To my family in Taiwan, who, always support all my efforts especially for my PhD
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This study covers three important research topics related to the application of self-assembly colloidal crystal by spin coating. The first topic describes the antireflection coatings on glass and semiconductor materials. Inspired by nature, the protruding nipples on moth eye can effectively reduce light reflection. Creating sub-300nm features with current lithography-based fabrication techniques (e.g., photolithography or interference lithography) is costly and is limited by either low resolution or small sample size. The spin-coating technology that combines the simplicity and cost benefit of bottom-up self-assembly with the scalability and compatibility of standard top-down microfabrication is used in creating non-close-packed moth eye antireflection coatings.

The second topic describes the templating fabrication of surface enhanced Raman scattering (SERS) active substrates. Wafer-scale metallic pyramid arrays with sharp nanotips can be replicated from silicon templates by a simple adhesive peeling process. The resulting nanopyramid arrays show stable surface enhancements for Raman scattering from benzenethiol molecules adsorbed at the metal surfaces. To further improve the reproducibility, we report a simple colloidal templating approach for fabricating surface-enhanced Raman scattering (SERS) substrates with highly
reproducible enhancement over wafer-sized areas. The substrates are produced by evaporating a thin layer of gold on highly ordered silica colloidal crystal-polymer nanocomposites created by a scalable spin-coating technology. The ordered inorganic-organic composite structure induces the formation of island-type gold films. Systematic measurements and statistical analysis show that the substrates exhibit high SERS reproducibility with less than 28% standard deviation over a 4 in. wafer surface. Finite element electromagnetic modeling has also been employed to simulate SERS enhancement from these structured substrates.

The third topic presented is the templated fabrication of sub-100nm nanostructures. Periodic polymer nanoposts and metal nanohole arrays with tunable size have been fabricated by templating from spin-coated two-dimensional non-close-packed colloidal crystal–polymer nanocomposites.
CHAPTER 1
INTRODUCTION

1.1 Top-Down and Bottom-Up Fabrication

Top-down fabrication has been widely used in the semiconductor industry to fabricate cheap and fast electronic devices which are the hallmark of modern life and technology. Photolithography is the most commonly used top-down technology to fabricate three dimensional components. Due to the light diffraction limit, feature sizes smaller than the wavelength of light cannot be achieved by conventional photolithography.\(^1\) Lithography techniques such as extreme ultraviolet light or soft X-rays lithography, electron beam lithography, and dip pen lithography have been used to generate smaller patterns.\(^2\) These high cost and low throughput techniques cannot be used for mass production and are only lab-oriented processes. Another challenge of top down fabrication is the choice of materials. The use of short wavelength as the exposure light source and smaller features size requires materials with suitable optical and mechanical properties.

Aside from top-down engineering technique, bottom-up nanofabrication offers a new paradigm for material fabrication. Complex structures found in nature are assembled with building blocks like atoms, protein, RNA and DNA. The self assembly building blocks can be made by organic, inorganic, polymeric and hybrid materials. Building blocks can be assembled into spheres and cubes, sheets and discs, wires and tubes, rings and spirals with nm to cm dimensions. A flowchart describing the ideas of self assembly is shown in Figure 1-1.
1.2 Colloidal Self-Assembly

The ability to synthesize monodisperse latex and silica nanoparticles by heterogeneous emulsion polymerizations and sol-gel chemistry, respectively with diameters in the range of tens of nanometer to several micrometers provides a new class of materials with a range of applications in chemistry and physics. A variety of methods, such as gravitational sedimentation, template assisted assembly, electrostatic repulsion, electric field induced assembly, robotic manipulation, Langmuir-Blodgett deposition, spin coating and capillary forces induced convective self-assembly have been developed to create both 3D and 2D colloidal crystals.

The application of the colloidal crystal has been widely exploited recently. One of the most appealing properties of these periodic dielectric lattices is 3D photonic crystals behavior. Colloidal crystals can function as the optical analog of the electronic semiconductor. The 3D colloidal crystal can also be used as a template for preparation of three-dimensionally ordered porous replicas, which are known as inverse opals. A wide variety of macroporous materials based on colloidal templates have been synthesized. The applications of these inverse opals include chemical and biological sensors, simultaneous chromatographic separation, optical sensing, power storage and generation, low-threshold laser, and full color displays.

Monolayer colloidal crystal can be used for lithographic patterning of surfaces, projection lithography, micromolds and surface relief patterns. Nanostructures such as nanodots, nanorings, nanoprisms, nanoholes, nanobowls, nanocrescent and hollow spheres nanostructures can be fabricated by two dimensional lithography. Applications include optical antennas, catalysts, chemical and biological sensors. The sizes, periodicities, and materials of these nanostructures can be controlled by adjusting the
size of the colloidal templates and the filling materials from organic, inorganic to polymeric materials.

1.3 Antireflection Coatings

Antireflection coatings (ARCs) are used in optical elements to reduce light reflection and enhance optical performance. A reduction in surface reflection is typically accomplished by the application of an antireflection coating of a quarter-wavelength optical thickness. When the index of refraction of the coating \((n_c)\) equals the square root of the product of the indices of the surrounding medium \((n_0)\) and the substrate \((n_s)\), that is, \(n_c = (n_s n_0)^{0.5}\) reflections are suppressed at wavelengths near the quarter-wavelength optical thickness. However, there are some limitations and problems when applying quarter-wavelength optical thickness as antireflection coatings. To achieve the effective antireflection coatings for glass, the refractive index must equal 1.2 while materials with the lowest refractive indices available are \(\sim 1.35\).\(^{33}\)

As for semiconductors, a single layer film can only reduce light reflection at a single wavelength. A stack of alternate high and low refractive index films, all one quarter wavelength thick is used to achieve broadband antireflection coatings. To achieve broadband antireflections requires very precise control of the thickness of each layer. Additionally, the potential mismatch of physical properties (such as thermal expansion coefficient) of each layer reduces the stability of the coating layers. By colloidal crystal templating, large area and cost effective broadband antireflection nanostructures can be generated.

1.4 Surface Plasmons and Surface Enhanced Raman Scattering

Surface plasmons are electromagnetic waves propagating at the interface between a dielectric and a conductor, evanescently confined in the perpendicular
direction. These electromagnetic surface waves arise via the coupling of the
electromagnetic fields to oscillations of the conductor’s electron plasma.\textsuperscript{34} The surface
plasmons dispersion can be obtained by solving Maxwell’s equation as shown in Figure
1-2. In order to couple light to surface plasmons, the momentum mismatch must be
overcome. A prism is typically used to excite surface plasmons on flat metal surfaces.
Periodic metal nanostructures are also used to generate surface plasmons.\textsuperscript{35} Recent
advances in nanotechnology allow metal to be structured to tailor surface plasmon
properties. Applications of surface plasmons have been exploited in optics\textsuperscript{36}, solar
cells,\textsuperscript{37} biological and chemical sensors\textsuperscript{35,38-39} and surface enhanced Raman
scattering.\textsuperscript{40}

Raman spectroscopy is a spectroscopic technique used to study vibrational and
other low-frequency modes in a system. It relies on inelastic scattering of
monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet
range. The incident photons are scattered inelastically by a molecular bond and shifted
in frequency by the energy of its characteristic molecular vibrations. Two types of
Raman scattering events, called Stokes and anti-Stokes scattering may result,
depending upon whether the incident light interacts with a molecule in the vibrational
ground state or an excited vibrational state as shown in Figure 1-3. Spontaneous
Raman scattering is typically very weak, and as a result the main difficulty of Raman
spectroscopy is separating the weak inelastically scattered light from the intense
Rayleigh scattered laser light. Surface enhancement Raman scattering was first
discovered by Fleischmann in 1974 but the prevailing explanation for the nature of the
single enhancement was proposed by Van Duyne in 1977.\textsuperscript{41} The mechanisms of SERS are sorted into two classes called chemical and electromagnetic enhancement.\textsuperscript{42}

The chemical enhancement can be explained by the new electronic states which arise from molecular-metal chemisorptions. Modified electronic states serve as resonant intermediate states in Raman scattering. When the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the adsorbate symmetrically fall about the Fermi level of the metal surface, charge transfer excitations can occur at about half the energy of the intrinsic intramolecular excitations of the adsorbate as shown in Figure 1-4.\textsuperscript{42} The electromagnetic field of the light at the adsorption surface can be greatly enhanced if surface plasmons are excited. The amplification of both incident laser field and scattered Raman field through their interaction with the surface constitute the electromagnetic SERS mechanism. The electromagnetic contribution to the Raman signals enhancement is the fourth power of the local electric field enhancement.

The most common types of SERS-active substrates are clusters of colloidal silver or gold nanoparticles in solution or dry on a surface.\textsuperscript{43-44} Although metal colloids exhibit the largest enhancement factor, the reproducibility of this type of SERS substrate remains a problem. The interparticle spacing which generates hot spots for SERS is difficult to control due to the stochastic distribution of the nanospheres on a substrate. By colloidal crystal templating fabrication, large-area and reproducible SERS active substrates can be easily fabricated.
Figure 1-1. A flowchart describes the self-assembly approach.

Figure 1-2. The dispersion curve for a SP mode shows the momentum mismatch problem that must be overcome in order to couple light and SP modes together, with the SP mode always lying beyond the light line, that is, it has greater momentum ($\hbar k_{SP}$) than a free space photon ($\hbar k_0$) of the same frequency $\omega$. 
Figure 1-3. Schematic diagram describes Raman Scattering.

Figure 1-4. A typical energy level diagram for a molecule adsorbed on a metal surface. The occupied and unoccupied molecular orbitals are broadened into resonances by their interaction with the metal states; orbital occupancy is determined by the Fermi energy. Possible charge transfer excitations are shown.
CHAPTER 2
SELF ASSEMBLY OF COLLOIDAL CRYSTALS BY SPIN COATING

Spin coating is a well-established technique in microfabrication for the formation of highly uniform thin films with adjustable thickness over large areas.\(^\text{45}\) It has already been utilized in making colloidal crystals, such as colloidal masks for nanosphere lithography.\(^\text{46-47}\) 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.\(^\text{48}\) 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 with strong capillary forces. To satisfy the vacuum requirements of dry 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, thereby releasing the colloidal crystals.

2.1 Experimental Procedure

A volume fraction of ca. 20% silica colloids with diameters of \(~ 30\text{ nm}\) to \(~ 2\text{ μm}\) 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 with 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 with continued spinning for a specific time needed to achieve a target thickness. The substrate is then transferred to a high intensity UV lamp to polymerize the monomer.

2.2 Results and Discussion

The self-assembled silica colloidal crystal-polymer nanocomposite films exhibit bright monochromatic six-arm diffraction (Figure 2-1), indicating the formation of hexagonally packed spheres parallel to the wafer surface. The long-range hexagonal ordering is confirmed by top-view scanning electron microscope (SEM) images of two samples consisting of 325 nm (Figure 2-1B and C) and 1320 nm (Figure 2-1D) silica spheres. The ordering perpendicular to the substrate surface is apparent in the cross sectional images shown in Figure 2-2. Most interestingly, the spin-coated colloidal crystals exhibit unusual non-close-packed (ncp) structures as revealed by magnified SEM images (Figure 2-2C and D). This is more apparent after the polymer matrix been selectively removed by oxygen plasma etching (Figure 2-3A 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 2-3C). 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 2-3 B)) calculated from SEM images similar to Figure 2-3A and C.

The spin-coated nanocomposite films exhibit excellent thickness uniformity with variation of less than 4% over a four-inch-diameter wafer. 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 2-2 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 multilayers can be 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 preceding layer (Figure2-2C) functions as a template, which aids in aligning the crystalline orientation of the subsequent multilayer.

As discussed above, the polymer matrix needs 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 2-3A, C and D show top- and side-view SEM images of monolayer and multilayer colloidal crystals after polymer matrix is removed. 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), only six-arm diffraction patterns with exact 60° angles between neighboring arms are observed, indicating the formation
of hexagonally ordered colloidal crystals. Unexpected results occur when the spin speed is higher than 6000 rpm. The alternating formation of hexagonal and square diffraction patterns is observed 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 2-4A 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 2-4B 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 2-4B. Further SEM characterization shows that the squarely arranged arrays cover the whole wafer surface and the crystal is 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.

The center-to-center nanoparticle distance can be controlled by adjusting the volume fraction of silica monomer dispersion as shown in Figure 2-5. As the volume fraction of the silica spheres increase, interparticle spacing decreases. Figure 2-6
shows the SEM images of top- and side- view of spin-coated colloidal crystal with volume fractions of 30% and 40%. Although increasing volume fraction can reduce interparticle spacing, it also increases the viscosity of silica ETPTA dispersion. For 50% volume fraction, the viscosity increases drastically and thus the silica ETPTA composite film is not uniform.

We attribute the unusual formation of non-close-packed colloidal crystals during spin-coating to the normal pressures produced by shear flows and monomer polymerization that squeeze shear aligned hexagonal layers of particles against substrates. Considering the low dielectric constant of the monomer (~ 3.0 at optical frequencies) and the small salt effect on the interparticle separation, the electrostatic repulsion between charged spheres plays only a minor role in determining the resulting microstructures. The shear forces created by spin-coating are crucial for aligning colloidal particles into hexagonally ordered crystals. The interactions of applied hydrodynamic, Brownian, and the colloidal forces determine the resulting microstructures. In sharp contrast to traditional rotational rocking-cuvette and parallel plate shear cells, the flow profile in the spin-coating process is not a uniform shear, with the shear maximum occurring at the substrate and rapidly decaying to a zero value at the free surface. Although shear aligned colloidal crystallization has been extensively studied, the effect of non-uniform shear on the formation of aligned microstructures has received little or no attention. Therefore, a detailed study on the underlying mechanisms of colloidal crystallization during spin-coating, which has yet to be fully understood, will provide new insights into shear-induced crystallization, melting and relaxation.
Figure 2-1. 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 2-2. Precise control over the nanocomposite thickness by spin coating. A) Monolayer, B) 2-layers, C) 5-layers and D) 41-layers.

Figure 2-4. 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 2-5. Interparticle spacing of spin-coated silica/ETPTA dispersion for different volume fraction.

Figure 2-6. SEM images of spin-coated silica monomer dispersion with different volume fraction. A) Top-view SEM image of 30% volume fraction, B) side view of A. C) 40% volume, D) side view of C.
CHAPTER 3
TEMPLATED FABRICATION OF ANTIREFLECTION COATINGS

3.1 Templated Antireflection Coatings on Glass Substrates

3.1.1 Templated Moth Eye Antireflection Coatings

Periodic optical microstructures are abundant in biological systems and have provided enormous inspiration for scientists to mimic natural structures for practical applications.\textsuperscript{55-59} To name just a few, \textit{Morpho} butterflies use multiple layers of cuticle and air as natural photonic crystals to produce striking blue color,\textsuperscript{56} inspiring the development of chemical sensors for detecting trace amount of vapors.\textsuperscript{58} Some nocturnal insects e.g., moths use arrays of non close packed nipples with sub 300 nm size as antireflection coatings (ARCs) to reduce reflectivity from their compound eyes.\textsuperscript{60} Artificial ARCs are widely used in monitors, car dashboards, optical components, and solar cells.\textsuperscript{33,61-63} Existing antireflection technologies, such as quarter-wavelength multilayer films and nanoporous coatings e.g., phase separated polymers and nanoparticle and polyelectrolyte multilayers often perform suboptimally or are expensive to implement.\textsuperscript{33,61-64}

Inspired by the natural photonic structures, moth-eye ARCs with subwavelength protrusion arrays have been widely explored.\textsuperscript{60,65} However, current lithography-based fabrication techniques (e.g., photolithography or interference lithography) in creating sub-300 nm features are costly and are limited by either low resolution or small sample size. Self-assembly in synthetic materials provides an inexpensive, simple to implement, inherently parallel, and high throughput alternative to lithography in creating periodic microstructures.\textsuperscript{28} Unfortunately, most of the traditional self assembly techniques are not compatible with standard microfabrication, impeding scale-up to an industrial-scale
fabrication. Additionally, conventional self-assembly is limited to the creation of close-packed structures, whereas natural moth-eye ARCs exhibit non-close-packing characteristics. The spin-coating technology that combines the simplicity and cost benefits of bottom-up self-assembly with the scalability and compatibility of standard top-down microfabrication is used in creating non-close-packed moth eye antireflection coatings.

**Experimental procedure.** A schematic outline of the templating procedures is shown in Figure 3-1. The fabrication of wafer-scale, non-close-packed colloidal crystals embedded in poly(ethoxylated trimethylolpropane triacrylate) (PETPTA) matrix is performed by spin coating technology. The resulting crystals can be easily and reproducibly created over arbitrarily large areas in minutes. The long-range periodic surface protrusions of the shear-aligned crystals similar to Figure 3-2 can be easily transferred to a poly(dimethylsiloxane) (PDMS Sylgard 184, Dow Corning) mold. The solidified PDMS mold can then be peeled off and put on top of ETPTA monomer supported by a glass slide with spacers (double-stick tape, thickness of ~0.1 mm) in between. ETPTA monomer is polymerized for 2 s using a Xenon pulsed UV curing system. After peeling off PDMS mold, ETPTA nipple arrays coated glass slide can be made. The flexible PDMS mold enables the creation of microstructured coatings on both planar and curved substrates.

The protrusion depth (~50 nm) of a replicated PETPTA array from the spin-coated nanocomposite film is shallow compared to the radius of templating silica spheres (180 nm), as revealed by the atomic force microscope AFM image (Figure 3-2A), and its corresponding depth profile (bottom curve) is shown in Figure 3-2D. The polymer matrix
of spin-coated nanocomposites can be plasma etched using an Unaxis Shuttlelock reactive ion etcher RIE inductively coupled plasma ICP operating at 40 mTorr oxygen pressure, 40 SCCM (SCCM denotes cubic centimeter per minute at STP flow rate), and 100 W to adjust the height of the protruded portions of silica spheres, resulting in good control over the depth of replicated nipples. Figure 3-2B and C show PETPTA nipple arrays replicated from the same nanocomposite sample, as shown in Figure 3-2A, after 20s and 45 s RIE etching, respectively. The shape of nipples in the latter sample is close to hemispherical, as revealed by the depth profile (top curve in Figure 3-2D.) The specular optical reflectivity of the replicated nipple arrays are evaluated using visible-near-IR reflectivity measurement at normal incidence. An Ocean Optics HR4000 high resolution fiber optic UV-visible-near-IR spectrometer with a reflection probe is used for reflectance measurements. The resulting reflectivity is calibrated using a STAN-SSL low-reflectivity specular reflectance standard Ocean Optics.

Figures 3-3 and Figure 3-4 illustrate the excellent control over the antireflection performance of the replicated nipple arrays by simply adjusting the RIE etching time (i.e., height of nipples). The hemispherical-like nipple arrays (dark gray curve in Figure 3-3) show significantly smaller reflectivity than that of a flat control sample (black curve) for the whole visible spectrum.

**Results and discussion.** A thin-film multilayer model has also been developed arrays and then compared with experimental spectra. The nipple lattice is assumed to be hexagonal and the distance between the centers of the neighboring nipples is $\sqrt{2}D$. Since the distance of the nipples is small with respect to the wavelength of light, light propagation is governed by the effective refractive index of the nipple array,
which can be calculated from effective medium theory.\textsuperscript{69} We first divide the whole hemisphere cap layer in 100 layers and calculate the effective refractive index for each layer. The reflectance of each layer can then be calculated using a matrix multiplication procedure for a stack of thin layers.\textsuperscript{69} Figure 3-3 shows that the simulated spectra (dotted lines) match the experimental spectra (solid line) and the reflection from the PETPTA/glass interface due to index mismatch might contribute to the small discrepancy between them.

The good and adjustable antireflection performance of the replicated nipple arrays can be explained by mapping the effective refractive index across the height of nipples (Figure 3-5). For featureless polymer film, the refractive index is sharply changed from 1.0 to 1.46 across the air-polymer interface, leading to high reflectance. For nipples with 50 nm height cross that are replicated directly from spin-coated nanocomposite without RIE etching, the effective refractive index is continuously changed from 1.0 nipple peaks to 1.09 nipple troughs, then sharply increased to 1.46, resulting in reduced reflectivity (Figure 3-4); while for hemispherical nipples (unfilled circle), the final step is moderate-from 1.20 to 1.46, thus leading to minimal reflectivity.

This simple yet scalable self-assembly approach for fabricating efficient moth-eye antireflection coatings with adjustable reflectivity and non-close-packed microstructures, which are not easily available by traditional self-assembly approaches. The specular reflection of nipple arrays matches the theoretical prediction using a thin-film multilayer model.

3.1.2 Templated Fabrication of Binary Arrays as Antireflection Coatings

Facile production of complex periodic nanostructures over a large area is of great technological importance in developing novel electronic, optical, and magnetic
devices. For instance, subwavelength-structured metal nanohole arrays exhibit extraordinary optical transmission, which is promising for realizing miniaturized devices for all-optical integrated circuits. Other than simple hexagonal and square arrays, complex nanohole geometries (e.g., binary arrays) have attracted great scientific and technological interest as they are promising structures for developing more efficient optical devices and biosensors, as well as a fundamental understanding of surface-plasmon-enabled optical transmission. Dielectric binary periodic nanostructures have also been explored for creating superhydrophobic and superoleophobic surfaces, photonic crystals, and antireflection coatings. However, creating periodic binary nanostructures with subwavelength-scale resolution is not a trivial task for the current nanofabrication techniques, such as electron beam lithography and focused ion beam. Although arbitrary nanostructures can be fabricated, attaining high-throughput and large-area fabrication in an inexpensive manner continues to be a major challenge with these top-down techniques.

Bottom-up self-assembly and subsequent templating nanofabrication provides a much simpler and inexpensive alternative to nanolithography in fabricating periodic nanostructures. Self-assembled block-copolymers and surfactants enable the creation of sub-50 nm periodic structures. Colloidal lithography provides a versatile approach for making a large variety of periodic microstructures by using self-assembled monolayer or multilayer colloidal crystals as deposition or etching masks. Binary periodic nanostructures, such as metal nanoparticle arrays, have recently been demonstrated by using angle-resolved colloidal lithography. Unfortunately, most of the current colloidal assembly techniques suffer from low throughput. It usually takes
hours to days to assemble a centimeter-sized crystal. In addition, current colloidal assembly techniques (e.g., convective self-assembly, gravitational deposition, and physical confinement) are not compatible with standard microfabrication, limiting the on-chip integration of practical devices. Moreover, only close-packed colloidal crystals are available through traditional self-assembly. But in many cases, non-close-packed crystals are preferred to expand the versatility of colloidal lithography. Furthermore, in conventional colloidal lithography, only self-assembled colloidal spheres are used as structural templates.

We show the scalable fabrication of binary periodic nanostructures by utilizing double-layer non-close-packed colloidal crystals as templates. Contrary to traditional colloidal lithography and our previous templating approaches, the polymer matrix between the spin-coated colloidal crystals has also been used as a sacrificial template to define the resulting periodic binary nanostructures, including intercalated arrays of silica spheres and polymer posts, gold nanohole arrays with binary sizes, and dimple-nipple antireflection coatings. We also show that binary-structured antireflection coatings exhibit better antireflective properties than unitary coatings.

**Experimental procedure.** By controlling the spin coating condition, a bilayer silica ETPTA nanocomposite can be fabricated. The resulting bilayer nanocomposite was etched by oxygen plasma etch at 40 mTorr pressure, 40 SCCM oxygen flow rate, and 100 W for 2 min to partially remove ETPTA polymer matrix for releasing the top-layer silica spheres of the spin-coated double-layer colloidal crystal. Both the bottom- and top-layer silica spheres were removed by dissolution in 2% hydrofluoric acid aqueous solution for 2 min. Poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning)
precursors were mixed and degassed and then poured over the resulting polymer post arrays with binary dimple-nipple structures. After curing at 80 °C for 30 min, the solidified PDMS mold was peeled off the polymer array and put on top of ETPTA monomer supported by a glass slide. The ETPTA monomer was photopolymerized for 4 s, using a Xenon pulsed UV curing system. The PDMS mold was finally removed to complete the fabrication process.

A HR4000 High Resolution Fiber Optic UV-vis spectrometer with a reflection probe was 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°. Absolute reflectivity was obtained as a ratio of the sample spectrum and 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.

In the current colloidal templating approach, we use double layer, non-close-packed colloidal crystals prepared by the well established spin-coating technique as structural templates. The spin-coating methodology is based on shear-aligning concentrated colloidal suspensions in a nonvolatile monomer. Contrary to conventional colloidal self-assemblies, spin-coating enables rapid production of wafer-scale (up to 8 in. in diameter) colloidal crystals with remarkably large domain sizes. Another unique property of the spin-coated colloidal crystals is their unusual non-close-packed crystalline structures. The spheres within each colloidal layer are hexagonally arranged
and are separated by \( \sim 1.4 \) times the particle diameter. The thickness of the shear-aligned colloidal crystals can be precisely controlled by adjusting the spin-coating conditions (e.g., spin speed and time). Most important, the shear-aligned colloidal crystals are embedded in a polymer matrix, which has a highly uniform thickness over wafer-scale areas. Here we demonstrate an approach that uses colloidal spheres as templates to generate periodic binary nanostructures that are not easily available by traditional top-down and bottom-up technologies.

The current colloidal templating technique is taken one step further by demonstrating the production of binary dimple-nipple antireflection coatings (ARCs) on glass substrates. Antireflection coatings are widely utilized in eliminating the “ghost images” for flat-panel displays, increasing the transmittance of optical lenses, reducing glaring from automobile dashboards, and enhancing the conversion efficiency of solar cells.\(^{33,61,64}\) The binary antireflective structure is inspired by the microstructured corneas of moths, which consist of hexagonal arrays of non-close-packed subwavelength nipples, similar to the protruded polymer posts as shown in Figure 3-2B. The height of the resulting nipples is at most the radius of the templating spheres, limiting the optical thickness and thus the antireflection performance of the unitary ARCs. By contrast, the optical thickness of the binary ARCs can almost be doubled. We expect this will lead to improved antireflective performance.

To generate binary ARCs, we first assemble double-layer, non-close-packed colloidal crystals (Figure 3-6A) by using the spin coating technology. The polymer matrix is then partially removed and the exposed silica spheres are dissolved in a 2% hydrofluoric acid aqueous solution, leaving behind a polymer dimple-nipple array as
shown by the top- and side-view SEM image in Figure 3-6B and C respectively. The resulting periodic binary structure can then be transferred to a poly(dimethylsiloxane) (PDMS) mold and then replicated to a thin layer of polymer (e.g., ETPTA) or sol-gel glass on a glass substrate by the well-established soft lithography technique. Figure 3-6D shows a side-view SEM image of a replicated ETPTA binary array. The specular optical reflection of the template polymer binary ARCs is evaluated by using UV-vis reflectivity measurement at normal incidence. The solid lines in Figure 3-7 show the experimental reflection spectra from a flat glass substrate and a glass slide covered with a polymer dimple-nipple ARC. For comparison with the new binary antireflective structure, the normal-incidence reflection from a glass slide coated with a unitary ETPTA hemispherical ARC as reported in our previous section is also shown (blue curve). The glass control sample exhibits ~4% single-surface reflection, while the binary ARC coated glass slide displays <0.5% reflectivity for the whole visible spectrum. It is also evident that the binary ARC shows improved antireflective performance over the unitary hemispherical ARC for most of the visible wavelengths.

**Results and discussion.** The experimental reflection measurement is complemented by theoretical calculation by using a rigorous coupled-wave analysis (RCWA) model. A coordinate system is set up with the z-axis perpendicular to the templated dimple-nipple surface so that the bottoms of the dimples are at \( z = 0 \) and the nipple tops at \( z = h \). We divide the dimple-nipple arrays into \( N = 100 \) horizontal layers with thickness \( (h)/(N) \). The dimple and nipple lattices are assumed to be hexagonal and the distance between the centers of the neighboring dimples and nipples is defined as \( 1.41D \), where \( D \) is the diameter of templating silica spheres. Other structural
parameters (e.g., dimple size and depth, nipple depth, size, and shape) are obtained from the side view SEM image as shown in Figure 3-6D. The fraction of ETPTA in each horizontal layer can then be determined by simple geometrical calculation. On the basis of the effective medium theory, the effective refractive index \( n(z^*) \) of the layer at height \( z^* \) can be approximated by \( n(z^*) \). \( f(z^*) = n_{ETPTA}^q + (1 - f(z^*))n_{air}^q \), where \( n_{ETPTA} = 1.46 \), \( n_{air} = 1.0 \), and \( q = 2/3 \).  

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 6 show the RCWA-simulated reflection spectra from a flat glass substrate and a binary ETPTA ARC. The simulated spectra agree reasonably well with the experimental results.

We show that the templated binary dimple-nipple antireflection coatings exhibit improved performance over unitary hemispherical nipples. This technique is scalable and compatible with standard microfabrication, promising a wide range of applications ranging from plasmonic devices to antireflection coatings for flat panel displays and solar cells.

3.2 Templating Antireflection Coatings on Semiconductor

3.2.1 Surface Texturing Silicon Wafers as Antireflection Coatings

Current production of solar cells is dominated by crystalline silicon modules,\(^{97-98}\) however, due to the high refractive index of silicon, more than 30% of incident light is reflected back, which greatly reduces the conversion efficiency of photovoltaic devices.\(^{64,99-100}\) To significantly suppress the reflective loss of solar cells, various antireflection techniques, such as quarter-wavelength multilayer films and nanoporous
coatings, have been developed.\textsuperscript{63,99,101} For crystalline silicon solar cells, silicon nitride films deposited by plasma enhanced chemical vapor deposition have become the industry standard for antireflection coatings (ARCs).\textsuperscript{99} Unfortunately, these existing techniques often perform suboptimally or are expensive to implement, impeding development of solar cells that can be made truly economically competitive with fossil fuels.

Inspired by the microstructured cornea of some nocturnal moths,\textsuperscript{60,65} subwavelength-structured gratings directly patterned on silicon substrates have been extensively explored both experimentally\textsuperscript{102-105} and theoretically\textsuperscript{106-108} for developing broadband ARCs. These gratings with a period smaller than the wavelength of incident light are intrinsically more stable and durable than multilayer ARCs since no foreign material is involved. Electron-beam lithography (EBL) is a common approach in fabricating subwavelength gratings.\textsuperscript{109} Unfortunately, the low throughput and the high cost of EBL raise big concerns. Interference lithography\textsuperscript{102-103} and nanoimprint lithography\textsuperscript{110} enable the creation of subwavelength antireflection structures over large areas; however, these techniques are still expensive to implement.

Spin coating technology provides a simpler and cheaper self assembly approach in creating wafer-scale subwavelength antireflection gratings on single-crystalline silicon substrates. Contrary to most bottom-up approaches,\textsuperscript{111-112} which are favorable for low-volume, laboratory-scale production, this nonlithographic technique is compatible with standard microfabrication, enabling large-scale production of subwavelength ARCs for solar collectors.
**Experimental procedure.** A schematic illustration of the fabrication procedures for making wafer-scale subwavelength inverted pyramid gratings on single-crystalline silicon wafers is shown in Figure 3-8. We start to generate non-close-packed colloidal monolayer on a (100) silicon wafer (test grade, n type, Montco Silicon Technologies) by the spin-coating technology. The non-close-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 3-9 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 long range 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.\(^{113}\)
The specular optical reflectivity of the replicated pyramid arrays is evaluated using visible-near-IR reflectivity measurement at normal incidence. The solid lines in Figure 3-10 show the measured normal-incidence specular reflection from a polished (100) silicon wafer and the sample, shown in Figure 3-9B, with 360 nm pyramidal pits. The flat silicon substrate exhibits high reflection (~35%) for visible and near infrared 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.

Results and discussion. The templated silicon subwavelength gratings exhibit lower reflection than colloid-based antireflection coatings on crystalline silicon solar cells. 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 ~2%–10%, 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. By contrast, the template pyramid arrays show relatively low reflection at short wavelengths (Figure 3-10).

A multilayer rigorous coupled wave analysis (RCWA) model 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, the effective refractive index $n(z^*)$ of the layer at level $z^*$ can be approximated by $n(z^*) = [f(z^*)\tilde{N}_{Si}^q + (1 - f(z^*)n_{air}^q)]^{1/q}$, where $f(z^*)$ is the fraction of silicon contained in the layer, $\tilde{N}_{Si} = n + ik$ is the complex refractive index of silicon ($n$ and $k$ are optical constants), $n_{air} = 1$, and $q = 2/3$. The optical constants of silicon which are functions of wavelengths are obtained from literature. 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 Figure 3-10. 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 Figure 3-11. 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,$^{60}$ 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 Figure 3-11. It is apparent that larger pyramids lead to lower reflection, matching our experimental observation.

### 3.2.2 Broadband Antireflection Coatings on Silicon Wafer

Subwavelength inverted pyramid arrays are anisotropically wet etched in single-crystal silicon wafers. Although this nonlithographic technique is much simpler and cheaper than PECVD deposition of SiNx ARCs, the antireflective performance of the templated ARCs is not as good as the commercial coatings. The normal-incidence reflection is higher than 10% for most solar wavelengths due to the limited depth of the inverted pyramids.$^{60}$ Additionally, the technique requires vacuum deposition of chromium which significantly increases the complexity and the cost for manufacturing ARCs on single-crystal silicon solar cells.

We use a bio-inspired templating technique for fabricating broadband moth-eye ARCs on SC silicon substrates. The resulting subwavelength-structured ARCs exhibit superior broadband antireflective performance than commercial SiNx coatings.
Experimental procedure. The schematic illustration of the templating procedures for making wafer-scale silicon nipple arrays is shown in Figure 3-13. Monolayer silica colloidal crystals with non-close-packed structures are created by the established spin-coating technique. The non-close-packed silica particles can be used as etching masks during a SF$_6$ reactive ion etching (RIE) process (40 mTorr chamber pressure, 26 SCCM SF$_6$, 5 SCCM O$_2$, 25 W) to pattern arrays of nipple-like structures directly on silicon wafers (test grade, $n$ type, (100), Montco Silicon Technologies). Under above RIE conditions, the etching selectivity between silicon and silica is more than 10:1.\textsuperscript{111} Templating silica spheres are finally removed by a hydrofluoric acid wash ~2% aqueous solution for 2 min.

Figure 3-14A shows a scanning electron microscope (SEM) image of a monolayer colloidal crystal consisting of 360 nm diameter silica spheres prepared by the spin-coating technique. The long-range hexagonal arrangement and the non-close-packed structure of silica particles are evident. Figure 3-14B shows a tilted SEM image of a sample after 9 min SF$_6$ etch. Due to the high etching selectivity between silicon and silica, the unprotected silicon is preferentially etched by reactive fluorine ions. The shrinkage of templating silica spheres is not significant. The RIE etching is isotropic, leading to the formation of nipple-like microstructures whose sizes and aspect ratios are determined by the templating silica sphere diameter and the RIE etching time. Figure 3-14C and D show tilted SEM images of silicon nipple arrays after 6 and 9 min RIE etching. The preservation of the hexagonal ordering and the interparticle distance of the original silica colloidal crystal are apparent for the templated nipple arrays. Subwavelength-scale nipples with aspect ratios as high as ~5.0 can be easily fabricated.
by this approach. The specular optical reflectivity of the templated silicon nipple arrays are evaluated using visible-near-IR reflectivity measurement at normal incidence. Figure 3-15 compares the normal-incidence reflection from a 15 min RIE-etched silicon nipple array sample, a bare SC silicon wafer, and a commercial SC silicon solar cell with PECVD-deposited SiNx ARC (Plastecs, Webster, MA). The polished SC silicon wafer shows more than 35% reflection for wavelengths from 350 to 850 nm (black solid line), agreeing well with previous measurement. The Plastecs SC silicon solar cell exhibits distinctive bluish color caused by the SiNx coating and presents the minimal reflection at around 700 nm (blue solid line). The templated nipple array shows excellent broadband antireflection property and the reflection is below 2.5% for a wide range of wavelengths (red solid line).

Results and discussion. The experimental reflection measurement is complemented by theoretical calculation using a rigorous coupled wave analysis RCWA model. A coordinate system is set up with z axis perpendicular to the nipple surface so that the array troughs are at \( z = 0 \) and the nipple peaks at \( z = h \). We divide the nipple arrays into \( N = 100 \) horizontal layers with thickness \( h/N \). 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 nipple lattice is assumed to be hexagonal and the distance between the centers of the neighboring troughs is defined as 1.41D, where D is the diameter of templating silica spheres. Therefore, the horizontal layer at level \( z^* \) contains a fraction \( f(z^*) \) of silicon with complex refractive index \( \tilde{N}_{si} = n + ik \), \( n \) and \( k \) are optical constants obtained from literature and a fraction \( 1 - f(z^*) \) of air with refractive index \( n_{air} = 1 \). The hexagonal
structure of the nipple arrays leads to the formula \( f(z^*) = \left[ \frac{\pi r^2}{\sqrt{3D^2}} \right] \). Based on the effective medium theory, the effective refractive index \( n(z^*) \) of the layer at height \( z^* \) can be approximated by \( n(z^*) = [f(z^*)\bar{N}_{Si}^q + (1 - f(z^*)n_{air}^q)]^{1/q} \), where \( q = 2/3 \). 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 3-15 show the RCWA-simulated reflection from a bare silicon wafer and a subwavelength nipple array with base radius of 210 nm and height of 800 nm templated from 360 nm silica spheres. It is evident that the simulated results agree reasonably well with the experimental spectra for both samples, though both the peak position and the reflection magnitude match with the RCWA calculation for flat silicon, while only magnitude matches with theoretical prediction for periodic nipple arrays. This is due to the limitation of the RCWA modeling where each layer is assumed to have a uniform refractive index, which is in fact a 2D periodic function at each layer. We further conduct optical modeling for the same subwavelength nipple array using another common simulation method—the thin film multilayer (TFM) model. The TFM model employs similar layer-slicing method as RCWA but a different matrix multiplication procedure to calculate the reflection from a stack of thin layers. The simulation results obtained from both models are compared in Figure 3-15. It is apparent that these two models generate almost identical results.

The resulting gratings exhibit excellent broadband antireflection properties. The specular optical reflection from the templated moth eye ARCs matches with theoretical
predictions using RCWA and TFM models. These biomimetic coatings are of great technological importance in improving the conversion efficiencies of crystalline silicon solar cells.

### 3.2.3 Biomimetic Subwavelength Antireflective Gratings on GaAs

Gallium arsenide (GaAs) is a technologically important semiconductor that has been widely used in optoelectronics, such as vertical cavity surface-emitting lasers, near-IR photodetectors, and highly efficient concentrator solar cells. However, owing to the high refractive index (RI) of GaAs ($n_{GaAs} = 3.6$ for visible wavelengths), more than 30% of incident light is reflected back from the substrate surface. This greatly reduces the efficiency of GaAs-based optoelectronic devices. To suppress the unwanted reflective losses, vacuum-deposited multilayer dielectric (e.g., MgF$_2$/ZnS) are used as antireflection coatings (ARCs). Unfortunately, these multilayer ARCs are expensive to fabricate owing to the stringent requirement of high vacuum, material selection, and layer thickness control. Additionally, thermal-mismatch-induced lamination and material diffusion of the multilayer ARCs limit the device performance at high power densities.

Inspired by the broadband antireflection of microstructured corneas of moths, which consist of non-close-packed arrays of sub-300 nm nipples, subwavelength antireflective structures have been extensively exploited. These structures can reduce reflection over a wider range of wavelengths and exhibit much improved thermal stability than conventional multilayer ARCs. However, scalable production of subwavelength ARCs is not a trivial task for the current top-down nanolithography technologies (e.g., electron-beam lithography and interference lithography). Bottom-up colloidal lithography, which uses self-assembled colloidal crystals as
deposition or etching masks to pattern periodic nanostructures\textsuperscript{85,89} provides a much simpler and inexpensive alternative to nanolithography in creating subwavelength gratings.\textsuperscript{64,125} Unfortunately, traditional colloidal assemblies suffer from low throughput, small areas, incompatibility with standard microfabrication, and limited close-packed crystal structures have been developed.

Significant obstacles have been encountered when we employ this nonlithographic spin coat technique to GaAs substrates. Only disordered colloidal monolayer can be assembled on GaAs by spin coating. This greatly reduces the uniformity and reproducibility of the antireflective performance of templated ARCs. We use a generalized single layer reduction (SLD) technique that enables reproducible production of monolayer colloidal crystals on a variety of substrates that otherwise lead to the formation of disordered crystals by the traditional spin-coating approach. We also demonstrate the scalable production of broadband ARCs on crystalline GaAs substrates, and their antireflective properties are characterized by both experimental measurements and theoretical simulation.

**Experimental procedure.** Figure 3-17A shows a typical scanning electron microscope (SEM) image of a colloidal monolayer consisting of 320 nm silica spheres prepared on a crystalline GaAs substrate (N-type, (100), University Wafer) by the standard spin-coating process. The particles are completely disordered as confirmed by the rings in the Fourier transform of the SEM image. Contrary to the direct formation of colloidal monolayer by spin coating, where the substrate plays a crucial role in determining the resulting crystalline quality, double-layer colloidal crystals are firstly assembled in SLD. Figure 3-17B shows a double-layer colloidal crystal prepared by spin
coating colloidal silica suspensions (20 vol. % in nonvolatile ethoxylated trimethylolpropane triacrylate monomer) at 8000 rpm for 90 s. The non-close-packed hexagonal arrangement for both the top- and bottom-layer particles is clearly evident. After removing the top-layer particles by sweeping using a clean room Q-tip under flowing water, crystalline colloidal monolayer with non-close-packed structure are formed as shown in Figure 3-17C. The distinctive six-arm Bragg diffraction star formed on the 2 in. (~5.08 cm) GaAs wafer (inset of Figure 3-17C) indicates the hexagonal ordering is over the whole wafer surface. The interparticle distance of the non-close-packed colloidal crystal 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 3-17D), $g(r)$, which is calculated as $g(r) = 1/\langle \rho \rangle dn(r, r + dr)/da(r, r + dr)$, where $dn$ counts the number of spheres that lie within a spherical shell, $dr$, of radius $r$ from an arbitrary origin; $da = 2\pi r dr$ for a particular radial distance $r$; and $\langle \rho \rangle$ is the average particle number density. Figure 3-17D also shows the positions of the oscillating PCF peaks agree well with those obtained from a perfect hexagonal lattice with $\sqrt{2}D$ interparticle distance. Preliminary results show the SLD technology can be easily and reproducibly applied to other important substrates, such as Ni, Cr, glass, and poly(methyl methacrylate). Only disordered monolayer is formed on these substrates by the traditional spin-coating technique.

The periodically arranged silica particles can then be used as etching masks during a BCl$_3$ reactive ion etch (RIE) process operating at 7.5 mTorr chamber pressure, 20 SCCM BCl$_3$, RIE=100 W, and inductively coupled plasma ICP=300 W on a Unaxis Shuttlelock reactive ion etcher to generate arrays of cone shaped nanopillars. Figure 3-
18A and B show the templated GaAs structures after 9.5 min RIE and removing templating silica particles by a 2% hydrofluoric acid wash. Interestingly, we observe the formation of mushroom-like microstructures. The “stems” of the mushrooms are cone-shaped and are caused by the isotropic etching of GaAs by reactive chlorine ions. The polymer wetting layer between the templating silica spheres and the substrate, which protects the GaAs surface immediately under the particles from being etched, causes the formation of the flat “caps” of the mushrooms. This unusual microstructure has been used to develop superoleophobic surface though it is not easily available by conventional top-down and bottom-up techniques. Longer dry etching leads to sharper conical stems and smaller caps as revealed by the SEM image of a 12 min etched sample in Figure 3-18C. The residual caps can finally be removed by a brief ultrasonication in acetone, resulting in the formation of conical GaAs gratings as shown in Figure 3-18D. The preservation of the long-range hexagonal ordering and the interparticle distance of the original silica colloidal monolayer throughout the templating process are clearly evident by comparing the SEM images of Figures 3-17 and 3-18. The specular reflectivity of the templated subwavelength gratings are evaluated using visible and near-IR reflectivity measurement at normal incidence by using an Ocean Optics HR4000 spectrometer. The solid curves in Figure 3-19 show the measured reflection from a bare GaAs wafer and the nanocone grating as shown in Figure 3-18D. The wafer exhibits >30% reflectivity, while much reduced reflection (~3%) is obtained for the templated subwavelength grating. Importantly, the resulting moth-eye ARCs on GaAs are broadband, exhibiting consistent low reflection over both visible and near-IR wavelengths.
Results and discussion. The optical measurement is complemented by theoretical simulation using a rigorous coupled-wave analysis (RCWA) model\textsuperscript{106}. A conical profile is used to simulate the templated nipples as shown in Figure 3-18D. We divide the cone array into 100 horizontal circular layers. The intercone distance is defined as 2D by the PCF calculation shown in Figure 3-17D. We can calculate the fraction of GaAs in each layer as \( f(z^*) = \frac{\pi r^*^2}{\sqrt{3}D^2} \) where \( z^* \) and \( r^* \) are the \( z \) coordinate and the bottom radius of the cone, respectively. Based on the effective medium theory, the effective RI \( n(z^*) \) of the layer at height \( z^* \) can be approximated by \( n(z^*) = [f(z^*)N_{\text{GaAs}}^q + (1 - f(z^*))n_{\text{air}}^q]^{1/q} \), where \( q=2/3 \).\textsuperscript{69,123} We can then calculate the total reflectance of the layered system by solving Maxwell’s equation to express the electromagnetic (EM) field in each layer and matching EM boundary conditions between neighboring layers. The complex RI of GaAs is used to calculate the resulting reflectance.\textsuperscript{127}

The curves with circles in Figure 3-19 show the simulated reflection from a flat GaAs wafer and an array of conical nipples templated from 320 nm silica spheres. The calculated spectrum for the featureless substrate has the same shape as the experimental result. The simulated reflection from the subwavelength nanocone array also agrees reasonably well with the experimental spectrum. The excellent broadband antireflection properties of the templated conical gratings can be understood by mapping the calculated effective RI at \( \lambda=700 \) nm across the height of 320 nm conical nipples (Figure 3-20). For bare wafer, the RI changes sharply from air (RI=1.0) to bulk GaAs (RI=3.772), while for templated nipples, the RI changes gradually from 1.0 to 3.41 and then to 3.772. As the reflection \( (R) \) from an interface between two materials with RI
of $n_1$ and $n_2$ is governed by Fresnel's equation $R = \left(\frac{n_1-n_2}{n_1+n_2}\right)^2$, the RI gradient exhibited by the conical nipples thus leads to very low reflection over a wide range of wavelengths. The technique is scalable and compatible with standard microfabrication, promising for developing more economic, efficient, and reliable GaAs-based optoelectronic devices.

Figure 3-1. Schematic illustration of the templating procedure from making moth eye antireflection coatings.
Figure 3-2. AFM images and corresponding depth profiles of replicated nipple arrays at different RIE etching times. A) 0 s. B) 20 s. C) 45 s. 360 nm diameter silica spheres are used as templates.

Figure 3-3. Experimental (solid) and calculated (dotted) specular optical reflectivity at normal incidence. Black: flat PETPTA. Light gray: 20 s RIE etch, 110 nm spherical cap. Dark gray: 45 s RIE etch, 180 nm hemispherical cap.
Figure 3-4. Dependence of the normal-incidence optical reflectivity at 600nm vs. RIE etching time performed on spin-coating colloidal crystal-polymer nanocomposite.

Figure 3-5. Comparison of the change of calculated effective refractive index from the nipple peaks (n_{eff}=n_{air}=1) to the nipple troughs (n_{eff}=n_{PETPTA}=1.46) between hemispherical (unfilled circle) and 50nm height spherical cap (cross) nipple arrays. The diameter of colloidal particles is 360nm.
Figure 3-6. SEM images illustrating the progressive fabrications procedures for binary dimple-nipple antireflection coatings: A) top-view image of a double-layer colloidal crystal template consisting of 340nm silica spheres, B) top-view image after removing silica spheres by wet etch, C) side-view image of the sample in panel B and D) replicated ETPTA binary array from the sample in panel B.

Figure 3-7. Experimental (solid) and RCWA-simulated (dotted) normal incidence specular reflection from a bare glass substrate (black), a glass slide covered with a templated ETPTA binary dimple-nipple array (red), and a glass slide coated with an ETPTA unitary hemispherical nipple array (blue).
Figure 3-8. Schematic illustration of the templating procedures for fabricating subwavelength-structured antireflection pyramid gratings on single-crystalline silicon.

Figure 3-9. 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 3-10. 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 3-11. 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 3-12. RCWA-simulated normal-incidence optical reflection at \(\lambda=600\) nm vs. inverted pyramid size. The 320 nm silica spheres are used as templates.

Figure 3-13. Schematic illustration of the templating procedures for fabrication moth-eye ARCs on silicon substrates.
Figure 3-14. SEM images of biomimetic antireflection coatings on silicon substrates. A) SEM images of a spin-coated monolayer non-close-packed colloidal crystal consisting of 360nm silica spheres. B) Tilted (20°) SEM image showing templating silica array and underneath silicon nipples etched by SF$_6$ RIE for 9min. C) Templated silicon nipple array after 6min of SF$_6$ etch. D) Silicon nipples after 9min SF$_6$ etch.

Figure 3-15. Experimental (solid) and RCWA-simulated (dotted) specular optical reflection at normal incidence for a flat silicon substrate (black lines), a commercial multicrystalline silicon solar cell (blue lines), and a 15-min etched nipple array (red lines).
Figure 3-16. Comparison between the calculated optical reflection at normal incidence by the RCWA model (red) and the thin-film multilayer model (blue) for an array of nipples with 210 nm base radius and 800 nm height.

Figure 3-17. SEM images of silica nanoparticles on GaAs. A) Disordered colloidal monolayer formed on GaAs by traditional spin coating. Inset, Fourier transform of the image. B) Double-layer colloidal crystals formed on GaAs. C) Monolayer colloidal crystal formed by SLD. Inset, photograph of a monolayer crystal formed on a 2 in. GaAs wafer illuminated with white light. D) Pair correlation function calculated from a low-magnification SEM image. For comparison, the PCF for an ideal hexagonal lattice with 2D interparticle distance is also shown (black lines).
Figure 3-18. SEM images of templated nanacones on GaAs substrates. A) Templated mushroom-like GaAs microstructures after 9.5 min BCl$_3$ RIE. B) Higher magnification image of A. C) Conical nipples formed after 12 min BCl$_3$ RIE. D) Same sample as C after a brief ultrasonication in acetone.

Figure 3-19. Experimental and RCWA-simulated specular reflection at normal incidence from a bare GaAs wafer and the conical grating as shown in Figure 3-18D.
Figure 3-20. Change of the calculated effective refractive index at $\lambda=700$ nm from the wafer surface (depth=0) to the bottom of templated GaAs nanocones with 320 nm height. The dotted line indicates the refractive index of bulk GaAs at the same wavelength.
CHAPTER 4
TEMPLATED FABRICATION OF SERS-ACTIVE SUBSTRATES

4.1 Templated Fabrication of Periodic Metallic Nanopyramid Arrays

Metallic substrates with periodic subwavelength structures exhibit unique surface plasmon properties that are of great scientific interest and considerable technological importance in developing nanophotonic devices, data storage, and biosensors. Metallic nanotips are particularly interesting as surface-enhanced Raman scattering (SERS) substrates because they can concentrate the electromagnetic field at the tip apex, resulting in a great enhancement of the Raman scattering intensity from molecules in the vicinity of the nanoscopic tips. Scanning probe microscopy (SPM) tips coated with noble metals (e.g., Au and Ag) have been shown to enhance Raman scattering by 3-6 orders of magnitude. The Raman enhancement factor of gold nanocrescent moons with sub-10 nm sharp edges, which are templated from sacrificial microspheres, is estimated to be larger than $1 \times 10^{10}$, making them promising for ultrasensitive biosensors. Other asymmetric metallic nanostructures, such as half shells, nanocups, nanoprisms, and nanorings, have also been developed for potential SERS applications. Unfortunately, precise control over the position, orientation, and spacing of these aspheric nanomaterials is not trivial and impedes the experimental reproducibility of SERS sensing.

Planar nanotip arrays with high tip density and aligned tip orientation are promising SERS substrates that could resolve the reproducibility issue of current tip-enhanced Raman spectroscopy. Electron-beam lithography (EBL) and focused ion-beam (FIB) lithography are two popular technologies used to create periodic metallic nanostructures with arbitrary patterns. Unfortunately, the high-cost and the low-throughput greatly
limit the implementation of these advanced lithographic techniques in practical application. Templated synthesis provides a much cheaper, simpler, and faster alternative to complex nanolithography in creating periodic metallic nanostructures. Examples include an array of metallic pyramids with nanoscale tips made by templated deposition of metals on anisotropically etched silicon pits, which are defined by phase-shifting photolithography and an array of submicrometer-scale particles with uniform periodic spacing and nearly uniform size and crystallographic orientations prepared by solid-state dewetting of gold thin films on oxidized silicon surfaces patterned with pyramidal pits by interference lithography. Other templates, such as block-copolymers, colloids, and even biological materials, have also been utilized in fabricating periodic metallic nanostructures with length scales ranging from nanometer to micrometer. However, most of these templating approaches either still require some sort of lithographic patterning or are not compatible with standard microfabrication, thereby impeding the cost-efficiency and scale-up of these unconventional methodologies.

We use metallic nanohole arrays templated from spin-coated two dimensional colloidal crystals to develop a new templating technique for fabricating wafer-scale, periodic metallic pyramid arrays with nanoscale tips and high tip density. Anisotropic KOH wet etching is utilized to transfer the periodic circular nanoholes into inverted pyramid arrays in (100) silicon wafers. These inverted pyramids can then be used as third-generation templates for replicating large-area metallic nanopyramid arrays by simple physical vapor deposition and adhesive peeling. This new nanofabrication approach is based solely on self-assembly and templated fabrication and no
lithographic patterning is involved in any step. Yet this technology is still scalable and compatible with standard microfabrication, enabling large-scale production of metallic nanostructures for potential SERS applications.

4.2.1 Experimental Procedure

The fabrication of wafer-scale, monolayer and non-close-packed colloidal crystal polymer nanocomposites is performed according to Chapter 2. In short, monodispersed silica colloids are dispersed in ETPTA to make final particle volume fraction of ~20%; 2 wt % Darocur 1173 is added as photoinitiator. The silica-ETPTA dispersion is dispensed on a 3-acryloxypropyl trichlorosilane (APTCS)-primed (100) silicon wafer and spin-coated at 8000 rpm for 6 min on a standard spin coater, yielding a hexagonally ordered colloidal monolayer. The monomer is then photopolymerized for 4 s using a Pulsed UV Curing System. The polymer matrix is fully removed using a reactive ion etcher operating at 40 mTorr oxygen pressure, 40 SCCM flow rate, and 100 W for 4 min. A 30 nm mask of chromium is deposited on the wafer using sputtering deposition at a deposition rate of 1.6 Å/s. The wafer is then rinsed in deionized water and rubbed with a cleanroom Q-tip to remove templating silica microspheres. Templating silica particles can also be removed by dissolving them in a 2 vol % hydrofluoric acid aqueous solution for 2-3 min. The removal of the particles creates a visible color change. The (100) silicon wafer covered by arrays of chromium nanoholes is then wet etched in a freshly prepared solution of 62.5 g KOH, 50 mL of anhydrous 2-propanol, and 200 mL of ultrapure water at 60 °C for various durations. The wafer is rinsed with deionized water and then wet etched with a chromium etchant (type 1020, Transene) to remove the chromium template. The etched wafers show iridescence under white light illumination. To create a nanopyramid array in gold, we sputtered the wafer with 500 nm of gold at a
deposition rate of \( \sim 5 \text{ Å/s} \). The layer of gold on the surface of the wafer can be easily peeled off with Scotch tape (3M), yielding a non-close-packed nanoparticle array in gold. To separate the metallic nanoparticle arrays from the silicon templates in a more reliable and reproducible way, we applied a thin layer of polyurethane adhesive (NOA 60, Norland Products) between the metalized wafer and a glass substrate. The adhesive is then polymerized by exposure to ultraviolet radiation. The silicon wafer templates can finally be peeled off, resulting in the formation of wafer-scale nanoparticle arrays supported on glass substrates.

Gold nanoparticle array samples are placed in a 5 mM solution of benzenethiol and 200 proof ethanol for 45 min and then rinsed in roughly 25 mL of 200 proof ethanol for several minutes. The samples are allowed to dry in air for 20 min, after which the Raman spectra are measured. A flat gold film sputtering-deposited on a glass slide using the same deposition condition is used as the control sample for Raman spectra measurements. Raman spectra are measured with a Renishaw inVia confocal Raman microscope using a 785 nm diode laser at 15 mW with an integration time of 10 s and a 40 \( \mu \text{m}^2 \) spot size.

4.2.2 Results and Discussion

In contrast with previous lithographic approaches to fabricating nanoparticle arrays,\textsuperscript{132,140} our method is simply based on colloidal self-assembly and templated synthesis. A schematic outline of the fabrication procedures is shown in Figure 4-1. We start from spin-coating concentrated silica-ETPTA monomer dispersions using a standard spin-coater. Wafer-scale, monolayer, hexagonally ordered colloidal arrays can be reproducibly made in minutes by controlling the spin speed and time. Following a
rapid photopolymerization of ETPTA monomer to immobilize silica particles, the polymer matrix are removed by a brief oxygen plasma etch. The resulting colloidal monolayer exhibits non-close-packed arrangement of particles with interparticle distance of ~1.4D, where D is the diameter of the silica spheres (see Figure 4-2A). Using this simple spin-coating method, silica particles with a wide range of sizes from ~100 nm to larger than 1 \( \mu \)m have been assembled into monolayer crystals. Manipulation of silica particle size enables control of the size and separation of nanopyramids in the templated arrays.

These shear-aligned, non-close-packed silica particles can then be utilized as deposition masks during conventional physical vapor deposition (e.g., sputtering, thermal evaporation, or electron-beam evaporation). The deposited metals, such as Cr or Ti/Au, fill the interstitials between silica spheres and accumulate on the top halves of particles as well. Because silica particles are loosely attached to the substrate, they can be easily removed by gentle rubbing with a cleanroom swab, leaving behind a metallic nanohole arrays as shown by the SEM image in Figure 4-2B. Templating silica spheres can also be removed by dissolving in a 2% hydrofluoric acid aqueous solution to lift off metals. We found that a thin layer of chromium (20-30 nm) is sufficient to sustain the KOH wet etching in the following step. These circular nanoholes retain the size and spacing of the templating silica spheres as well as their hexagonal long-range ordering. Under white light illumination, these templated nanohole arrays function as diffraction gratings, exhibiting strong iridescence. Shape and edge roughness of the templated nanoholes determine the qualities of the resulting inverted pyramids in silicon, thus precautions need to be taken to ensure circular shapes and smooth edges of the metallic nanoholes. Slower PVD deposition rate helps to reduce the grain size and the
roughness of edges, whereas thermal or EB evaporation, which is more unidirectional in deposition, is better than sputtering in maintaining the circular shapes of nanoholes.\textsuperscript{45}

We then use templated chromium nanohole arrays as second-generation etching masks to create inverted pyramid arrays in (100) silicon wafers through anisotropic etching in an aqueous solution containing KOH and 2-propanol. It is well-known that KOH is a wet etchant that attacks silicon preferentially in the <100> plane, producing characteristic anisotropic V-shape pitches with 54.7° sidewalls.\textsuperscript{45} Images A and B in Figure 4-3 show SEM images of pyramidal pits that are templated from 320 nm silica spheres and etched at 60 °C for 120 and 420 s, respectively. The long-range hexagonal ordering of these pits is obvious from the SEM images and is further confirmed by the hexagonally arranged dots in the fast Fourier transform (FFT) of these images (insets of images A and B in Figure 4-3). Another interesting feature of the calculated FFTs is the two sets of four-arm stars with exact 90° angles between neighboring arms surrounding the central dots, characteristic of square pyramidal pits. The orthogonal crosses at the centers of the pits also verify the inverted pyramidal structures. The spacing between neighboring pits is the same as that of the original non-close-packed colloidal arrays (Figure 4-2A), whereas the pit size (252 ± 28 nm) for the 120 s sample is smaller than the size of the nanoholes (~320 nm). This indicates that the etching reaction starts from the center of the nanoholes and then propagates to the edges; otherwise, the spacing between neighboring nanoholes could not be retained in the templated pyramidal pits.

For longer etching duration, undercutting of silicon underneath the chromium nanoholes occurs. This leads to larger inverted pyramids (Figure 4-3B) with well-defined square bases. For shorter etching time (Figure 4-3A), the corners of the square bases
are not as sharp as those of over etched ones. We also notice that there are some rectangular shaped pyramids in the anisotropic etched samples that are replicated from noncircular (e.g., oblate) nanoholes. The size and depth of the inverted pyramidal pits can be easily controlled by adjusting the wet etching duration. Figure 4-3C shows the dependence of the size of the pyramids vs. different etching time at 60 °C. More than 100 pyramids are measured using SEM to arrive at the reported size and size distribution of each sample. If we rise the reaction temperature to 80 °C, which is commonly used in anisotropic etching of silicon for micromachining, the etching reaction becomes so vigorous that the precise control over the dimensions of the pyramids is more difficult.

For certain KOH etched samples, we find unwanted particle precipitation on the surface of the silicon wafer as well as in the pyramidal pits. Figure 4-4 shows a typical SEM image of such particles precipitated on an anisotropically etched n-type silicon wafer. Though these particles are sparsely distributed on the wafer surface, they affect the uniformity of the resulting gold nanopyramid arrays by creating random defects in the pyramids. Previous study shows that these particles are iron oxide precipitated from the reaction of iron impurities in KOH pellets with hydroxide ions. A brief etching (1 min) in 2 M HCl aqueous solution at room temperature can easily remove these unwanted particles.

We then use the inverted silicon pyramids as the third generation templates to replicate metallic nanopyramid arrays. Conventional PVD deposition is carried out to deposit various metals in the silicon pits and form continuous metal films on the surface of the silicon wafer. For metals with weak adhesion to silicon, such as Au, Ag, Pt, and
Pd, the deposited films can be adhered onto a glass substrate using a thin layer of polyurethane adhesive, followed by peeling off the silicon templates. The resulting wafer-scale nanop pyramid arrays exhibit striking diffractive colors and a characteristic six-arm diffractive star (Figure 4-5A). The adjacent arms of the diffraction star form exact 60° angles, a result indicating the formation of long-range hexagonal ordering.\textsuperscript{8,49} Figure 4-5B shows a typical top-view SEM image of a replicated Au nanop pyramid array. The hexagonal ordering of nanop pyramids is clearly evident from the image. However, the periodic nanop pyramids are polycrystalline, as is clear from the SEM images. The typical domain size is several hundred micrometers, limited by the single-crystal domain sizes of the original spin-coated monolayer colloidal crystal. Our previous results show that spin-coated monolayer crystals have much smaller single-crystal domains than multilayer crystals made by the same spin-coating process. The gold pyramids are faithful replica of the original inverted silicon templates, indicating that no breaking of sharp tips occurred during the film peeling off procedure. Most of the pyramids have sub-10 nm sharp tips revealed by the magnified SEM image shown in the insets of images B and C in Figure 4-5 and the side-view SEM image in Figure 4-5C. The spacing between neighboring nanop pyramids measured using SEM is the same as the original non-close-packed colloidal arrays. By a simple geometrical calculation, we estimate the nanotip density is about 6x10\textsuperscript{8} tips cm\textsuperscript{-2} for 300 nm templating silica spheres. For metals with strong adhesion to silicon, such as Cr, Ni, and Al, the surface of silicon pits can be modified by octadecyl silane (ODS) to reduce the metal adhesion and facilitate the film peeling,\textsuperscript{149} or a thin film of Au can be predeposited as a sacrificial layer before the deposition of adhesive metals. KOH/IPA wet etching can also be used
to dissolve the silicon templates to release the metallic nanopyramid arrays provided the metals can survive the chemical etching.\textsuperscript{141}

We evaluate the performance of our gold nanopyramid arrays as SERS substrates using benzenethiol as a model compound (Figure 4-6). In addition to the excellent affinity to gold surfaces, benzenethiol molecules have a large Raman cross-section, presumably as a result of chemical enhancement alongside electromagnetic enhancement.\textsuperscript{128} The templated gold nanopyramid array sample (red curve) gives a strong Raman signal of adsorbed benzenethiol molecules. The positions of Raman peaks agree well with those in the literature for benzenethiol on gold substrates.\textsuperscript{128,150-151} In control experiments, no SERS spectra are observed for benzenethiol molecules adsorbed on the flat sputtered gold films deposited under the same conditions on glass substrates (blue curve). The SERS enhancement factor for the gold nanopyramid substrate is estimated to be $\sim 7 \times 10^5$ using the method described in the literature by comparing the Raman intensity for two peaks at 1080 and 1581 cm$^{-1}$.\textsuperscript{150-151} Previous results show that the greatest SERS enhancements occur when localized plasmon resonances on the structured metallic surfaces are present at both the excitation wavelength and Raman scattered wavelength.\textsuperscript{151} Here the structural parameters of the gold nanopyramid arrays (e.g., pyramid size, separation, and height), which greatly affect the plasmon resonances, have not been optimized yet. We believe the SERS enhancement factor of our periodic substrates can be further improved by tailoring the structures of the templated nanopyramid arrays to match the optimal SERS requirements.
4.2 Wafer-Scale SERS Substrates with Highly Reproducible Enhancement

Using spin-coated monolayer colloidal crystals as templates, we have fabricated periodic gold nanopyramid arrays with nanoscale sharp tips. They have also been demonstrated as SERS-active substrates with a high enhancement factor (up to $10^8$). However, the fabrication process involves multiple steps (e.g., metal deposition, mask liftoff, and KOH anisotropic etch), and each step could introduce some defects and uncertainties. The accumulation of defects results in poor reproducibility and large variation (>100%) in SERS enhancement over wafer-scale areas. Here, we report a much simpler templating technology that only requires a single metal deposition step for creating SERS substrates with high reproducibility over large areas. The new methodology leverages the high uniformity of the spin-coated colloidal arrays and well-established physical vapor deposition techniques.

4.2.1 Experimental Procedure

The fabrication of wafer-scale, non-close-packed silica colloidal crystal-polymer nanocomposite is performed by following the established spin-coating procedures. In short, Stöber silica colloids are first dispersed in an ETPTA monomer (with 2 wt % Darocur 1173 photoinitiator) to make a final particle volume fraction of 20%. The colloidal suspension is disposed on an APTCS-primed silicon wafer and spin-coated at 300 rpm for 1 min, 800 rpm for 1 min, 1500 rpm for 20 s, 3000 rpm for 20 s, and 7000 rpm for 2 min. The ETPTA monomer is rapidly polymerized for 12 s by using a pulsed UV curing system. Two nanometer chromium and 18 nm gold are finally deposited on the surface of the colloidal crystal-polymer nanocomposite by electron beam evaporation at a typical deposition rate of 0.1 nm/s from graphite crucibles at $2.5 \times 10^{-6}$ mbar.
A calibrated halogen light source is used to illuminate the sample for reflection measurement. The beam spot size is about 3 mm on the sample surface. Measurements are performed at normal incidence, and the cone angle of collection is less than 5°. Absolute reflectivity is obtained as a ratio of the sample spectrum and reference spectrum. The reference spectrum is the optical density obtained from an aluminum-sputtered (1000 nm thickness) silicon wafer.

The gold-coated nanocomposite is immersed in a 5 mM solution of benzenethiol in 200 proof ethanol for 2 days and then dried in air for 20 min. Raman spectra are obtained using a 50X objective and a 785nm diode laser at 0.5 mW with an integration time of 10 s and a 40 μm² spot size.

In the finite-element method (FEM) model, we suppose that the gold coated nanocomposite is placed horizontally, so that the interface between the substrate and the medium (air) is parallel to the \(xz\) plane while the hemispherical protrusions are along the \(y\) axis. The total electromagnetic fields \(E = E_{\text{inc}} + E_{\text{scatter}}\) and \(H = H_{\text{inc}} + H_{\text{scatter}}\) should satisfy Maxwell’s equations within medium and scatter (gold) domains:

\[
\nabla \times (\nabla \times E) - \omega^2 \varepsilon \mu E = 0 \\
\nabla \times (\nabla \times H) - \omega^2 \varepsilon \mu H = 0
\]

where \(\varepsilon\) and \(\mu\) are domain-dependent permittivity and permeability, respectively, and \(\omega\) is the light frequency. Continuity of tangential components of \(E\) and \(H\) across the interface between air and gold leads to the following boundary conditions with \(n\) as the interfacial normal vector:

\[
(E_1 - E_2) \times n = 0 \\
(H_1 - H_2) \times n = 0
\]
We then employ FEM under Comsol Multiphysics environment to solve eqs 1 and 2 for each substance (air and gold). Ten boundary layers around the medium and scatter domains are artificially constructed first. The “perfect matched layers” (PML) boundary approach is then used to define the boundary conditions for the bounded domains in order to obtain high resolution numerical solutions. The electronic and magnetic conductivity of each boundary layer can be set artificially so that little or no electromagnetic radiation will be reflected back into the domain of scatter. To simulate electromagnetic fields in the newly augmented domains, we solved Maxwell eq 1 in all subdomains. The boundary condition (eq 2) still holds for all internal interfaces. As to the outer boundaries of the PML layers, a low-reflection boundary condition (eq 3) is used to minimize residual reflection and attenuate the wave quickly within the layers

\[ n \times (\nabla \times H_z) - j \omega H_z = 0 \]  

(3)

After solving Maxwell eq 1 together with boundary conditions (eqs 2 and 3), the two-dimensional electric field can be used to calculate the order of magnitude of the Raman enhancement factor \([\log G(x, y)]\) as

\[ G(x, y) = \log \left( \left| \frac{E(x, y)}{E_0} \right|^4 \right) \]

where \(E(x, y)\) and \(E_0\) are the electric field amplitude at location \((x, y)\) and the incident field, respectively.

**4.2.2 Results and Discussion**

Contrary to traditional colloidal self-assembly technologies, which usually take days or even weeks to assemble centimeter-sized colloidal crystals as templates for making SERS substrates, the spin-coating technology is rapid and scalable. We have demonstrated that wafer-sized (up to 8 in. diameter) colloidal crystals can be fabricated
in minutes. In this methodology, monodispersed silica particles with diameter ranging from tens of nanometers to several micrometers are dispersed in a nonvolatile ETPTA monomer and then shear aligned to form highly ordered colloidal crystals by using standard spin-coating equipment. After photopolymerization of ETPTA monomers, the colloidal arrays are embedded in a polymer matrix, and the spheres of the top layer protrude out of the film, forming a periodic surface. The resulting colloidal crystal-polymer nanocomposites exhibit highly uniform thickness and remarkably large single-crystalline domain size over the whole wafer area. Another unique property of the shear-aligned colloidal crystal is the unusual non-closed-packed structure. The interparticle distance between neighboring colloids is fixed at $\sim 1.4$ times of the particle diameter.

The SERS-active substrate is fabricated by subsequent deposition of a 2 nm layer of chromium and an 18 nm layer of gold on the spin-coated nanocomposite by electron beam evaporation. Figure 4-7 shows a photograph of a metalized nanocomposite consisting of 320 nm silica spheres on a 4 in. silicon wafer illuminated with white light. The nanocomposite film is prepared by spin-coating a colloidal suspension at 7000 rpm for 2 min, having a thickness of 3 monolayers. The metalized sample exhibits a brilliant six arm diffraction star with exact 60° angles between neighboring arms. This pattern is caused by Bragg diffraction of visible light by the hexagonally ordered colloidal arrays. Some defects (e.g., comets) caused by large airborne solid particles are apparent on the wafer. Many of these defects can be avoided by conducting spin-coating in a cleanroom.
Long-range hexagonal ordering and non-closed-packing of the metalized colloidal crystal are evident in the typical top-view SEM image as shown in Figure 4-8A. Extensive SEM examination reveals that periodic colloidal arrays with similar crystalline structure and quality uniformly cover the whole wafer surface. Interestingly, the magnified SEM image in Figure 4-8B illustrates that the gold coating on the nanocomposite is rough and gold islands of tens-of-nanometer-scale size and sub-10 nm gaps are clearly evident. The side-view SEM image in Figure 4-8C further confirms the granular microstructure of the deposited gold layer, and the protrusion depths of the spheres are measured to be ~80 nm.

Although island-type and discontinuous gold and silver films have been extensively studied for a wide range of applications such as molecular electronics and SERS,\textsuperscript{157-162} the formation of gold islands on the colloidal crystal-polymer nanocomposite is still somewhat unusual. As demonstrated in early studies, only when the metal film is thin (<10 nm nominal thickness for gold and <20 nm nominal thickness for silver), the surface condensation and nucleation of evaporated metal can induce the formation of island-type films.\textsuperscript{159,161} However, the thickness of the evaporated gold on the spin-coated nanocomposite is 18 nm, which is above the threshold for the formation of discontinuous films.\textsuperscript{163} Control experiments show that evaporated gold of similar thickness forms continuous films on flat glass substrates. It is known that a thin (~80 nm) polymer wetting layer uniformly covers the protruded spheres of the spin-coated nanocomposite. To evaluate the effect of this polymer layer on the formation of gold islands, we selectively remove the polymer layer on the protruded silica spheres by a brief oxygen plasma etch (40 mTorr oxygen pressure, 40 SCCM flow rate, and 100 W
for 15, 30, and 45 s) and then deposit chromium and gold with similar thicknesses as the nanocomposite sample. AFM images show that the resulting metal films are continuous and smooth. This indicates that the polymer wetting layer plays a crucial role in the formation of gold islands during the evaporation of a metal film.

We have also compared the AFM images and corresponding depth profiles of the metalized nanocomposite and the same sample after wet-etching the gold and chromium layers in Figure 4-9. The metalized sample exhibits a rough and granular surface, and the root mean squared surface roughness ($R_{\text{rms}}$) is measured to be 3.\textsuperscript{162} After removing the metal coating, the nanocomposite surface is smooth and the roughness is reduced to 1.05, which is almost identical to that of a newly spin-coated sample. This suggests that the formation of gold islands is not because of the surface buckling of the polymer nanocomposite caused by the deposition of metals. The depth profiles in panels B and D of Figure 4-9 show that the protrusion depths of the silica spheres retain after metal evaporation, indicating conformal deposition of metals on the surface of the nanocomposite. Although the underlying mechanism for the formation of gold islands during evaporation of relatively thick metals has yet to be fully understood and is still under investigation, the creation of discontinuous metal films with periodic microstructures over wafer-scale areas could find important technological applications in nanoelectronics, electromechanical devices (e.g., strain gauge), and biosensors.\textsuperscript{157-159} We focus on the application of these structured metal films as reproducible SERS substrates. Figure 4-10 compares the SER spectra of benzenethiol molecules adsorbed on a continuous gold control sample and an 18 nm gold-coated nanocomposite consisting of 400 nm silica spheres. Benzenethiol is chosen as the model molecule
because of its ability to assemble into dense monolayer on gold and its large Raman cross section. Because of its ability to assemble into dense monolayer on gold and its large Raman cross section, the periodic, island-type gold film shows strong and distinctive SERS peaks, whose positions and relative amplitude match with those in the literature for benzenethiol molecules adsorbed on structured gold surfaces, while the flat gold control sample does not display clear SERS signal. The assignment of the SERS peaks to different vibrational modes is shown in Table 4-1. The SERS enhancement factor, $G$, is calculated using the method described in the literature by comparing the Raman intensity (after baseline subtraction) for various vibrational peaks obtained for a pure benzenethiol liquid ($I_{bulk}$) and at the metalized nanocomposite surface ($I_{surf}$) as:

$$G = \frac{C_\infty N_A \sigma h I_{surf}}{R I_{bulk}}$$

where $C_\infty$ is 9.8 M, $N_A$ is Avogadro’s number, $\sigma$ is the gold surface area covered by benzenethiol molecules (0.45 nmol cm$^{-2}$), $h$ is the confocal length of the spectrometer ($\sim$88 μm determined for the 50X objective used in the experiment), and $R$ is the surface roughness ($\sim$3.5 measured by AFM).

We have systematically investigated the reproducibility of SERS enhancement over 4 in. diameter samples consisting of 320 and 400 nm silica spheres. Four concentric rings with radii of 0.5, 1.6, 2.7, and 3.8 cm separate the 4 in. wafers into five regions designated as R0, R1, R2, R3, and R4, respectively. In each region, we have randomly obtained at least 10 SER spectra, and the average Raman counts and corresponding standard deviation for different SERS peaks are listed in Table 1. From the Table 4-1, it is evident that the SERS enhancement is reproducible from place to place within each region. We have also calculated the standard deviation of the averaged Raman counts for each vibrational mode across the 4 in. wafer. The results
are 19.4% (1575 cm⁻¹), 16.2% (1074 cm⁻¹), 14.2% (1023 cm⁻¹), 22.0% (1000 cm⁻¹),
13.8% (695 cm⁻¹), and 15.5% (419 cm⁻¹) for the 320 nm sample and 22.1% (1575 cm⁻¹),
20.9% (1074 cm⁻¹), 25.9% (1023 cm⁻¹), 23.0% (1000 cm⁻¹), 24.7% (695 cm⁻¹), and
27.6% (419 cm⁻¹) for the 400 nm sample. We therefore conclude that the templated
substrates exhibit high SERS reproducibility with less than 28% standard deviation over
a 4 in. wafer surface.

From the SERS measurements, we have also found that the peak position for any
specific vibrational mode is almost identical with less than 1 nm variation from place to
place on the 320 and 400 nm samples. Therefore, we arithmetically average the SER
spectra from the five regions of the two 4 in. samples and show the results in Figure 4-
11. We have also calculated the SERS enhancement factors using the averaged
Raman intensity for different peaks, and the results are listed in Table 4-2. Because of a
high scattering background for pure benzenethiol, the peaks at 1575 and 1074 cm⁻¹ are
beyond the detection limit of the spectrometer. Therefore, we only list SERS
enhancement factors for other four peaks in Table 4-2. It is apparent from Table 4-2 that
a SERS enhancement factor on the order of 10⁷ can be achieved, and the 400 nm
sample exhibits a slight higher enhancement. It is also interesting to notice that for 320
nm silica spheres the enhancement factor tends to increase from the center of the wafer
(R0 region) to the edge (R4 region), while this trend is reversed for 400 nm silica
spheres. We speculate that the crystalline parameters (e.g., interparticle separation,
particle protrusion depth, and single crystalline domain size) could be slightly different
from center to edge due to the nonuniform shear stress during the spin coating process.
It is well-known that SERS enhancement is sensitive to the structural parameters of the samples.

To help understand the enhancement mechanism, we have conducted optical reflection measurements at normal incidence and finite element electromagnetic modeling. It is well-known that localized (Mie scattering-based, surrounding metal nanoparticles)\textsuperscript{166,167} and delocalized (Bragg scattering-based, covering micrometer-scale areas)\textsuperscript{166-167}, surface plasmons play important roles in determining the amplitude of SERS enhancement. Bartlett et al. have demonstrated that periodically structured metallic nanovoids prepared by electrochemical deposition exhibit strong and reproducible SERS enhancement, even though the metal films are not rough.\textsuperscript{150-151} They have also shown that greatest SERS enhancement occurs when surface plasmon resonances on structured metallic surfaces are present at the excitation wavelength and Raman scattered wavelength.\textsuperscript{150-151} Compared to other metal island SERS substrates,\textsuperscript{157-160,162} which typically only exhibit localized surface plasmon resonance, our periodic metal films could support localized and delocalized surface plasmons. The former is originated from the metal islands, while the latter is caused by the Bragg scattering from the periodic structure whose lattice constant matches with the wavelength of operating light. To evaluate the surface plasmon resonance of metalized nanocomposites, we measured optical reflection at normal incidence. Figure 4-12 shows the reflection spectra obtained at eight random locations on a metalized nanocomposite consisting of 400 nm silica spheres. The position of the laser excitation wavelength, 785 nm, is also indicated by the dashed line. The absorbance valleys (peaked at ∼600 and 800 nm) in the reflection spectra could be attributed to the interference of the incident light with
delocalized and localized surface plasmons as well as the colloidal multilayers.\textsuperscript{166} It is evident that the position of the excitation laser almost coincides with the absorbance valley located at $\sim$800 nm. This could result in high SERS enhancement as shown in Figure 4-11B.

To further evaluate the contribution of the delocalized surface plasmons to the overall SERS enhancement, we calculated the electric field amplitude distribution and corresponding Raman enhancement factors surrounding arrays of gold hemispherical protrusions using the Comsol Multiphysics software.\textsuperscript{154} Because the periodic array is symmetric, we construct a simplified two dimensional model which can be considered as sections through a three-dimensional array at the point of maximal enhancement (Figure 4-13A). Figure 4-13A shows the calculated distribution of a SERS enhancement factor around two adjacent hemispherical protrusions with a templating sphere diameter of 320 nm and interprotrusion distance of 1.4 $\times$ 320 nm. The simulation results show that the maximal SERS enhancement factors occur at the top of the semicircles. The spatial distribution of the enhancement factors around the two semicircles is asymmetric, indicating strong electromagnetic interaction between the neighboring scatters. Figure 4-13B illustrates that a larger array (12 semicircles) results in higher enhancement ($\sim 10^{4.6}$), and Figure 4-13C demonstrates that the maximal enhancement factor reaches a plateau when the array has more than 12 scatters. In real SERS experiments, the laser spot ($\sim 40 \, \mu m^2$) covers $\sim 250$ protrusions. It should be noted that the current electromagnetic modeling represents a significant simplification of the real case as the contributions from the localized surface plasmons caused by isolated gold islands and the charge transfer mechanism, which arises from the electronic interaction
between the adsorbed molecules and metal surface,\textsuperscript{168} are not being considered. This could explain the large discrepancy between the experimental and calculated SERS enhancement. Indeed, the continuous and smooth gold films deposited on the oxygen plasma-etched nanocomposites exhibit a much lower SERS enhancement factor ($<10^5$) than that of the discontinuous films. We have developed a simple and scalable bottom-up approach for fabricating periodically structured surfaces that can serve as substrates for depositing gold island films with reproducible SERS enhancement over wafer-sized areas.

Figure 4-1. Schematic illustration of the templating procedures for making periodic metallic nanopyramid arrays.
Figure 4-2. Photograph of a gold-coated colloidal crystal-polymer nanocomposite consisting of 320 nm silica spheres on a 4 in. silicon wafer illuminated with white light.

Figure 4-3. Inverted pyramid arrays anisotropically etched in (100) silicon wafer. A) SEM image of a sample etch at 60 °C for 120s. The inset showing a Fourier transform of the image. B) SEM image of a sample etch at 60 °C for 420s. The inset showing a Fourier transform of the image. C) Average size and size distribution of inverted pyramids etched at 60 °C for various durations.
Figure 4-4. SEM image of particles precipitation on KOH etched silicon.

Figure 4-5. Periodic gold nanop pyramid array. A) Photograph of a 4 in. gold nanop pyramid array templated from 320 nm silica spheres illuminated with white light. B) Top-view SEM image of a replicated gold nanop pyramid array. The inset showing a magnified SEM image of a single nanop pyramid. C) Side-view SEM image of the same gold nanop pyramid array as in B. A magnified pyramid is shown in the inset.
Figure 4-6. Raman spectra of benzenethiol adsorbed on a gold nanopyramid arrays (red curve) replicated from a silicon inverted pyramid array that is templated from 320 nm silica spheres and etched at 60 °C for 210s and a flat gold control sample (blue curve).

Figure 4-7. Photograph of a gold-coated colloidal crystal-polymer nanocomposite consisting of 320 nm silica spheres on a 4 in. silicon wafer illuminated with white light.
Figure 4-8. Scanning electron microscope (SEM) images of the gold coated nanocomposite as shown in Figure 4-7. A) Top view. B) Magnified top view. C) Tilted view (45°).

Figure 4-9. Tapping mode atomic force microscope (AFM) images and corresponding depth profiles. (A and B) Metalized nanocomposite consisting of 320 nm silica spheres. (C and D) Same sample after dissolving the metal coating.
Figure 4-10. SER spectra obtained on a gold-coated nanocomposite consisting of 400 nm silica spheres (red) and a flat gold control sample on glass (black). The spectra were taken using a 785 nm diode laser at 0.5 mW with an integration time of 10s.

Table 4-1. Assignment of SERS peaks and corresponding average counts

<table>
<thead>
<tr>
<th>peak (cm(^{-1}))</th>
<th>assignment</th>
<th>region</th>
<th>320nm</th>
<th>400nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1575</td>
<td>a(_1), (\nu(C-C-C))</td>
<td>R0</td>
<td>3099±698 (22.5%)</td>
<td>7460±1799 (24.1%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R1</td>
<td>3606±862 (23.9%)</td>
<td>7060±1542 (21.8%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R2</td>
<td>3370±772 (22.9%)</td>
<td>5162±776 (15%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R3</td>
<td>4499±590 (13.1%)</td>
<td>5521±901 (16.3%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R4</td>
<td>4853±624 (12.9%)</td>
<td>4368±715 (16.4%)</td>
</tr>
<tr>
<td>1074</td>
<td>a(_1), (\nu(C-C-C)) and (\nu(C-S))</td>
<td>R0</td>
<td>5505±1208 (21.9%)</td>
<td>10850±704 (6.5%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R1</td>
<td>6424±1282 (20%)</td>
<td>11969±1863 (15.6%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R2</td>
<td>6841±1135 (16.6%)</td>
<td>8135±1414 (17.4%)</td>
</tr>
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<td></td>
<td>R3</td>
<td>8170±999 (12.2%)</td>
<td>8280±1155 (13.9%)</td>
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<tr>
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<td></td>
<td>R4</td>
<td>8103±1241 (15.3%)</td>
<td>7489±971 (13%)</td>
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<td>1023</td>
<td>a(_1), (\nu(C-H))</td>
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<td>3480±841 (24.2%)</td>
<td>7604±850 (11.2%)</td>
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<td>R1</td>
<td>4016±969 (24.1%)</td>
<td>7712±1261 (16.4%)</td>
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<tr>
<td></td>
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<td>R2</td>
<td>4270±811 (19%)</td>
<td>5123±1032 (20.1%)</td>
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<tr>
<td></td>
<td></td>
<td>R3</td>
<td>4939±668 (13.5%)</td>
<td>5141±904 (17.6%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R4</td>
<td>4890±920 (18.8%)</td>
<td>4389±729 (16.6%)</td>
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<tr>
<td>1000</td>
<td>a(_1), (\nu(C-C-C))</td>
<td>R0</td>
<td>4100±1000 (24.4%)</td>
<td>9164±897 (9.8%)</td>
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<tr>
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<td></td>
<td>R1</td>
<td>4910±1177 (24%)</td>
<td>8801±1397 (15.9%)</td>
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<tr>
<td></td>
<td></td>
<td>R2</td>
<td>5183±918 (17.7%)</td>
<td>6345±1123 (17.7%)</td>
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<tr>
<td></td>
<td></td>
<td>R3</td>
<td>6222±774 (12.4%)</td>
<td>6381±1004 (15.7%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R4</td>
<td>7221±1136 (15.7%)</td>
<td>5409±792 (14.6%)</td>
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Table 4-1. Continued.

<table>
<thead>
<tr>
<th>peak (cm$^{-1}$)</th>
<th>assignment</th>
<th>region</th>
<th>Raman counts</th>
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<tr>
<td>695</td>
<td>a1, $\nu$(C-C-C) and $\nu$(C-S)</td>
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<td>1112±197 (17.7%)</td>
<td>2179±458 (21%)</td>
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<tr>
<td></td>
<td></td>
<td>R1</td>
<td>1207±301 (24.9%)</td>
<td>2190±552 (25.2%)</td>
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<tr>
<td></td>
<td></td>
<td>R2</td>
<td>1180±267 (22.6%)</td>
<td>1607±343 (21.3%)</td>
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<tr>
<td></td>
<td></td>
<td>R3</td>
<td>1337±223 (16.7%)</td>
<td>1222±213 (17.4%)</td>
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<tr>
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<td></td>
<td>R4</td>
<td>1560±381 (24.4%)</td>
<td>1500±330 (22%)</td>
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<tr>
<td>419</td>
<td>a1, $\nu$(C-C-C) and $\nu$(C-S)</td>
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<td>3970±1041 (26.2%)</td>
<td>8142±1815 (22.3%)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>R1</td>
<td>4972±970 (19.5%)</td>
<td>8067±1135 (14.1%)</td>
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<tr>
<td></td>
<td></td>
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<td>5777±1312 (22.7%)</td>
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<td>R3</td>
<td>6076±1010 (16.6%)</td>
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<td>R4</td>
<td>5697±1286 (22.6%)</td>
<td>6356±749 (11.8%)</td>
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Peaks and Raman counts recorded for benzenethiol molecules adsorbed on five areas (R0-R4) of 4 in. nanocomposites consisting of 320 and 400 nm silica spheres.

Figure 4-11. Arithmetically averaged SER spectra recorded for benzenethiol molecules adsorbed on five areas (R0-R4) of 4 in. nanocomposites consisting of A) 320 and B) 400 nm silica spheres. Spectra were taken using a 785 nm diode laser at 0.5 mW with an integration time of 10s.

Table 4-2. Assignment of SERS peaks and Raman enhancement factors

<table>
<thead>
<tr>
<th>peak/(cm$^{-1}$)</th>
<th>assignment</th>
<th>region</th>
<th>enhancement factor</th>
<th>320nm</th>
<th>400nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1023</td>
<td>a1, $\nu$(C-H)</td>
<td>R0</td>
<td>2.2×10$^7$</td>
<td>4.8×10$^7$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>R1</td>
<td>2.6×10$^7$</td>
<td>4.9×10$^7$</td>
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<tr>
<td></td>
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<td>R2</td>
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<td>3.3×10$^7$</td>
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<td></td>
<td></td>
<td>R3</td>
<td>3.2×10$^7$</td>
<td>3.3×10$^7$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>R4</td>
<td>3.1×10$^7$</td>
<td>2.8×10$^7$</td>
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Table 4.2 Continued.

<table>
<thead>
<tr>
<th>peak/(cm$^{-1}$)</th>
<th>assignment</th>
<th>region</th>
<th>enhancement factor</th>
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<td></td>
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<tr>
<td>1023</td>
<td>a1, $\nu$(C-H)</td>
<td>R0</td>
<td>$2.2 \times 10^7$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$6.5 \times 10^6$</td>
</tr>
<tr>
<td>1000</td>
<td>a1, $\nu$(C-C-C)</td>
<td>R0</td>
<td>$7.8 \times 10^6$</td>
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<td></td>
<td></td>
<td></td>
<td>$8.2 \times 10^6$</td>
</tr>
<tr>
<td>695</td>
<td>a1, $\nu$(C-C-C) and $\nu$(C-S)</td>
<td>R0</td>
<td>$1.1 \times 10^7$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$1.2 \times 10^7$</td>
</tr>
<tr>
<td>419</td>
<td>a1, $\nu$(C-C-C) and $\nu$(C-S)</td>
<td>R0</td>
<td>$4.9 \times 10^7$</td>
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<td></td>
<td></td>
<td></td>
<td>$6.2 \times 10^7$</td>
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<td>$6.6 \times 10^7$</td>
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<td>$7.5 \times 10^7$</td>
</tr>
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<td></td>
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<td>$7.1 \times 10^7$</td>
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Peaks and Raman enhancement factors were calculated for benzenethiol molecules adsorbed on five areas (R0-R4) of 4 in. nanocomposites consisting of 320 and 400nm silica spheres.

Figure 4-12. Normal incidence reflection spectra obtained at eight locations on a 4 in. metalized nanocomposite consisting of 400nm silica spheres.
Figure 4-13. Simulated Raman enhancement around gold semispherical protrusions templated from 320 nm silica spheres at $\lambda=785$ nm. A) 2 scatters. B) 12 scatters. C) Simulated order of magnitude of maximal SERS enhancement factor ($\log G_{\text{max}}$) versus number of scatters.
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), information storage, efficient light-emitting diodes, and biosensors, as well as fundamental understanding of surface plasmon enabled optical transmission and diffraction. 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. 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. Attaining high throughput and large-area fabrication continues to be a major challenge with these top-down techniques.

Bottom-up self-assembly and templated 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.\textsuperscript{12,86,177}

Although the spin coat technology has been demonstrated to generate wafer-scale non-close-packed 2D and 3D arrays, 2D submicrometer-scale particles (<100 nm) have not been achieved reproducibly in large area by spin coat technology. Here we report a flexible and scalable non-lithographic approach for fabricating large-area sub-100 nm periodic nanostructures using submicrometer-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 cm\textsuperscript{2} area.

### 5.1 Experimental Procedure

Figure 5-1 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 5-1). 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 5-2A, 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 5-2 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 5-2D 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 5-3 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 5-4A 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.

5.2 Results and Discussion

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 5-4C and D. Due to different substrate wettability, 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 5-4D). 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 5-4B 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. In summary, we have developed a simple yet scalable templating nanofabrication technique that enables the creation of periodic nanostructures with tunable feature size.

Figure 5-1. 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 nanocomposites as templates.
Figure 5-2. 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 5-3. SEM image of an array of gold nanoholes with 89 nm diameter templated from a monolayer nanocomposite consisting of 360 nm silica spheres.
Figure 5-4. SEM images of micro-candles. A) and B) Top- and side-view SEM images of an array of silicon “micro-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 6
CONCLUSIONS AND RECOMMENDATIONS

This dissertation covers three research topics which demonstrate the important applications of templating nanostructure by spin coating technology. The conclusions associated with the antireflection coatings presented in Section 6.1. The conclusions associated with the SERS-active substrates are presented in Section 6.2. The conclusion associated sub-100nm structures are presented in section 6.3. The recommendations for further study are presented in section 6.4.

6.1 Antireflection Coatings

Antireflection coatings templated from spin-coated colloidal arrays are generated on glass substrates and semiconductor wafers. Bio-inspired moth eye structures are generated by surface templating using PDMS to transfer nanostructure on glass substrates. Binary array antireflection coatings are fabricated using two layers silica/ETPTA nanocomposite. This dimple and nipple binary nanostructures can further reduced reflection to below 0.5% in the visible light range. By using 2 dimensional non-close-packed colloidal crystals as etching masks, nanostructures can be generated on Si and GaAs wafer surfaces that greatly reduced the reflection. These cost effective and large-area broadband antireflection coatings on Si and GaAs are expected to enhance optical performances of optical devices.

6.2 SERS-Active Substrates

Two types of SERS-active substrates are fabricated by spin coating technology. Gold nanopyramid arrays with sharp tips that can concentrate electromagnetic waves are used as SERS-active substrates with an enhancement factor of $\sim 7 \times 10^5$. Further
improvements are made by using gold-coated polymer pyramids and electrochemical SERS to increase enhancement factor up to $10^8$.

A highly reproducible SERS-active substrate is demonstrated. It leverages the uniformity of spin-coated colloidal arrays and conventional physical vapor deposition techniques. The formation of discontinuous, island-type metal films with periodic microstructures over large areas could lead to important technological applications in nanoelectronics, electromechanical devices, and biosensors.

### 6.3 Sub-100nm Nanostructures

Sub-100 nm metal nanohole arrays, which have important technological applications in integrated nanophotonics and bio-microanalysis, can be easily templated over a large area. The polymer wetting layer between the spin-coated colloidal monolayer and the substrate also plays a crucial role in determining the shape of the templated microstructures that have broad applications ranging from plasmonics to broadband antireflection coatings for solar cells.

### 6.4 Recommendations

Future work should focus on the colloidal assembly mechanism by shear aligning force. This cost effective spin coat technology is beneficial to both academic and industry because it can quickly (in several minutes) assemble 2 and 3 dimensional colloidal crystal in large scale (up to 8 in. wafer) and is compatible with current microfabrication technology. A better understanding of the formation mechanism could lead to tuning the colloidal structures which could further extend its applications.

Another future work is to fabricate real solar cells based on the antireflection coatings we have developed. Our work has shown that the reflection is greatly reduced in the visible range by templating from spin-coated made colloidal crystals on both glass
and semiconductor materials. This reduction of reflection can increase the absorption of photons and hence increase the photon electron conversion efficiency.

Light transmission measurement through templated nanohole arrays should also be conducted. The combination of extraordinary transmission and high conductivity makes gold nanohole arrays a potential candidate for transparent electrodes.
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BIOGRAPHICAL SKETCH

Chih-Hung Sun grew up in Hsinchu, Taiwan. He received his bachelor's degree at the National Taiwan University in 2001 and his master degree at National Tsing Hua University in 2003. He started his military service in July 2003, and he was discharged in January 2005. He began his graduate studies at the University of Florida in August 2006 and joined Professor Peng Jiang's nanostructured material research group to pursue a doctorate degree. He graduated in the fall of 2009 after spending three and half years being educated in chemical engineering and material science.