silica nanoparticles is clearly evident from the SEM image and its fast-Fourier transform (inset of figure 3-2A). The magnified SEM image in figure 3-2B shows that the spin-coated colloidal crystal is non-close-packed and that the spheres of the top layer fill in the triangularly arranged
crevices made by the nontouching spheres of the second layer. Underneath, hexagonally packed layers throughout the film thickness exhibit similar intralayer non-close-packed structures and good registry between neighboring layers. One of the great advantages of the current spin-coating technique is that the thickness of the spincoated colloidal crystals can be easily controlled by adjusting the spin speed and duration. Ellipsometry measurements showed that uniform films with thickness ranging from a single monolayer to hundreds of layers could be created over a 2 inch diameter wafer. Figure 3-2C shows an SEM image of a monolayer non-closepacked colloidal crystal consisting of 70 nm particles prepared by spin-coating at 10 000 rpm for 26 min. The interparticle distance of the non-close-packed colloidal crystal is determined to be $1.41D$, where $D$ is the diameter of the silica spheres, by the first peak of the pair correlation function (PCF; see figure 3-2D), $g(r)$, which is calculated from a lower-magnification image as in figure 3-2C as $g(r) = 1/\langle \rho \rangle dn(r, r + dr)/da(r, r + dr)$, where $\langle \rho \rangle$ is the average particle number density and $r$ is the particle radius. To calculate the PCF, Scion Image software was utilized to extract the particle coordinates. Figure 3-2D shows that the positions of the oscillating PCF peaks agree well with those obtained from a perfect hexagonal lattice with $\sqrt{2}D$ interparticle distance. This distance is the same as that of spin-coated crystals made of submicrometer-sized particles, suggesting a similar shear-induced ordering mechanism for the observed colloidal crystallization process. As revealed by previous shear-induced colloidal crystallization studies, the high shear rate ($>103$) in the spin-coating process can lead to a sliding layer mechanism, in which 2D hexagonally packed colloidal layers are readily formed due to the coupling of the centrifugal and viscous forces.\textsuperscript{120,121} This shear-alignment process is
usually associated with the reduction of the viscosity of the colloidal suspensions (i.e., shear thinning) due to the reduced resistance when layers of ordered spheres glide over one another.\textsuperscript{120,121} Figure 3-3 shows the comparison of the shear thinning behavior for colloidal suspensions using spheres with diameters of 350 and 70 nm at the same particle volume fraction (0.20). It is apparent that a higher shear rate is required to achieve low relative viscosity for 70 nm particles compared to 350 nm spheres, indicating that a higher spin speed is necessary to crystallize smaller particles. This agrees with our experimental observation that the crystallization of 70 nm particles only occurs at high spin speed (≥10 000 rpm). This result correlates well with early shear-annealing studies.\textsuperscript{121,122} Electrostatic repulsion between silica nanoparticles could contribute to the observed non-close-packed structure as zeta potential measurements show that the nanoparticles are charged (\(\zeta = -44.8 \pm 3.2\) mV) in the silica–ETPTA suspensions.

3.3 Templated Sub-100 nm Periodic Nipple Arrays

The current spin-coating technique for assembling sub-100 nm diameter particles over a large area was taken one step further by using the non-close-packed colloidal monolayers as templates to pattern self-cleaning, broadband antireflection coatings directly on crystalline silicon substrates. The silica nanoparticles were used as etching masks during a chlorine RIE process operating at 3 mTorr pressure, 20 SCCM flow rate, and 50 W to generate silicon nanopillars underneath them (see the tilted SEM image in figure 3-4A). Figures 3-4B and C show top-view and side-view SEM images of an array of templated nanopillars after dissolving silica nanoparticles in a 2% hydrofluoric acid aqueous solution. The preservation of the hexagonal ordering and the interparticle distance of the templating silica monolayer are apparent for the resulting
nanopillar arrays. The depth of the templated nanopillars can be controlled by changing the RIE duration. Figure 3-4D shows a cross-sectional SEM image of an array of silicon nanopillars with aspect ratio of ~6.0 after 20 min of Cl₂ RIE. Shallow dimples are formed on the top surfaces of the pillars due to the shrinkage of the templating silica nanoparticles during prolonged etching that makes the silica particles too small to protect the silicon underneath from being etched. The number density of the templated nanopillars (1.5 × 10¹⁰ pillars cm⁻²) is more than one order of magnitude higher than that of the samples templated from submicrometer-scale particles.⁵⁴

The templated silicon nanopillar arrays were dark, and no angle-dependent diffraction was observed as the periodicity of the nanopillar arrays is much smaller than the wavelength of visible light. The specular reflection of the templated nanopillar arrays was evaluated using visible–near-infrared reflectivity measurement at normal incidence and theoretical calculation based on a rigorous coupled-wave analysis (RCWA) model.³¹ An HR4000 high-resolution fiber optic UV–Vis spectrometer and an NIR-512 spectrometer (both from Ocean Optics) with reflection probes were used for reflectance measurements. A calibrated halogen light source was used to illuminate the sample. The beam spot size was about 3 mm on the sample surface. Measurements were performed at normal incidence and the cone angle of collection was less than 5°. The absolute reflectivity was obtained as the ratio of the sample spectrum to the reference spectrum. The reference spectrum was the optical density obtained from an aluminum sputtered (1000 nm thickness) silicon wafer. The final value of absolute reflectivity was the average of several measurements obtained from different spots on the sample surface. The resulting reflectivity was calibrated using an Ocean Optics STAN-SSL low-
reflectivity specular reflectance standard for templated pillar arrays and an STAN-SSH high-reflectivity specular reflectance standard for flat silicon wafers.

Figure 3-5 compares the specular reflection from a flat silicon wafer, a commercial crystalline silicon solar cell with vapor-deposited silicon nitride (SiNx) antireflection coating, and the templated nanopillar array as shown in figure 3-4D. The normal-incidence reflection is greatly reduced from >30% for a flat silicon wafer to <2.5% for the templated nanopillar array. It is also apparent that the nanopillar ARC exhibits excellent broadband antireflection property, better than commercial ARC on the crystalline silicon solar cell, which shows reduced reflection only around 600–800 nm.26

Figure 3-5 shows that the simulated spectra (dotted lines) for both the flat silicon substrate and the templated nanopillar array agree well with the experimental results. The excellent broadband antireflection of the nanopillar ARCs is due to the refractive index gradient across the air and silicon interface.32 Figure 3-6 shows the calculated effective refractive index at \( \lambda = 700 \) nm across the height of 400 nm nanopillars. For the bare wafer, the refractive index (RI) changes sharply from air (RI = 1.0) to bulk silicon (RI = 3.774), while for templated nanopillars, the RI changes gradually from 1.0 to 3.439 and then to 3.774. This refractive index gradient leads to very low reflection over a wide range of wavelengths. The templated nanopillars with high aspect ratio can trap a high fraction of air in the trough area between nanopillars, making the silicon surface superhydrophobic.17 This is promising for developing self-cleaning ARCs for silicon solar cells. The hydrophobicity of silicon nanopillars can be further improved by functionalization with fluorosilane through the well-established silane coupling reaction.34 Here, silicon nanopillars were chemically modified by reacting with a 4.4 ×
A $10^{-3}$ M solution of (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane (Gelest) in hexane/CCl₄(v/v:70/30) for 2 h at room temperature. The resulting surfaces were rinsed with dichloromethane and ethanol and then dried under air. Figure 3-7 shows a water drop profile on a fluorosilane-modified silicon nanopillar array. The surface is superhydrophobic and the measured apparent water contact angle is 158°, significantly enhanced from ~108° on a fluorinated flat silicon wafer. The utilization of nanoparticles instead of submicrometer-sized particles as templates to generate moth-eye ARCs facilitates the elimination of unwanted Bragg diffraction and simultaneously enhances the film hydrophobicity.¹⁷,³²

### 3.4 Templated Sub-100 nm Polymer Dots Arrays and Metal Holes Arrays

Subwavelength periodic metal nanohole arrays are of great scientific interest and considerable technological importance in developing miniaturized optical devices for all-optical integrated circuits (e.g., optical waveguides, switches, and couplers),¹²³,¹²⁴ information storage,¹²⁵ efficient light-emitting diodes,¹²⁶ and biosensors,¹²⁷ as well as fundamental understanding of surface plasmon enabled optical transmission and diffraction.¹²⁸ Zero-mode waveguiding through arrays of sub-100 nm nanoholes perforated in a metal film has also been demonstrated as a simple and highly parallel method for single-molecule bioanalysis at high concentrations.⁸,¹²⁷ Unfortunately, these important applications have been greatly impeded by the expensive and complex nanofabrication techniques (e.g., electronbeam, focused ion beam, and interference lithography) in creating subwavelength nanohole arrays.⁸,¹¹⁷,¹²⁸ Attaining high throughput and large-area fabrication continues to be a major challenge with these top-down techniques.
Bottom-up self-assembly and templating nanofabrication provide a much simpler, faster, and inexpensive alternative to nanolithography in generating periodic nanostructures. For instance, self-assembled monolayer or multilayer colloidal crystals are used as templates to create a large variety of functional periodic nanostructures including nanohole arrays. However, most of the available bottom-up approaches suffer from low throughput and incompatibility with mature microfabrication, limiting mass-production and on-chip integration of practical devices. Furthermore, only close-packed colloidal crystals are available through traditional self-assembly, whereas non close-packed crystals are needed to template nanohole arrays.

Here we report a flexible and scalable non-lithographic approach for fabricating large-area sub-100 nm periodic nanostructures using submicrometre-sized particles as templates. The resulting nanofeature size can be easily adjusted by controlling the templating conditions. Sub-100 nm patterns, whose size is only ~20% of the original templating sphere diameter, can be fabricated over an 80 cm² area.

Figure 3-8 shows a schematic outline of the new templating procedure for making periodic metal nanohole arrays. The established spin-coating technique is utilized to create a monolayer of non-close-packed silica colloidal crystals embedded in a thin layer of polymer matrix as structural templates. In the spin-coating technique, monodisperse silica particles are dispersed in non-volatile ethoxylated trimethylolpropane triacrylate (ETPTA, Sartomer) monomers to form stable dispersions with a particle volume fraction of ~20%. The dispersions are then spin-coated on planar substrates (e.g., glass and silicon wafer) using standard spin-coating equipment. Both
multilayer and monolayer colloidal crystals with non-close-packed structures can be formed by simply tuning the spin-coating speed and time. The ETPTA monomers can then be polymerized by exposure to ultraviolet radiation to immobilize the shear-aligned particle arrays.

The resulting colloidal crystal–polymer nanocomposite has a thin polymer wetting layer (~100 nm thick) between the silica monolayer and the substrate. The current templating technique is aimed at utilizing this polymer wetting layer to transfer the hexagonal patterns of spin-coated colloidal monolayers consisting of submicrometre-sized particles into arrays of nanoholes with a sub-100 nm diameter (Figure 3-8). In this approach, conventional oxygen plasma etching is firstly applied to partially remove the polymer matrix between the non-close-packed colloidal arrays. Silica particles function as etching masks during the oxygen plasma etching process. They protect the polymer wetting layer immediately underneath them to form polymer posts whose size can be easily adjusted by controlling the etching conditions. The templating silica particles can then be removed by dissolving in a 2% hydrofluoric acid aqueous solution for 2 min. A thin layer of metal can finally be deposited between the exposed polymer posts, followed by lifting-off polymer templates to form hexagonal arrays of metal nanoholes with tunable size.

Figure 3-9A,B and C show top-view scanning electron microscope (SEM) images of the templated polymer posts after oxygen plasma etching operating at 40 mTorr pressure, 40 sccm flow rate, and 100W on a Unaxis Shuttlelock RIE/ICP reactive ion etcher for 2, 6, and 8 min, respectively, followed by hydrofluoric acid wash to remove the templating silica particles. It is evident that the resulting polymer posts retain the
long-range hexagonal ordering and the inter-particle distance of the original non close-packed colloidal monolayer consisting of 360 nm silica spheres. The cross-sections of the posts are round-shaped for all three above conditions, indicating uniform etching of ETPTA from the peripheries of the templated posts.

It is also apparent from Figure 3-9 A-C that longer etching duration leads to smaller polymer posts. We determine the size and size distribution of the templated posts by averaging over 100 posts using image analysis software (Scion Image). Figure 3-9D shows the dependence of the size of the templated posts on the oxygen plasma etching time. The measured size standard deviation is around 10%, which is a little bit worse than that of the templating silica spheres (~5–7%). Importantly, much smaller polymer posts (as small as 55 nm) than the original templating silica spheres (360 nm) can be achieved. This represents ~85% shrinkage of the template size. When longer plasma etching duration (49 min) is applied, the polymer posts become too narrow to support the silica particles, resulting in the collapse of the particles and subsequent complete etching of the polymer posts.

After removing the silica particles by hydrofluoric acid wash, the polymer posts can be used as sacrificial deposition masks to template metal nanohole arrays with tunable size. A thin layer of metal is deposited by traditional physical vapor deposition techniques (e.g., electron-beam evaporation and sputtering) to fill up the spacing between the non close-packed polymer posts. As the adhesion between the polymer and the substrate is quite low, the posts can be easily removed by a gentle sweeping using a cleanroom Q-tip under flowing water, resulting in the formation of wafer-scale periodic nanohole arrays. Figure 3-10 shows a SEM image of a templated gold
nanohole array with 89±13 nm diameter. The nanoholes keep the same long-range hexagonal ordering and inter-particle distance as the original monolayer colloidal crystal template.

Besides providing a much simpler approach than nanolithography for generating sub-100 nm nanohole arrays, the new templating nanofabrication approach enables creation of complex micropatterns that are not easily available by traditional top-down techniques. Figure 3-11A and B show top- and side-view SEM images of arrays of “micro-candles” templated from spin-coated colloidal monolayers. In this approach, non-close-packed silica particles are firstly used as etching masks during oxygen plasma etching to pattern polymer posts underneath them as described above. The released silica spheres can then be utilized as etching masks for the second time during chlorine reactive ion etching (RIE, 5 mTorr pressure, 20 SCCM chlorine flow rate, and 80 W) to generate ordered arrays of silicon pillars. The polymer posts are not affected by the chlorine RIE process, forming “candle wicks” on top of the templated silicon pillars after removing the templating silica particles by a brief hydrofluoric acid wash.

The height of the polymer posts can also affect the spatial distribution of the reactive ions during the above particle masked RIE process, resulting in the formation of unusual “candle-stand shaped” micropatterns in a gallium antimonide (GaSb) substrate as shown in Figure 3-11C and D. Due to different substrate wettabilities, the polymer wetting layer on a GaSb wafer (~500 nm thick) is much thicker than that on a silicon or a glass substrate (~100 nm). The shadowing effect created by the templating silica spheres is then significantly affected by the different polymer spacer height. On a silicon wafer, the templating silica particles are close to the substrate surface, resulting in
effective shadowing of the regions underneath the particles. This leads to the formation of pillars with vertical sidewalls and almost the same diameter as that of silica spheres. While for a GaSb substrate under similar chlorine RIE conditions, the tall polymer posts between the substrate and the templating particles change the spatial distribution of the reactive chlorine ions, leading to the formation of tapered pillars with flat circular caps (Figure 3-11D). The cap size is similar to that of the templating silica spheres. GaSb pillars with a high aspect ratio and vertical sidewalls resembling the silicon pillars as shown in Figure 3-11B have previously been fabricated using lithographically patterned photoresist as an etching mask under similar chlorine RIE conditions as described above. This verifies the importance of the polymer posts in controlling the shape of the templated microstructures during the particle-masked dry etching process.
Figure 3-1. TEM image of silica nanoparticles synthesized by the microemulsion method.

Figure 3-2. A) SEM image of a multilayer colloidal crystal. The inset showing a Fourier transform of the image. B) Higher-magnification SEM image of the sample in (A). C) Spin-coated monolayer colloidal crystal. D) Pair correlation function (PCF) calculated from a lower-magnification SEM image of the monolayer sample in (C). For comparison, the PCF for an ideal hexagonal lattice with $\sqrt{2}D$ center-to-center distance is also shown (black lines).
Figure 3-3. Shear thinning behavior of silica–ETPTA suspensions using 70 and 350 nm particles at a volume fraction of 0.2.

Figure 3-4. A) Tilted-view (20°) SEM image showing the templating silica nanoparticles and the underneath silicon nanopillars after brief Cl₂ RIE. B) Top-view SEM image of a templated silicon nanopillar array after 15 min RIE. C) Tilted-view (20°) SEM image of the sample in (B). D) Cross-sectional SEM image of silicon nanopillars etched for 20 min.
Figure 3-5. Experimental and simulated specular reflection at normal incidence from a flat silicon wafer (black), a commercial single-crystalline silicon solar cell with SiNx antireflection coating (blue), and the templated silicon nanopillar array as shown in figure 3-4(D) (red).

Figure 3-6. Change of the calculated effective refractive index at $\lambda = 700$ nm from the wafer surface (depth = 0) to the bottom of templated silicon pillars with 400 nm height.
Figure 3-7. Water drop profile on a fluorosilane-modified silicon nanopillar array prepared by Cl₂ RIE for 20 min using 70 nm silica nanoparticles as templates.

Figure 3-8. Schematic illustration of the fabrication procedures for making periodic arrays of metal nanoholes with tunable size by using monolayer non close-packed colloidal crystal-polymer nanocomposite as templates.
Figure 3-9. Templated polymer posts with adjustable size. A–C) SEM images of polymer posts with diameters of 202±10 nm, 78±7 nm, and 70±10 nm after 2, 6, and 8 min oxygen plasma etching, respectively. D) Size dependence of the templated polymer posts on the oxygen plasma etching time. 360 nm silica spheres are used as the original templates.

Figure 3-10. SEM image of an array of gold nanoholes with 89 nm diameter templated from a monolayer nanocomposite consisting of 360 nm silica spheres.
Figure 3-11. A) and B) Top- and side-view SEM images of an array of silicon “micron-candles” templated from a spin-coated 2-D colloidal crystal. C) and D) Top- and side-view SEM images of a templated array of GaSb “micro-candle stands”.

CHAPTER 4
THE PRODUCTION OF GRAPHENE SHEETS

4.1 Introduction

Graphene – a flat monolayer of carbon atoms tightly packed into a two-dimensional honeycomb lattice – is the basic building block for graphitic materials of all other dimensionalities. It can be wrapped up into 0D fullerenes, rolled into 1D nanotubes or stacked into 3D graphite (Figure 4-1). Graphene has been made by several different methods. The epitaxial growth of graphene by chemical vapor deposition (CVD), such as the decomposition of ethylene on nickel surfaces, is the most general way to make graphene. Large area graphene films of single and few layers graphene have been generated by CVD growth on metal substrates and graphene-type carbon materials have been produced by substrate-free CVD and radio-frequency PECVD. Another approach is the micromechanical exfoliation of graphite. This approach, which is also known as the ‘Scotch tape’ or peel-off method, followed on micromechanical exfoliation from patterned graphite and has yielded small samples of graphene that are useful for fundamental study. Another method is epitaxial growth on electrically insulating surfaces such as SiC and the other is the creation of colloidal suspensions.

Graphite is inexpensive and available in large quantity in natural world, which makes the production of graphene from colloidal suspensions made from graphite much more attractive and economical than from CVD techniques. This approach is both scalable to afford the high volume production and versatile to apply various chemical functionalizations. These advantages mean that the colloidal suspension method for producing graphite-derived graphene could be used for a wide range of applications.
Since graphite does not readily exfoliate to yield individual graphene sheets, people had made graphene sheets from graphite oxide. Graphite oxide has been mainly produced by the Staudenmaier\textsuperscript{148} and Hummers\textsuperscript{149} methods. All these methods involve oxidation of graphite in the presence of strong acids and oxidants. The level of the oxidation can be varied on the basis of the method, the reaction conditions and the precursor graphite used.

Figure 4-2 shows the general chemical structure of graphite oxide (GO).\textsuperscript{151} The \textit{sp}\textsuperscript{2}-bonded carbon network of graphite is strongly broken and a significant fraction of this graphitic network is bonded to hydroxyl groups or participates in epoxide groups.\textsuperscript{150-153} Small parts of carboxylic or carbonyl groups are thought to distribute in the edges of the layers in graphite oxide. GO is thus composed of a layered structure of graphene oxide sheets that are strongly hydrophilic so that intercalation of water molecules between the layers readily occurs.\textsuperscript{154} The interlayer spacing between the graphene oxide sheets increases reversibly from 6 to 12 Å with the increase of relative humidity. Besides, graphite oxide can be completely exfoliated to generate aqueous colloidal suspensions of graphene oxide sheets by simple sonication.\textsuperscript{155} The measurement of the surface zeta potential of graphene oxide sheets\textsuperscript{156} shows that they are negatively charged when dispersed in water. This suggests that electrostatic repulsion between negatively charged graphene oxide sheets could produce a stable aqueous suspension of them.

Although the homogeneous colloidal suspensions of graphene oxide can be generated, the resultant graphene oxide is electrically insulating due to disruption of the carbon networks. Several chemical approaches have been used for the reduction of the
graphene oxide by reductants, such as hydrazine\textsuperscript{157-159} and dimethylhydrazine,\textsuperscript{160} to produce electrically conducting graphene sheets. When dried, the final black powder became electrically conductive (powder conductivity $\sim 200$ Sm\textsuperscript{-1}).\textsuperscript{157} However, the resulting conducting graphene sheets agglomerate together when the aqueous graphene oxide suspension was reduced by hydrazine at the pH value of 10.\textsuperscript{157} In order to improve this problem, an aqueous suspension of reduced graphene oxide sheets under basic conditions (pH~10) was proposed.\textsuperscript{156} The graphene oxide sheets were reduced by hydrazine and excess hydrazine was removed by dialysis. Basic environment converts neutral carboxylic groups to negatively charged carboxylate groups so that these negatively charged sheets don’t agglomerate during the reduction process by hydrazine. Paper-like graphene paper had been made by filtration and shows good electrical conductivity ($\sim 7200$ Sm\textsuperscript{-1}).\textsuperscript{156} Elemental analysis of the reduced graphene oxides measured by combustion revealed the ratio of carbon and oxygen atoms is around 10, indicating a significant amount of oxygen exist and the reduced graphene oxide is different from pristine graphene.

Thermal exfoliation of graphite oxide is another way to obtain reduced graphene sheets. Rapid heating up to 1050°C exfoliates and reduces graphite oxide, producing highly-agglomerated fluffy black powders.\textsuperscript{161,162} These sheets whose atomic C/O ratio is about 10.3 have a similar oxygen content to that of hydrazine-reduced graphene oxide, and its electrical conductivity is around 2000 Sm\textsuperscript{-1}.

4.2 Graphene Sheets from Colloidal Suspensions made from Graphite

4.2.1 Oxidation of Graphite to Make Graphite Oxide

Staudenmaier method. Graphite oxide (GO) was prepared according to the Staudenmaier\textsuperscript{148} method. A reaction flask containing a magnetic stir bar was charged
with sulfuric acid (87.5 mL) and nitric acid (45 mL) and cooled by immersion in an ice bath. The acid mixture was stirred and allowed to cool for 15 min, and then natural flake graphite (5 g), nominally ~45 µm across (Asbury Carbons, Asbury, NJ), was added under vigorous stirring. After the graphite powder was well dispersed, potassium chlorate (55 g) was added slowly over 15 min to avoid sudden increases in temperature. The reaction flask was loosely capped to allow evolution of gas from the reaction mixture and allowed to stir for 120 hour at room temperature. On completion of the reaction, the mixture was poured into 2 L of deionized water and filtered. The GO was redispersed and washed in a 5% solution of HCl. The filtrate was tested with barium chloride for the presence of sulphate ions. The HCl wash was repeated until this test was negative. The GO was then washed repeatedly with deionized water until the pH of the filtrate was neutral. The GO slurry was then stored in an oven at 60°C for 24 hour.

**Modified Hummers method.** GO was synthesized from natural flake graphite (~45 µm, Asbury Carbons, Asbury, NJ) by the method of Hummers and Offeman. It was found that, prior to the GO preparation, an additional graphite oxidation procedure was needed. Otherwise, incompletely oxidized graphite-core/GO-shell particles were always observed in the final product. The graphite powder (10 g) was put into an 80°C solution of concentrated H₂SO₄ (150 mL), K₂S₂O₈ (5 g), and P₂O₅ (5 g). The resultant dark blue mixture was thermally isolated and allowed to cool to room temperature over a period of 6 h. The mixture was then carefully diluted with distilled water, filtered, and washed on the filter until the rinse water pH became neutral. The product was dried in air at ambient temperature overnight. This preoxidized graphite was then subjected to oxidation by Hummers’ method. The oxidized graphite powder
(20 g) was put into cold (0°C) concentrated H₂SO₄ (230 mL). KMnO₄ (30 g) was added gradually with stirring and cooling, so that the temperature of the mixture was not allowed to reach 20°C. The mixture was then stirred at 35°C for 2 h, and distilled water (460 mL) was added. In 15 min, the reaction was terminated by the addition of a large amount of distilled water (1.4 L) and 30% H₂O₂ solution (25 mL), after which the color of the mixture changed to bright yellow. The mixture was filtered and washed with 1:10 HCl solution (2.5 L) in order to remove metal ions. The GO product was suspended in distilled water to give a viscous, brown, 2% dispersion, which was subjected to dialysis to completely remove metal ions and acids. The resulting 0.5% w/v GO dispersion, which is stable for a period of years, was used to prepare exfoliated GO.

**Results and Discussions.** Complete oxidation is monitored by the total disappearance of the 0.34 nm intergraphene spacing and the appearance of a new one with a 0.65-0.75 nm range depending on the water content of GO, as determined by X-ray diffraction (XRD) measurement. In terms of structure, the disappearance of the 0.34 nm has been reported previously. Figure 4-3 shows the XRD data for graphite and GO made by Staudenmaier method and Modified Hummers method. Note that the d-spacing for the GO made by Staudenmaier method (GO-ST) appears at a value very close to the native graphite values for the 0002 peak while a broad peak corresponding to the 0.7 nm GO interlayer separation is partially retained. Relative to native graphite, the peak at 2θ~27° is now broad, presumably because of the incomplete oxidation of graphite. Only the shell of the graphite had been oxidized but the core part still maintained graphitic stacking. For the GO made by modified Hummers method (GO-MH), the peak at 2θ~11° corresponding to the 0.7 nm interlayer spacing is narrow and
no other peaks are shown in the curve. This means the increase of c-axis spacing to 0.7 nm and the appropriate level of oxidation for the elimination of the 0.34 nm graphite interlayer spacing have been successfully achieved by modified Hummers method.

4.2.2 Thermal Exfoliation of Graphite Oxide into Graphene Sheets

Graphite oxide (GO) (200 mg) prepared as described above was placed in an alumina boat and inserted into a 1-inch outer diameter, 24-inches long quartz tube that was open at one end. The other end of the quartz tube was sealed using a stainless steel flange. An argon (Ar) inlet was then inserted through the flange. The sample was flushed with Ar for 10 min, and then the quartz tube was quickly inserted into a Lindberg tube furnace preheated to 1050°C and held in the furnace for 30 sec.

Figure 4-4 shows 200 mg graphite oxide in an alumina boat inserted into a quartz tube and Figure 4-5 shows a 500-1000 fold volume expansion after the rapid heat treatment of GO. To determine the composition of the evolved gases that cause the rapid expansion, a series of TGA/DSC experiments were performed where the outlet gas is analyzed by FTIR. Small amounts of water are lost during the initial heating stage and there is a dramatic mass loss accompanied by an exothermic DSC peak. These features correspond to the decomposition of oxygen-containing groups in the GO. The products of this decomposition are found to be CO₂ (wavenumbers 2360 cm⁻¹ and 690 cm⁻¹) and H₂O (wavenumbers 1340-1900 cm⁻¹ and 3550-4000 cm⁻¹) as expected. The absence of sulfur, nitrogen, and chlorine-containing compounds indicates that the intercalating species are not present in the washed material and therefore do not participate in the exfoliation. The mass lost during the thermal decomposition is approximately 30% of the initial GO mass.
Imaging of graphene sheets (GS) by atomic force microscopy (AFM) was performed with special emphasis on sheet thickness, morphological features, and lateral dimensions. For the most accurate determination of the sheet thickness, tapping mode was applied on the measurement. Samples of GS were prepared by loading a 20 mL scintillation vial with 1 mg of graphene and 10 mL of dimethylformamide (DMF) as the dispersion medium. The suspension was ultrasonicated for 30 min. This suspension was diluted to a concentration of 0.02 mg/mL. The final suspension was spincoated at 5000 rpm on a piece of silicon wafer. The AFM image of the exfoliated graphene sheets is shown in Figure 4-6. The flat areas of the sheet have an average height of about 1-2 nm and several large wrinkles with peak heights up to tens of nm. Figure 4-7 shows the height of the line scanning in Figure 4-4.

Transmission electron microscope (TEM) imaging of GS was performed on a JEOL 200CX microscope at 200 keV to characterize graphene sheets. The TEM samples were prepared by dispensing one drop of graphene suspension with concentration ~ 0.01 mg/mL on 300 mesh copper TEM grids covered with thin amorphous carbon films. The TEM images of the GS in low magnification are shown in Figure 4-8 and 4-9. The graphene sheets in both figures have random shapes and wrinkled paper-like structures with an area of several µm².

Figure 4-10 shows the XRD data for graphite and GS. The disappearance of the c-axis spacing by oxidation to 0.7 nm and the 0.34 nm graphite interlayer spacing proves that GS have been successfully exfoliated by rapid thermal expansion.
Figure 4-1. Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite.\textsuperscript{129}

Figure 4-2. Chemical structure of graphite oxide.\textsuperscript{151}
Figure 4-3. XRD measurements data of graphite, GO-ST and GO-MH.

Figure 4-4. Photograph of 200 mg graphite oxide in an alumina boat inserted into a quartz tube.
Figure 4-5. Thermally-exfoliated graphene sheet after rapid heating up to 1050°C.

Figure 4-6. AFM image of a single exfoliated graphene sheet.
Figure 4-7. The height of the line scan in the single graphene in figure 4-6.

Figure 4-8. TEM Image of a single exfoliated graphene sheet.
Figure 4-9. TEM Image of a single exfoliated graphene sheet.

Figure 4-10. XRD measurements data of graphite and exfoliated graphene sheets.
CHAPTER 5
GRAPHENE – CHITOSAN NANOCOMPOSITES

5.1 Introduction

Graphene – a two-dimensional single layer of carbon atoms bonded together in a hexagonal lattice – has stimulated a vast amount of research in recent years. Its remarkable properties including high values of Young’s modulus (~1100 GPa),\textsuperscript{164} thermal conductivity (~5000 Wm\(^{-1}\)K\(^{-1}\))\textsuperscript{165} and specific surface area (~2630 m\(^2\)g\(^{-1}\))\textsuperscript{166} make it an excellent carbon-based nanofiller material for polymer-based nanocomposites. Traditional lightweight polymer-based composites with high-performance could be developed for several applications\textsuperscript{167} by dispersing strong, highly stiff fibers in a polymer matrix, but these composite structures contain a significant quantity (~60 vol\%) of filler bound in a polymer matrix.\textsuperscript{167} In nanocomposites, significant changes in properties are possible at very low loadings (<2 vol\%) of such nanifiller as exfoliated nanoclays, graphite nanoplatelets and carbon nanotubes. This performance is achieved, not only by using the inherent properties of the nanofiller, but more importantly by optimizing the dispersion, interface chemistry and nanoscale morphology to utilize the enormous surface area per unit volume that nanofillers have. Even at low volume fractions, the huge interfacial area generated by well-dispersed nanoparticles can affect the behavior of the surrounding polymer host,\textsuperscript{168-170} creating a continuous network of dramatically altered polymer chains,\textsuperscript{171,172} and changing the thermal and mechanical properties of the matrix.

Nanocomposites have great potential to exceed the performance of conventional composites due to its nanoscale fillers at low loading. However, maximal mechanical enhancement can only be achieved when the nanofiller is homogeneously dispersed in
the polymer matrix and the external tensile load is efficiently transferred via a strong interaction at the interface between the filler and the matrix. Here we present a simple approach for the preparation of graphene-polymer composites via complete thermal exfoliation of graphite and dispersion of functionalized graphene sheets within polymer matrix.

5.2 Chitosan Biopolymer

Chitosan is a linear β-1,4-linked polysaccharide obtained by the partial deacetylation of chitin and its structure is very similar to cellulose. It is formally a copolymer composed of glucosamine and N-acetylglucosamine due to incomplete chitin deacetylation. Chitosan does not refer to a single well-defined structure and can differ in molecular weight, degree of acetylation, and sequence. As a result of these structural differences, the properties of chitosan like the pKa can also vary somewhat. The behavior of a typical chitosan is with a degree of acetylation of 20% or less and a molecular weight on the order of 200 kDa. The unique structural feature of chitosan is the presence of the primary amine at the C-2 position of the glucosamine residues. Few biological polymers have such a high content of primary amines, and these amines provide important functional properties to chitosan that can be utilized for biofabrication.

The pH value substantially alters the charged state and properties of chitosan. At low pH, these amines are protonated and positively charged, and chitosan is a water-soluble cationic polyelectrolyte. When dissolved and carried with the positive charge of –NH₃⁺ groups, the chitosan can adhere to negatively charged surfaces or adsorb negatively charged materials. It is commonly used to disperse nanomaterials and immobilize enzymes for constructing biosensors due to its excellent capability for film formation, nontoxicity, biocompatibility, mechanical strength, and good water
At high pH, chitosan’s amines become deprotonated and the polymer loses its charge and becomes insoluble. Importantly, chitosan’s pKa is near neutrality, and the soluble-insoluble transition occurs at pHs between 6 and 6.5 which is a particularly convenient range for biological applications. At high pH, chitosan’s electrostatic repulsions are reduced allowing the formation of inter-polymer associations, such as liquid crystalline domains or network junctions, that can yield fibers, films, or hydrogels, depending on the conditions used to initiate the soluble-insoluble transition. Finally, Figure 5-1 indicates that chitosan’s amines are reactive allowing a range of chemistries to be employed to graft substituents to functionalize chitosan or to cross-link the chitosan backbone to confer elasticity.

5.3 Graphene – Chitosan Nanocomposites

5.3.1 Functionalization of Graphene Sheets

In order to reinforce efficiently the chitosan matrix with graphene, the homogenous dispersion of graphene in the chitosan matrix and the strong interfacial interactions between the graphene and chitosan are required. The feasible route to harnessing the poor dispersibility for applications would be to incorporate graphene sheets in a composite material via hydrogen bonding interaction. The covalent functionalization of graphene sheets not only improves dispersibility of graphene sheets, but also reinforces interfacial interactions required between the graphene and the matrix. Here a facile method was utilized to functionalize graphene sheets with 3-Aminopropyltriethoxysilane (APTES) before incorporating graphene sheets into polymer matrix.

To begin with, thermally-exfoliated graphene sheets (1 mg) and N,N’-Dicyclohexyl-carbodiimide (5 mg) were dispersed in 3-Aminopropyltriethoxysilane (APTES) (10 mL)
followed by ultrasonication for 1 hour. The homogeneous mixture was then put in an oven at 70°C for 24 hour. The resulting APTES-functionalized graphene sheets were centrifuged and dispersed with ethanol for three times to remove residue APTES.

In Figure 5-2, the right vial shows APTES-functionalized graphene sheets can be well dispersed in ethanol without any agglomeration but the graphene sheets without functionalization in the left vial show severe agglomeration. These silane moieties are grafted onto the graphene sheets via S_N2 nucleophilic displacement reaction between epoxy groups of graphene sheets and amino moieties of APTES. Those silane moieties of the functionalized graphene sheets can help graphene sheets easily disperse in ethanol without agglomeration. Given that other functional groups like hydroxyl and carboxylic groups are unlikely to be reduced under the given conditions, these groups should therefore remain in the exfoliated graphene sheets.

5.3.2 Preparation of Graphene – Chitosan Nanocomposite Film

To form the nanocomposite films, 0.5 wt% of chitosan were dissolved in an aqueous solution of 2 wt% acetic acid for 24 hour before use. The APTES-functionalized graphene sheets in ethanol dispersion was gradually added to the chitosan solution and ultrasonicated for 10 min. Finally, this homogeneous graphene/chitosan solution was poured into a glass beaker and kept in an oven at 60°C under vacuum for 48 hours. The nanocomposite film was then peeled off from the beaker for mechanical testing. A series of graphene – chitosan nanocomposite films with different graphene weight percentage were similarly prepared.

Figure 5-3 shows a photograph image of the final graphene – chitosan nanocomposite film with 4.76 wt% of graphene sheets. The uniform black color of this composite film indicates graphene sheets can be homogeneously dispersed in the
polymer matrix without agglomeration. Figure 5-5 also shows the cross-sectional SEM image of this film, which is pretty uniform and its thickness is around 15 µm. When enlarging this cross-sectional image, which is shown in Figure 5-6, we found out graphene sheets not only homogeneously disperse in the polymer matrix but align parallel to the surface of the composite film, indicating once the external force is applied to this composite film, the load can be successfully transferred to those stiff graphene sheets via the interfacial interactions between the graphene and chitosan. This might be because in the graphene/chitosan suspension, the primary amine groups in the chitosan and the secondary amine groups in the APTES-functionalized graphene sheets have been protonated and become positively charged, which makes the suspension very stable during the evaporation process. Thus when ethanol and water slowly evaporate from the suspension, the charge balance can achieve and sustain the dispersibility and alignment of graphene sheets in the chitosan matrix. Also, in the bottom side of the composite film contacting the container, there exists a thin wetting layer containing only chitosan polymer, which is shown in the top of the composite film that have been flipped over in Figure 5-5. This might be because during the evaporation process, the volume of the suspension gradually shrunk with the removal of the ethanol and water, forcing the graphene sheets and chitosan polyelectrolyte down to the bottom of the container. Thus when most of the solvent had been evaporated, the bottom polymer matrix quickly dried due to higher temperature before graphene sheets diffused into this region, forming a thin polymer wetting layer without any graphene sheets.

Figure 5-6 shows the tensile strength measurements of the composite films with different graphene weight percent. The yield strength of the pure chitosan polymer film
is about 60 MPa. As we incorporate graphene nanofillers with chitosan matrix, the yield strength gradually increases with the graphene percent in the composite film. However, when the graphene content exceeds 5 wt%, the tensile strength starts to decrease and even to be lower than that of the pure chitosan film when containing 6.98 wt% of graphene. Based on our results, the highest yield strength of 125 MPa can be reached at 4.76 wt% of graphene content. When the graphene content is higher than 5 wt%, we found out the wetting layer became thicker than that of the film with lower nanfiller content, indicating graphene sheets tend to agglomerate at higher concentration. This could be why the measured tensile strength decreases with the increase of graphene percent as the concentration of graphene is above 5 wt%. Although the detailed mechanism of forming these nanocomposite films still needs to be investigated further, we have demonstrated the self-assembling layered structure of graphene – chitosan composite via a simple evaporation method.
Figure 5-1. Schematic illustrating chitosan’s versatility for fabrication. At low pH (less than about 6), chitosan’s amines are protonated conferring polycationic behavior to chitosan. At higher pH (above about 6.5), chitosan’s amines are deprotonated and reactive. Also at higher pH, chitosan can undergo interpolymer associations that can lead to fiber and network (i.e., film and gel) formation.\textsuperscript{176}

Figure 5-2. Photographs of (left) unfunctionalized graphene sheets and (right) APTES-functionalized graphene sheets dispersions in ethanol/0.05 mg/mL

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Figure 5-3. Photograph of graphene – chitosan nanocomposite film (4.76 wt%).

Figure 5-4. Cross-sectional SEM image of graphene – chitosan nanocomposite film (4.76 wt%).
Figure 5-5. Cross-sectional SEM image of graphene – chitosan nanocomposite film (4.76 wt%).

Figure 5-6. Tensile strength measurements of graphene – chitosan nanocomposite film at different graphene contents.
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