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TEMPLATE REPLICATION OF NANOMATERIALS

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by
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This thesis focuses on one central theme, the template replication of nanomaterials. The first half of this thesis focuses on studying new properties that emerge in nanostructured materials prepared by existing template replication strategies. The second half of this thesis focuses on the development of novel strategies to synthesize nanomaterials by replication of nanoscale templates.

Chapter 1 of this thesis presents an introduction to the synthesis of nanomaterials by template replication. Top down and bottom up approaches are covered in this chapter.

Chapter 2 of this thesis presents the different techniques used to characterize the materials studied in this thesis.

Chapter 3 presents the optical properties of one-dimensional metallic gratings coupled to a one-dimensional photonic crystal. Light incident upon a periodically corrugated metal/dielectric interface can generate surface plasmon-polariton (SPP) waves. This effect is used in many sensing applications. Similar metallodielectric nanostructures are used for light trapping in solar cells, but the gains are modest because SPP waves can be excited only at specific angles and with one linear polarization state of incident light. Here we report the optical absorptance of a metallic grating coupled to silicon oxide/oxynitride layers with a periodically varying refractive index, *i.e.*, a 1D photonic crystal. These structures show a dramatic enhancement relative to those employing a homogeneous dielectric material. Multiple SPP waves can be activated, and both *s-* and *p-*polarized incident light can be efficiently trapped. Many SPP modes are weakly bound and display field enhancements that extend throughout the dielectric layers. These modes have significantly longer propagation lengths than the single SPP modes excited at the interface of a metallic grating and a uniform dielectric. These results suggest that metallic gratings coupled to photonic crystals could have utility for light trapping in photovoltaics, sensing, and other
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Chapter 4 in this dissertation presents data which demonstrates that the resonance frequency of multiple SPP waves can be tuned by varying the periodicity of the metallic grating. In this study only p-polarized incident light was considered in the visible and near-infrared regimes. When the absorptance was plotted against the angle of incidence, the excitation of an SPP wave was indicated by an absorptance peak whose angular location did not change with the number of periods (beyond a threshold) of the photonic crystal. A decrease in the period of the metal grating resulted in shifting the excitation of the SPP waves to smaller wavelengths. The metallic gratings used in this study were prepared by template replication process.

Chapter 5 in this dissertation presents a new method of fabricating wafer scale metallic gratings. By combining nanosphere lithography with template stripping, silicon wafers were patterned with hexagonal arrays of nanowells or pillars. These silicon masters were then replicated in gold by metal evaporation, resulting in wafer-scale hexagonal gratings for plasmonic applications. In the nanosphere lithography step, two-dimensional colloidal crystals of 510 nm diameter polystyrene spheres were assembled at the air-water interface and transferred to silicon wafers. The spheres were etched in oxygen plasma in order to define their size for masking of the silicon wafer. For fabrication of metallic nano-pillar arrays, an alumina film was grown over the nanosphere layer and the spheres were then removed by bath sonication. The well pattern was defined in the silicon wafer by reactive ion etching in a chlorine plasma. For fabrication of metal nano-well arrays, the nanosphere monolayer was used directly as a mask and exposed areas of the silicon wafer were plasma-etched anistropically in SF₆/Ar. Both techniques could be used to produce sub-wavelength metal replica structures with controlled pillar or well diameter, depth and profile, on the wafer scale, without the use of direct writing techniques to fabricate masks or masters.
Chapter 6 presents a new method of preparing microporous titania particles replicated from Metal-organic frameworks (MOFs) templates. Metal-organic frameworks provide access to structures with nanoscale pores, the size and connectivity of which can be controlled by combining the appropriate metals and linkers. Microporous titania replicas were made from the MOF template HKUST-1 by dehydration, infiltration with titanium isopropoxide, and subsequent hydrothermal treatment at 200 °C. Etching of the MOF with 1M aqueous HCl followed by 5% H$_2$O$_2$ yielded a titania replica that retained the morphology of the parent HKUST-1 crystals and contained partially ordered micropores as well as disordered mesopores. Interestingly, the synthesis of porous titania from the HKUST-1 template stabilized the formation of brookite, a rare titania polymorph.
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Chapter 1 Introduction to solids patterned on the nanoscale

1.1 Introduction

In nature, atoms assemble together into ordered patterns forming solids known as crystals. In the past century, solid state physics has shown that the crystal structure and bond length dictate the chemical and physical properties exhibited by solid materials. Materials with tunable periodicity and crystal structures can also be prepared on length scales larger than atomic ordering. Like their atomic analogues, these materials also exhibit properties that are dictated by crystal structure and length scale of periodicity.

One such method of preparing these materials is template replication. Usually, the material of interest is infiltrated into a template with the desired crystal structure and periodicity, or the template is used as a projection mask. Finally, the template is removed yielding a replica or inverse structure. In this thesis, materials prepared by this approach will be denoted as templated materials. Templates can be prepared by a variety of techniques. For instance, mesoporous silica, metal organic frameworks, block copolymers, and particle layers can be used as a bottom up method to replicate materials. Another approach known as top down methods require the direct writing of the structure into a template using techniques such as electron beam lithography, photolithography and/or ion beam lithography. These approaches will be covered in greater detail in the subsequent sections of this thesis.
1.2 Bottom up strategies to templated materials

1.2.1 Introduction to bottom up replication of solids

Bottom up strategies for preparing porous materials by replication allow precise control over parameters such as surface area, pore size, pore geometry, and interfacial properties. The flexibility in varying these parameters allow these materials to be useful for heterogeneous catalysis, photovoltaics, electrochemical energy storage, gas separation, sensors, and several other applications. Porous materials are classified according to their pore size; microporous materials contain pores sizes smaller than 2 nm, mesoporous materials contain pore sizes between 2 nm and 50 nm, and macroporous materials contain pore sizes greater than 50 nm. Various synthetic strategies have been developed to synthesize porous materials with ordered and disordered pore geometries. Ordered porous solid are usually prepared by replication from soft templates such as surfactants or block copolymers, or from hard templates such as carbon or silica.

Soft templating is carried out by evaporation induced self-assembly of a metal precursor solution with surfactants or block copolymers. Usually a polymeric metal alkoxide sol with a surfactant or block copolymer below the critical micelle concentration is prepared as the precursor solution. This mixture is coated onto a substrate by dip coating or spin coating. Gradual solvent evaporation leads to an increase in the concentration of the surfactant above the critical micelle concentration. Micelles self-assemble into various geometries when the concentration is higher than the critical micelle concentration. This self-assembly process allows micelles to serve as the structure directing template for ordered porous nanostructures. The initial surfactant concentration is a critical parameter for controlling the morphology of the micelle template. The polymeric metal alkoxide sol and surfactant micelles are co-assembled onto the
substrate, yielding an organic/inorganic composite. The organic template can then be removed by calcination, solvent extraction, or ultraviolet degradation. Finally the film is exposed to a heat treatment step to solidify the sol if calcination was not used to remove the template. Care must be taken during high temperature processing steps to inhibit structural collapse and/or pore sintering. It is important to note that there are very few examples of ordered microporous solids prepared by replication of a template.

The hard template route to porous materials involves the use of porous solids as templates. In this approach an ordered porous solid with empty pores is infiltrated with a precursor molecule. The replicated material is then obtained by removal of the template through selective etching or calcination. A wide variety of templates such as zeolites, colloidal crystals, ordered porous silica and ordered porous carbon have been used as the template for preparation of ordered porous particles and thin films. Care must be taken to inhibit structural collapse and/or pore sintering during high temperature processing steps for mesoporous and especially microporous materials. The precursor materials used for infiltration of the template’s pores must be smaller than the size of the pore (to allow for high loading) and not react with the template.

Colloidal particle multilayers (opals) and monolayers can also be used as templates to prepare a wide variety of nanostructured materials. Materials replicated from colloidal crystals are used to prepare inverse opals, ideally with ~74% void space. Particle monolayers (usually silica or polystyrene) can be used to prepare isolated hexagonal nanoparticle arrays, nanodome arrays, nanorod arrays, nanodisk arrays, nanowell arrays, nanopyramid arrays, nanohole arrays, and several other kinds of two-dimensionally periodic structures.
1.2.2 Metal organic frameworks as templates for microporous solids

Metal–organic frameworks (MOFs) are solids that offer control of pore size and geometry by selecting the appropriate molecular building units. Recently, there have been several reports of preparing nanoporous carbon from MOF templates by direct carbonization or by infiltration of a carbon precursor followed by calcination and etching of the template. In both cases the replicated carbon particles usually retain the macroscale morphology of the MOF template; however the ordered pore structure of MOF is destroyed. The replicated carbons exhibit surface area ranging from 200- 3000 m$^2$/g, the high surface area results primarily from disordered micropores. Nanoporous carbon prepared by this method has been used as supercapacitors, H$_2$ storage, toxic gas sensors, and electrocatalysis.

The pore diameter of the MOF derived carbon is close to that of the parent MOF, however the low thermal stability of the MOF results in the loss of pore ordering. In order to increase the thermal stability of the MOF, a strategy involving the functionalization of the MOFs pore walls with silane was adopted. In this approach 3-aminopropyltriethoxysilane was coordinated to the pores by attachment to unsaturated chromium sites. Resorcinol was then infiltrated into the MOF pores and the composite was calcined at 650 C under an inert atmosphere. Finally the carbon/MOF composite was treated with hydrofluoric acid to remove transition metal species. The low angle XRD pattern of the replicated carbon shows three weakly intense reflections. All three reflections of the carbon replica were observed to shift to higher angles, indicating that the replica shrunk during pyrolysis. Replicas cast from unmodified MOFs exhibited a single broad peak at low angles, this indicative of incomplete replication.
Figure 1-1. A schematic depicting the replication of a MOF with furfuryl alcohol as a carbon precursor. (ref. 21)

Figure 1-2. Low angle XRD patterns of a) silane modified MIL-101, MOF/Carbon composite (A-P-20), its carbon replica (A-C-20), and directly calcined silane modified MIL-101 (A-650). b) unmodified MIL-101, its carbon replica cast from a solution with 20% resorcinol concentration (A-C-20), its carbon replica cast from a solution with 50% resorcinol concentration (B-C-50), its carbon replica cast from a solution with 20% resorcinol concentration (B-C-20), and directly calcined unmodified MIL-101 (B-650). (ref. 21)
1.3 Top down strategies to replicated solids

1.3.1 Introduction to top down replication

Today, methods such as electron beam lithography, focused ion beam lithography, nano-imprint lithography and scanning probe lithography are used to prepare patterned nanostructured materials on length scales from tens of nanometers to many hundreds of nanometers.\textsuperscript{28,30} There are two types of categories for lithography, processes that require masks and processes that do not require masks (maskless lithography).

Optical lithography and nano-imprint are widely used lithographic processes with high pattern throughput. They are excellent tools for large scale manufacturing of a fixed pattern. However, these processes are not suitable for a laboratory type setting due to high mask related costs. Electron beam, scanning probe lithography and focused ion beam lithography are maskless type lithographic approaches. For pattern fabrication, a beam focused to a few tens of nanometers is scanned on a sample to imprint the desired pattern into photoresist (electron beam) or directly into the substrate (focused ion beam, scanning probe). These methods have inherently low throughput, but are more suitable for use in a laboratory type setting due to the absence of mask related costs.\textsuperscript{28}

Wet etching or dry etching is one strategy used to transfer the lithographically defined pattern into the substrate. Wet etching is an isotropic etchant, resulting in significant undercut under the template.\textsuperscript{30} Due to this problem; it is difficult to control the lateral dimension and depth independently of each other. Structures that span many microns can tolerate such methods. However, when precise control of dimensions is needed, which is often the case in materials with length scales spanning tens to hundreds of nanometers, undercut cannot be tolerated. Dry etching
is used instead of wet etching because anisotropic etching (no undercut) is possible with this technique.30

1.3.2 Template stripping of patterned noble metal films

Metallic thin films with periodic nanoscale texturing are usually prepared by expensive lithographic techniques.28, 30 Recently numerous lithographic strategies have been developed to reduce fabrication costs.15, 30 Of all the newly developed techniques, template stripping is one of the most promising techniques for low cost fabrication of patterned metal films.15 Template stripping is a technique that takes advantage of the good wettability and poor adhesion of noble metals to oxide surfaces. In a typical process, metal is evaporated over a patterned silicon wafer with its native oxide, the exposed part of the metal film is then attached to a substrate with an epoxy resin glue, and finally the substrate is removed from the silicon film yielding a metal replica of the silicon pattern. Patterned metals prepared by this technique are much smoother than those made by techniques such as lift off; the RMS surface roughness of template stripped gold is ~ .19 nm whereas as evaporated gold has an RMS surface roughness of ~2.2 nm.15 The smoother surfaces of the metal films are desirable because it reduces parasitic absorption by the metal film. The main drawback of the template technique is that patterned silicon is usually prepared by standard lithographic techniques, which are quite expensive. The size of the patterned area on the silicon template is usually on the order of a 5-10 mm, because the cost scales with pattern size with conventional lithographic techniques.
**Figure 1-3.** Schematic representation of the template replication of patterned metallic films by template stripping. (ref. 30).

**Figure 1-4.** a) SEM image of silver grating prepared by lift off. b) SEM image of gold evaporated over a patterned silicon template. Note how the film facing the patterned silicon is smoother than the as evaporated metal.
1.3 Dissertation Overview

In this dissertation I will present the work we have intensively researched for the past 4 years. Chapter 2 will summarize techniques that were used to fabricate and characterize nanostructured templated materials. Chapters 3 and 4 focus on studying new properties that emerge in nanostructured materials prepared by existing template replication strategies. Chapter 5 and 6 focuses on the development of new replication strategies to create exotic nanostructures.

Muhammad Faryad and Akhlesh Lakhtakia performed electromagnetic simulations; these results are included chapters 3 and 4. Liu Liu assisted me in preparing one of the gratings used in chapter 3. Greg Barber grew the dielectric layers used in chapters 3 and 4. Atsushi Kondo synthesized the metal organic framework templates and helped develop etch chemistry for removal of the MOF templates, these results were used in chapter 6.

References


Chapter 2 Characterization of Materials

2.1 Introduction

Structuring materials at the nanoscale is a powerful tool for creating “new materials” from old materials. A number of complementary techniques are typically used to synthesize and interrogate the properties of nanostructured materials. This chapter will introduce the more specialized techniques we have used to synthesize and characterize templated materials. General techniques such as X-ray diffraction, electron microscopy, scanning probe microscopy, and UV-visible spectroscopy will not be covered in this thesis because descriptions of them can be found in many textbooks and other sources.

2.2 Ellipsometry

2.2.1 Introduction to Ellipsometry

Spectroscopic ellipsometry is a technique used to determine the refractive index and thickness of thin films and bulk materials. An ellipsometer operates by measuring the change in the polarization state of linearly polarized light reflected from a film. The amplitude and phase of the electric field component of $s$ and $p$ polarized light are altered, and therefore the reflected beam is usually elliptically polarized. The ellipsometer measures two parameters, the amplitude ratio ($\psi$) and phase difference ($\Delta$) as a function of wavelength, often at multiple angles of incidence. The angles of incidence are chosen to constrain the fit to the optical constants and structure of the film and to maximize the sensitivity of the measurement. The optical constants and film thicknesses determined are usually averaged across a few angles of incidence. Typically, a rotating analyzer is used to determine the polarization state of the outgoing light. The amount of
Figure 2-1. A schematic diagram showing incident linearly polarized light reflecting off a film surface as elliptically polarized light. (www.jawoollam.com)
light passed through the rotating polarizer relative to the incident intensity is dependent on the
electric field orientation of the light reflected from the sample. Once this signal reaches the
detector, it is converted into an electrical signal to determine the reflected polarization. Finally,
this signal is compared to the polarization of the initial light signal to determine the polarization
change of the reflected light. Spectra are usually collected and fitted at multiple angles, and the
thicknesses and dielectric functions determined at these angles are averaged. Because it is
fundamentally an interferometric technique, ellipsometry is capable of measuring sub-nanometer
variations in film thickness. The optical response measured is dependent on the optical properties,
thickness and surface roughness of the material.

2.2.2 Propagation of Light in Materials

Photons can reflect and transmit when they reach interfaces between materials. When
light enters a material, the propagation direction of light generally changes due to refraction. This
change in direction is interpreted as a variation in the speed of light within the medium of
propagation. Snell’s law (equation 2-1) can be used to describe the refraction of light at a single
interface.

\[ N_i \sin \theta_i = N_t \sin \theta_t \]  

(2-1)

Here \( N_i \) is the complex refractive index of light in medium 1, \( N_t \) is the complex refractive index in
medium 2, and \( \theta_i \) and \( \theta_t \) are the angles of incidence and transmission, respectively. The complex
refractive index is defined as

\[ N = n + ik \]  

(2-2)
Figure 2-2. Photons refract and reflect at each interface of the film. This causes interference of the beams which leads to differences in beam intensity and phase delay. (www.jawoollam.com)
Where $n$ is the ratio of the speed of light in vacuum to the speed of light propagation within the material, and $k$ is the extinction coefficient.

The reflected and transmitted beam intensities can be determined by Fresnel’s equations (equations 2-3 through 2-6). Two equations are needed to describe transmittance (denoted as $t$) and two equations are needed to describe reflection (denoted as $r$). A total of four equations are needed because $s$ and $p$ polarized light have different boundary conditions. $S$ polarization is defined as light with its electric field vector oriented normal to the plane of incidence, while $p$ polarized light is defined as light having its electric field vector oriented parallel to the plane of incidence.

\[
\begin{align*}
    r_p &= \frac{E_{tp}}{E_{ip}} = \frac{N_i \cos \theta_i - N_t \cos \theta_t}{N_i \cos \theta_i - N_t \cos \theta_t} \\
    t_p &= \frac{E_{tp}}{E_{ip}} = \frac{2N_i \cos \theta_i}{N_i \cos \theta_i - N_t \cos \theta_t} \\
    r_s &= \frac{E_{ts}}{E_{is}} = \frac{N_i \cos \theta_i - N_t \cos \theta_t}{N_i \cos \theta_i + N_t \cos \theta_t} \\
    t_s &= \frac{E_{ts}}{E_{is}} = \frac{2N_i \cos \theta_i}{N_i \cos \theta_i + N_t \cos \theta_t}
\end{align*}
\]

Here the subscript $i$ stands for material 1, the subscript $t$ stands for material 2, $E$ stands for electric field, the subscript $s$ stands for $s$ polarized light, the subscript $p$ stands for $p$ polarized light, and $N$ stands for the complex refractive index.

\[\rho = \frac{r_p}{r_s} = \tan(\psi)e^{i\Delta} \quad (2-7)\]

2.2.3 Analysis of Ellipsometry Data

The fundamental equation used in ellipsometry defines the ratio of the reflection coefficients of $s$ and $p$ polarized light. This ratio is commonly written as:

\[\rho = \frac{r_p}{r_s} = \tan(\psi)e^{i\Delta}\]
When a single interface present (i.e. a bulk substrate), $\psi$ and $\Delta$ can be directly calculated from the following equation.

$$\rho = \tan(\psi) e^{i\Delta} = \frac{N_t \cos \theta_i - N_i \cos \theta_t}{N_t \cos \theta_i + N_i \cos \theta_t}$$

(2-8)

where $N_o$ and $N_i$ are the complex refractive indices of air and the sample respectively, and $\theta_i$ and $\theta_t$ are the angles of incident and transmitted light, respectively. The complex refractive index of air, the angle of incidence, $\psi$, and $\Delta$ are known quantities. The transmission angle can be substituted as a function of $N_o$, $N_i$ and $\theta_i$ by using Snell’s law. Finally, solving equation 2-8 for $N_t$ yields the following equation

$$N_t = N_i \tan \theta_i \sqrt{1 - \frac{4\rho}{(1+\rho)^2} \sin \theta_i}$$

(2-9)

This equation is used to determine the complex refractive index for an infinitely thick film.

Problems that involve more than one interface are quite complex. Multi-interface problems are usually solved numerically.

### 2.2.4 Dielectric Function Models

The experimentally collected data must be fit to a model to determine the optical properties and refractive index of multi-interface samples. The model is used to calculate the predicted response of the system. The initial model chosen for fitting is dependent on the type of material used. It is important to note that the number of unknown properties cannot exceed the amount of data points collected. When the refractive indices are not known, they must be modeled according to the optical properties of the sample. We use the CompleteEASE software package to fit the dielectric models to the experimental data.

Absorption of light leads to electric polarization in the materials, this can be described by various models, such as the Lorentz model, Tauc-Lorentz model (this model is typically used for
amorphous materials), Harmonic Oscillator Approximation model, and Model Dielectric Function model. For wavelengths where the material is not absorbing, the dielectric functions can be determined with the Sellmeier model, or Cauchy model. For free carrier absorption, the dielectric functions are usually determined with the Drude model.

The Sellmeier model is usually preferred over the Cauchy model for determining the dielectric functions of non-absorbing materials, because the latter does not correct for non-realistic dispersion. The Sellmeier model is represented as

\[ n^2 = A + \sum_{j} \frac{B_j \lambda^2}{\lambda^2 - \lambda_0^2} \]  

(2-10)

Where \( A \) and \( B_j \) represent analytical parameters used in the data analysis, and where \( \lambda_0 \) is the resonant wavelength of the material, these terms are used to describe the refractive index over a range of wavelengths.

The Drude model is widely used to describe free carrier absorption in semiconductors and free electrons in metals. The drude model is represented as

\[ \varepsilon = N^2 = 1 - \frac{E_p^2}{E^2 - i\Gamma E} \]  

(2-11)

where \( E_p \) represents the plasma energy, \( \Gamma \) is proportional to the broadening parameter of angular frequency, and \( E \) is the photon energy. The Drude model is valid at frequencies below the plasma frequency.
Figure 2-3. This schematic shows which regions models are used to determine the dielectric functions.
2.2 Porosity Measurements

2.2.1 Nitrogen Gas Sorption Isotherms

Nitrogen gas adsorption/desorption at 77K is the most widely used technique for determining pore volume, pore size distributions and surface area of porous materials.\textsuperscript{2,3} When a gas molecule comes into contact with the surface of a solid material, it can physisorb onto the surface of the material. Physisorption of gases in porous solids is governed by fluid-pore interactions, fluid-fluid interactions, and the effects of pore confinement on the thermodynamic stability of gases within the pore.\textsuperscript{2,3} The interplay between the interactions of these parameters influences the shape of the gas adsorption isotherm. The adsorption isotherms can be used to determine the pore classification.\textsuperscript{2,4} Porous materials are classified according to their pore size; microporous materials contain pores sizes smaller than 2 nm, mesoporous materials contain pore sizes between 2 nm and 50 nm, and macroporous materials contain pore sizes greater than 50 nm.\textsuperscript{5}

The adsorption isotherm relates pressure with the adsorption of a specific gas. The vertical axis shows the amount of gas adsorbed; while the horizontal axis shows the relative pressure (P/P\textsubscript{o}), where P\textsubscript{o} is the gas’s saturation pressure. There are six different shapes to the adsorption isotherms as defined by the IUPAC (Figure 2-4); the shape of the adsorption isotherm is dependent on the pore sizes and the interactions adsorbate and adsorbent.\textsuperscript{2-4} Steep uptakes of gas at low partial pressures P/P\textsubscript{o} < 0.2 is usually indicative of the presence of micropores. More specifically, small micropores with diameters ~2-3 gas molecules in diameter are observed to fill at P/P\textsubscript{o} < 0.01, while larger micropores fill over P/P\textsubscript{o} ~ 0.02-0.2. The steep uptake at low partial pressures occurs because the behavior is almost completely dominated by interactions between the gas and pore wall. The interactions between the gas and the pore wall are very strong because...
Figure 2-4. This graph shows the different types of adsorption isotherms as defined by IUPAC. I) Microporous materials. II) Nonporous materials III) Nonporous materials and materials with weak interactions between the adsorbate and adsorbent. IV) Mesoporous materials. V) Porous materials and materials with weak interactions between the adsorbate and adsorbent. VI) Homogeneous surface materials. (ref. 4)
the adsorption potentials on the opposite sides of the pore walls overlap in micropores. In mesoporous materials, the sorption behavior is dominated by interactions between the fluid and pore wall, and by fluid-fluid interactions. These interactions lead to multilayer adsorption and the capillary condensation within the pores at $P/P_o > 2$. It is characteristic for mesoporous materials to display hysteresis loops in the adsorption desorption isotherm due to capillary condensation.

### 2.2.1 Determination of Surface Area by the BET Method

There are a variety of models used to fit adsorption isotherms to determine the surface area, pore size distribution, and pore volume of a material. The Brunauer, Emmet and Teller (BET) method is one of the most popular methods for determining monolayer surface area of solids with mesopores or larger pore sizes. There are two stages used to determine the BET surface area. Firstly, one of the sorption isotherm is transformed into a BET plot; this plot is used to determine the monolayer capacity (volume), $n_m$. This variable is calculated using the following equation:

$$\frac{1}{n \left( \frac{P}{P_0} \right) - 1} = \frac{1}{n_m C} + \left[ \frac{C-1}{n_m C} \right] \left( \frac{P}{P_0} \right)$$

(2-12)

Where $C$ is an empirical constant which is dependent on the strength of interaction between the adsorbent-adsorbate interactions, and $P/P_o$ is the gas partial pressure normalized to its saturation pressure. This equation is only valid assuming the following conditions: 1) The heat of adsorption is constant for the first monolayer. 2) The interactions of adsorbed molecules laterally are negligible. 3) Multilayer adsorption can occur on the already formed molecular monolayer. 4) The heat of adsorption of all additional monolayers over the first monolayer is equal to the heat of condensation. After the monolayer capacity is determined, the surface area ($S$) can be calculated with the following equation:
where \( N_A \) is Avogadro’s number and \( \sigma \) is the gas’s molecular cross section. Finally the surface area is normalized to the sample’s weight when its pores are empty, yielding the specific surface area. If the BET method is applied to a material with micropores, an apparent BET surface area is given.

### 2.2.2 Determination of Mesopore Size Distribution by the Barret-Joyner-Halenda (BJH) Method

\[
\ln \frac{P}{P_0} = \frac{-2 \gamma \cos \theta}{RT \Delta \rho (r_p - r_c)}
\]  

(2-14)

The mesopore size distribution can be calculated from a variety of methods. In this thesis the Barrett-Joyner-Halenda (BJH) method will be discussed.\(^7\) BJH theory is based on the modified Kelvin equation (eq. 2-10) which predicts the pressure at which the adsorbate will condense or evaporate in a pore as a function of size.\(^8\) In the modified Kelvin equation shown here, the pore is assumed to be spherical. The variable \( r_p \) is the pore radius, \( r_c \) is the adsorbed multilayer film thickness prior to condensation, \( \Delta \rho \) is the density difference of the liquid and gas phase, \( \theta \) is the contact angle of the liquid meniscus against the pore wall, \( R \) is the universal gas constant, and \( T \) is the temperature. The BJH method requires 14 steps, beginning with the Kelvin equation, to determine the micropore size distribution.\(^8\) This is beyond the scope of this thesis, so the calculation steps will not be shown here. Details of this calculation can be found in reference \(^8\).

Methods based on the modified Kelvin equation assume the fluid behavior is bulk-like, therefore the interactions between the fluid and pore wall are neglected. Neglecting this parameter can cause errors as high as 20% for pores smaller than 10 nm. The equation is more accurate for larger mesopores due to weaker fluid-pore wall interactions.\(^2, \ 3, \ 8\)
2.2.3 Micropore Size Distribution and Pore Volume Determination

The micropore size distribution can be calculated by a variety of methods. In this thesis only the Horvath-Kawazoe (HK) method will be discussed. This method relates the pore size to the relative pressure in which the pores are filled by the adsorbate. First the pore width, \( L \), is calculated from the following equation (the equation below is only valid for oxide type materials; slight variations of this equations is needed for non-oxide materials) as a function of partial pressure:

\[
\ln \frac{P}{P_0} = \frac{21.77}{(L-0.64)} \left( \frac{1.847 \times 10^{-3}}{(L-0.32)^2} - \frac{2.54 \times 10^{-7}}{(L-0.32)^9} - 0.04981 \right)
\] (2-15)

After this, the amounts of gas adsorbed (\( n \)) for various values of partial pressures are estimated. The differential of the adsorbed amount with respect to the pore width (\( \frac{dn}{dL} \)) is plotted vs. \( L \), yielding the micropore size distribution. The HK method is not applicable for calculating micropore diameters larger than 1.5 nm. The HK method assumes abrupt pore filling; therefore it treats the filling of partially filled pores as the filling of new pores; this leads to some inaccuracies in the pore size distribution calculated by this method.

\[
\log W = \log (V_0 \rho) - K \log \left( \frac{P}{P_0} \right)
\] (2-16)

The micropore volume can also be calculated by a variety of methods, but in this thesis only the Dubinin–Radushkevich method will be discussed. Here \( W \) is the weight absorbed, \( \rho \) is the liquid adsorbate density (extracted from the sorption isotherm), \( K \) is a constant determined by the shape of the pore size distribution, and \( V_0 \) is the micropore volume. A plot of \( \log W \) vs. \( \log (V_0 \rho) \) should give a straight line, and the intercept of this straight line can be used to calculate the micropore volume.
2.3 Lithographic Techniques

Photolithography and electron beam lithography (EBL) are the primary techniques used to prepare patterns on substrates. In an industrial setting, photolithography equipment is able to reach resolutions of ~32 nm. However, at the Penn State Nanofabrication Facility, the photolithography equipment is only capable of achieving ~600 nm resolution. We used electron beam lithography to fabricate metallic gratings since our samples had feature sizes below 600 nm. In our process, we use electron beam lithography to define the pattern of interest in a photoresist layer. We then utilize reactive ion etching to transfer the pattern into a silicon wafer. Finally, the patterned silicon wafer was used as a template to replicate noble metal gratings.

2.3.1 Synthesis of Metallic Gratings by Electron Beam Lithography

Electron beam lithography is a widely used technique to prepare nanostructured materials. It is a very flexible approach which can prepare patterns with dimensions from 7 nm- several microns. EBL prepares patterns by exposing an electron sensitive resist material to a focused, high energy electron beam. Exposure to the beam alters the material’s properties; it allows the chemically region to be selectively dissolved in a solvent (positive resist) or withstand dissolving in a solvent (negative resist). The resultant pattern embedded in the photoresist is used as a mask. This mask can then be used as a template for etching into the underlying substrate, or as a region where some material can be selectively grown.

In our process we etched the underlying silicon layer with reactive ion etching, yielding a silicon grating. We then used the silicon grating as a template to replicate noble metal gratings as shown in Figure 2-5. We typically evaporate a metal such as gold or silver over the patterned metal grating, we then attach an epoxy resin glue to the topside of the gold surface to adhere it to
a substrate, finally we strip off the substrate and the gold is removed from the patterned silicon yielding a metallic grating.

2.3.2 Reactive Ion Etching

Reactive ion etching is used to transfer the pattern from the photoresist into the silicon. Reactive ion etching utilizes plasma to remove material from a masked area of the silicon wafer, allowing one to imprint the pattern of the mask into a substrate. The depth of this imprinted pattern can is usually controlled by the etch time.

For our samples we used chlorine gas to etch into the silicon wafer. We specifically chose chlorine because it allows one to etch an anisotropic profile into the silicon wafer.\textsuperscript{11} Gases such as CF\textsubscript{4} are isotropic etchants; isotropic etchants etch under the mask layer, leading to undercut.\textsuperscript{11} Anisotropic etchants allow the depth and duty cycle of the grating to be controlled independently.

2.3.3 Nanosphere Lithography

Nanosphere Lithography is an inexpensive technique which allows one to produce various nanostructure arrays with controlled shape, sizes, and periodicity.\textsuperscript{12} Usually polystyrene or silica spheres are assembled as a hexagonally close-packed monolayer on a substrate of choice.\textsuperscript{12, 13} The diameter of the spheres controls the periodicity of the structure cast from the sphere template. The close-packed polystyrene spheres are usually assembled by drop casting, spin coating, or by shadow sphere lithography.\textsuperscript{14-16} In the first two cases, the meniscus of the evaporating solvent forces the spheres to self-assemble into a close-packed layer.\textsuperscript{17}
Figure 2-5. Process flow for fabrication of metallic gratings by template stripping.

Figure 2-6. The image on the left shows the etch profile for isotropic etching; there is significant undercut below the mask. The image on the right shows the etch profile for anisotropic etching.
We prepared close-packed polystyrene monolayers by the shadow lithography method.\textsuperscript{16} In brief, the spheres are floated at the air-water interface and driven together by the addition of surfactant to the water surface. The floating monolayer is allowed to dry over a substrate, and after elimination of the liquid the closed packed monolayer is transferred to the substrate. Both techniques create polycrystalline films, and these films usually have some line defects and point defects.

The close-packed monolayers can be used to fabricate a variety of nanostructures.\textsuperscript{12, 19-21} If a material is directly evaporated over the close-packed monolayer, ordered particle arrays will be formed. The beads can also be shrunken by oxygen etching, followed by evaporation of a material over the template yielding a nano-hole array. The technique is quite flexible, and allows one to prepare various ordered patterned nanostructures over large areas.
Figure 2-7. Processes of sphere assembly into ordered, close-packed films. a) This image depicts assembly of particles by meniscus forces. This technique can be used to grow particle monolayers and multilayers. b) This schematic depicts the shadow sphere lithography process; it shows a closed packed polystyrene monolayer floating on top of the air-water interface. (ref. 18)
References


Chapter 3 Broadband light absorption with multiple surface plasmon polariton waves excited at the interface of a metallic grating and photonic crystal

3.1 Introduction

A one-dimensional (1D) metallic grating is an efficient reflector of light, except when the magnetic field vector of the incident light is parallel to the grating lines and the angle of incidence \( \theta \) has a particular value. Then, enhanced light absorption arises from the excitation of collective oscillations of conduction electrons near the grating’s surface. The coupling generates quasiparticles called surface plasmons that are confined to the vicinity of the metal/air interface. This resonant phenomenon can be analyzed classically in terms of a surface-plasmon wave by solving Maxwell’s equations for time-harmonic fields. A similar phenomenon occurs when the air above the grating is replaced by a homogeneous, isotropic dielectric material of sufficient thickness. Then the quasiparticles are called surface plasmon-polaritons (SPP) and their classical equivalent is the SPP wave.

SPP waves are commonly exploited for sensing\(^1\) and biosensing\(^2\), optical filtering\(^3\), and optical data storage.\(^4\) But perhaps their most exciting applications in recent years have been for photovoltaics\(^5\), photoelectrochemical cells\(^6\), solar fuel production\(^7\), and solar thermal photovoltaics.\(^8\) Resonant absorption manifested as the excitation of SPP waves has now been investigated for more than three decades as a way of maximizing the conversion of solar light into electricity. It is used in metal grating-backed thin layers of crystalline silicon (\(\sim 5 \mu m \) thick)\(^9\) and amorphous silicon (\(\sim 0.5 \mu m \) thick),\(^10\) which can replace traditionally much thicker (\(\sim 100-\mu m \)) layers of crystalline silicon.

Resonant absorption at the interface of a 1D metallic grating and a homogeneous dielectric material occurs with \(p\)-polarized light (\(i.e., \) light with its magnetic field vector parallel
to the grating lines) but not with s-polarized light (electric field vector parallel to the grating lines). \textsuperscript{2,11} Thus, the SPP-wave mode is \textit{p} polarized but cannot be \textit{s} polarized. The optical energy is confined to a sub-wavelength thickness in the dielectric material, \textsuperscript{5,11,12} and only a single SPP-wave mode can be excited at any given free-space wavelength $\lambda_o$ over a narrow range of the angle of incidence.\textsuperscript{1,11} Hence, the experimental absorptance $A$ ($A=1-R-T$, where $R$ and $T$ are the reflectance and transmittance, respectively) of unpolarized broadband light is considerably less than 50\% when a 1D metallic grating is employed.\textsuperscript{5} To address this problem of polarization sensitivity, light trapping structures that have angular insensitivity and broadband absorption have been researched in recent years. These structures typically employ two-dimensional (2D) metallic gratings that lower the polarization sensitivity by converting some of the $s$-polarized light to $p$-polarized light.\textsuperscript{12,17} A strategy to decrease angular sensitivity is to employ metal-insulator-metal (MIM) layers.\textsuperscript{14-16} However, MIM structures are highly dissipative because of short SPP-wave propagation lengths and large confinement factors.\textsuperscript{11} Because of the loss of optical energy within the metal, these structures are of limited use for photovoltaics, which can be efficient only if most of the light is absorbed within the semiconductor.\textsuperscript{9,10}

The trapping of light by grating structures can become more efficient if the homogeneous dielectric material is replaced by a periodic multilayer, \textit{i.e.}, a 1D photonic crystal (PC) with piecewise homogeneous refractive index in the thickness direction. In this case, some recent studies have shown that both incident $p$- and $s$-polarized light can excite SPP waves,\textsuperscript{18,19} even when the wave vector of the incident light is wholly perpendicular to the grating lines. In these reports, the metal/dielectric interface was planar and a prism-coupled configuration,\textsuperscript{20-22} widely used for optical sensing, was employed. Only a \textit{single} $p$-polarized SPP-wave mode and at most a \textit{single} $s$-polarized SPP-wave mode were observed experimentally at any $\lambda_o$ within the photonic bandgap of the periodic multilayer. However, a theoretical study on a canonical boundary-value problem has shown that if the dielectric material has a sinusoidally graded refractive index in the
thickness direction, then multiple $p$-polarized and multiple $s$-polarized SPP-wave modes can be excited at specific wavelengths with high efficiency.$^{23,24}$ This prediction was shown theoretically to hold well when the periodic dielectric is backed by a metallic grating,$^{25}$ but it has not been experimentally validated.

In this paper, we provide the first experimental evidence that multiple $p$- and multiple $s$-polarized SPP-wave modes can be excited over a broad spectral range, in a 1D PC backed by a 1D metallic grating. In our experiments, the wave vector of the incident light was oriented perpendicular to grating lines, so that incident $p$- (resp. $s$-) polarized light could excite only $p$ (resp. $s$) polarized SPP-wave modes. The chosen PC was a non-absorbing, periodic dielectric material of two or three period thickness. Accompanying theoretical results show that many of the SPP-wave modes are weakly localized to the interface of the metal and the PC, display field enhancements that spread throughout the entire two or three periods of the PC, and have very long propagation lengths (on the order of hundreds of micrometers). The latter implies that less energy will be dissipated in the metal when the non-absorbing dielectric material is replaced by a light absorber, such as the semiconductor layers of a photovoltaic cell. Not only SPP-wave modes but also waveguide modes (whose characteristics depend strongly on the thickness of the 1D PC)$^{25,26}$ are excited and evidently contribute to broadband absorptance. The efficient coupling of light into these structures has strong implications for performance enhancement of sensors,$^1$ photovoltaics,$^2$ and solar thermal photovoltaics.$^8$
3.2 Materials and Methods

3.2.1 Fabrication of metallic gratings.

Metallic gratings were fabricated as described in detail elsewhere. In brief, silicon wafers were patterned by electron beam lithography on ZEP520A photoresist (Zeon, Tokyo) with the inverse pattern of the desired metallic grating. The pattern in the photoresist was transferred into the silicon by inductively coupled reactive ion etching on a Versalock 700 (Plasma-Therm, St. Petersburg, FL) with pure Cl₂ gas. The photoresist dissolved in Nano strip, a commercially available resist remover, with the assistance of a bath sonicator. Gold was thermally evaporated on the patterned silicon wafer at room temperature with a base pressure <1x10⁻⁶ at 0.1 nm/s. The gold film was attached to a glass slide using EpoTek 377 epoxy (Epoxy Technology, Billerica, MA). The epoxy resin was cured by a seven-day thermal treatment at 125 °C. The gold film was released from the silicon wafer with a razor blade yielding a gold grating glued to a glass slide. All gratings used in this work were 6 x 6 mm in size.

3.2.2 Fabrication of periodic dielectric multilayers.

Periodic multilayers of silicon oxide/oxynitride were grown directly on the gold gratings by plasma-enhanced chemical vapor deposition on a Cluster Tool (Applied Materials, Santa Clara, CA) at a susceptor temperature of 220 °C. Ammonia, silane and nitrous oxide were used in varying ratios to deposit layers with specific refractive indices. All layers were deposited at a pressure of 3.5 Torr and a power density of 0.955 W/cm².
3.2.3 Electron microscopy.

SEM images were collected on a Leo 1530 FESEM (Carl Zeiss, Oberkochen, Germany), and TEM images were collected on a Phillips 420 TEM (Phillips, Amsterdam, The Netherlands).

3.2.4 Optical characterization of dielectric and gold layers.

The complex refractive index of each layer, whether dielectric or metallic, was calculated from data obtained by using an RC2 spectroscopic ellipsometer (Woollam, Lincoln, NE). For these measurements, a thin film of the same nominal thickness and composition as those grown for the multilayer structures (Fig. 1) was deposited under identical conditions on a glass slide or silicon wafer. The spot size used for collection of the data was 3.5 x 3.5 mm.

3.2.5 Parameters for theoretical simulations.

For computation of absorptances using the rigorous coupled-wave approach of the structure containing gold gratings of 350 nm period, 80% duty cycle, 50 nm depth, the unit cell profile of the gratings was approximated by a sinusoid, as suggested by cross-sectional views (not presented) of the grating shown in Fig. 1b. The grating region was divided into 2-nm-thick slices parallel to the mean plane of the metal/dielectric interface, and each slice was considered to be homogeneous. For computations, 31 Floquet harmonics were used.

3.2.6 Measurements of specular and non-specular reflectances.

Specular reflectance measurements were performed on a Lambda 950 UV-Visible spectrometer (Perkin Elmer, Waltham, MA) with a Universal Reflectance accessory.
Measurements were performed in steps of 1 nm for $\lambda_o$ and 1° for $\theta$. The non-specular reflectance of order -1 was measured using a dual rotary stage arrangement. Monochromatic light, in 5 nm intervals, was selected from a broadband source (150 W Xe arc lamp, Oriel-Newport) through a single pass monochromator. The intensity of the monochromatic beam was determined from the specular reflectance from a calibrated silver mirror in place of the grating and a silicon photodiode (Hamamatsu Corporation, S1226-44BQ, 3.6 mm x 3.6 mm) at a nominal distance of 110 mm from the mirror/grating plane. At this distance, the silicon photodiode detector occupies a subtended angle of approximately 1.9°. The intensity of the non-specular, -1 order reflected light was measured using the same silicon photodiode. The intensity of the non-specularly reflected light was obtained from the ratio of the grating-detector current to the calibrated current measured from the Ag mirror.

### 3.3 Results and Discussion

#### 3.3.1 1D Grating/Periodic Dielectric Structures

The test structure used in this study is shown schematically in Figure 3-1. Here, light is incident from air on a 1D PC that consists of 9 different layers in each period and is backed by a 1D metallic grating. The dielectric layer neighboring the grating and filling its troughs is made of silicon nitride ($\text{Si}_3\text{N}_4$); the next 7 layers are made of silicon oxynitride {($\text{Si}_3\text{N}_4$)$_a$(SiO$_2$)$_{1-a}$}, each with a different value of $a$; and the 9th (top) layer is made of silicon oxide (SiO$_2$). Figure 3-2 gives the measured refractive indexes of all nine dielectric materials as functions of $\lambda_o$. The imaginary part of the refractive index was below $10^{-4}$ in the spectral regime studied for all the dielectric materials, and it was therefore ignored in the calculations.
Top-down scanning electron microscope (SEM) images and cross-sectional transmission electron microscope (TEM) images of structures fabricated and characterized in this study are shown in Figure 3-4-1 b-e. Whereas the vapor-deposited dielectric layers in the shallow grating structure shown in Figure 3-4-1d appear more or less planar, those shown in Figure 3-1e, which is a structure with a deeper metallic grating, are more conformal.

Due to the periodicity of the metallic grating, the Bloch theorem\textsuperscript{27,28} mandates that the reflected and the transmitted fields must contain both specular and non-specular components when the structure is illuminated by a monochromatic plane wave. Furthermore, the fields induced inside the structure must consist of Floquet harmonics of negative, zero, and positive orders.\textsuperscript{29} It is the panoply of Fourier harmonics that facilitates the excitation of multiple SPP-wave modes in the grating-coupled configuration under investigation.\textsuperscript{30-32} Because the metallic gratings are \textasciitilde200 nm thick, they do not transmit light in the wavelength range studied and hence \(T=0\) in all experiments.

Calculations of the reflected field were made for \(0^\circ < \theta < 70^\circ\) (where \(0^\circ\) is defined as normal incidence) for \(\lambda_0\) between 400 and 1000 nm using the rigorous coupled-wave approach.\textsuperscript{25,29} The measured refractive index of the dielectric materials, shown in Figure 3-2, was used in the calculations along with the data in Figure 3-3 for the metallic grating. Over most of the domain chosen for the calculations and for incident light of both \(p\)- and \(s\)-polarization states, the non-specular reflected components were very weak for the structure that has a shallow grating (Fig. 3-1 d), as can be deduced from comparing Figures 3-4 and 3-5. Accordingly, only the specular reflectances \(R_{0p}\) and \(R_{0s}\) were measured at angles between 9 and 55\(^\circ\) in order to determine the absorptances \(A_p \approx 1 - R_{0p}\) and \(A_s \approx 1 - R_{0s}\). We calculated absorptances for the structure shown in Figure 3-1d when the PC contained either two or three periods. Peaks in the plots of \(A_p\) and \(A_s\) vs. \(\theta\) (resp. \(\lambda_0\)) for fixed \(\lambda_0\) (resp. \(\theta\)) were identified. Each absorptance peak whose \(\lambda_0\)-location (at a fixed \(\theta\)) or \(\theta\)-location (at a fixed \(\lambda_0\)) depended very weakly on the number
Figure 3-1. (a) Schematic of a 1D metallic grating coupled to a multilayer dielectric material, which forms one period of a 1D PC. (b) Top down SEM image of a gold grating (350 nm period, 80% duty cycle, 50 nm depth). (c) Top down SEM image of a gold grating (350 nm period, 50% duty cycle, 93 nm depth). (d) Cross-sectional TEM image of a gold grating (350 nm period, 80% duty cycle, 50 nm depth) coupled to a 1D PC with two periods, each consisting of nine layers. (e) Cross-sectional TEM image of a gold grating (350 nm period, 50% duty cycle, 93 nm depth) coupled to a 1D PC with three periods, each consisting of nine layers. The dielectric layers in (d) exhibit some roughness but are quite planar, but those in (e) are quite conformal to the metallic grating. The thickness direction is along the z-axis, the grating plane is the xz plane, the grating lines are directed along the y-axis, the propagation direction of the incident light lies wholly in the xz plane with the angle of incidence $\theta$ measured with respect to the z-axis, and SPP waves propagate along the x-axis in the xy plane.
of periods of the PC beyond a threshold indicated the excitation of an SPP-wave mode, which we then confirmed by the solution of a canonical boundary-value problem. At a fixed $\lambda_o$, we also determined the order $n$ of the Floquet harmonic corresponding to each excited SPP-wave mode from the canonical boundary-value problem.

### 3.3.2 Excitation of Multiple SPP Waves in Shallow 1D Grating Structures.

Figure 3-4 compares experimental and theoretical results for a gold metallic grating with a period of 350 nm and 50 nm tall rectangular raised sections that span 80% (duty cycle) of each period. The metallic grating is shown alone in Figure 3-1b and the entire structure comprising the grating and the PC is shown in cross-section in Figure 3-1d. Figures 3-4a and 3-4d show the calculated $\theta$-locations and $\lambda_o$-locations of $p$- and $s$-polarized SPP-wave modes for $\lambda_o$ between 400 and 1000 nm. As many as ten $p$- and eight $s$-polarized SPP-wave modes are theoretically possible for this structure. Density plots of theoretically predicted and experimentally measured absorptances as functions of $\theta$ and $\lambda_o$ are presented in Figures 3-4 b,c and 3-4e,f for incident $p$- and $s$-polarized light, respectively, for the two-period PC backed by the grating. The loci of absorptance peaks in the contour plots in Figures 3-4b,c closely resemble the lines in Figure 3-4a, and the same statement can be made for Figure 3-4e,f and 3-4d. Remarkably, the experimental data confirm the existence of nine of ten $p$-polarized SPP-wave modes predicted theoretically. All four modes identified by $n = -1$, two of three modes identified by $n = +1$, and one of three modes identified by $n = -2$ in Figure 3-4a are clearly evident in Figure 3-4c. The existence of the two other modes identified by $n = -2$ in Figure 3-4a can be discerned experimentally in a high-resolution version of Figure 3-4c, but their excitation is weak because of the strong background absorption at $\lambda_o < 500$ nm caused by waveguide modes superimposed on the interband transitions of gold. The onset of gold’s interband transitions lies below $\lambda_o < 600$ nm, but the
Refractive indexes ($n_d$) of nine silicon oxide/oxynitride layers, measured by spectroscopic ellipsometry. The first layer in each period of the PC is the one closest to the metallic grating and the ninth layer is the farthest.

Figure 3-3. Real ($n_m$) and imaginary ($k_m$) parts of the refractive index of gold, determined by spectroscopic ellipsometry.
Figure 3-4. Optical absorptance of a gold grating (350 nm period, 80% duty cycle, 50 nm depth) coupled to a 1D PC. (a,d) Calculated angles of incidence for absorptance peaks vs. free-space wavelength $\lambda_o$ when either (a) $p$-polarized or (d) $s$-polarized SPP waves are excited. (b,c) Density plots of absorptance as a function of $\theta$ and $\lambda_o$ for incident $p$-polarized light obtained by (b) theory and (c) experiment. (e,f) Density plots of absorptance as a function of $\theta$ and $\lambda_o$ for incident $s$-polarized light obtained by (e) theory and (f) experiment.
Figure 3-5. Calculated optical absorptance of a gold grating (350 nm period, 80% duty cycle, 50 nm depth) coupled to a two- or three-period thick PC. The total reflectance and transmittance (including specular and non-specular components) were calculated using the rigorous coupled wave approximation and then absorptance was computed as $A = 1 - (\text{total reflectance}) - (\text{total transmittance})$. (a,b) Density plots of absorptance as a function of $\theta$ and $\lambda_o$ for incident $p$-polarized light for (a) two- and (b) three-period PCs. (c,d) Density plots of absorptance as a function of $\theta$ and $\lambda_o$ for incident $s$-polarized light for (c) two- and (d) three-period PCs. Comparison of the results with those in Figure 3-4 shows that the effect of non-specular reflectance is negligible for this structure which has a shallow grating.
transitions do not completely dominate the signal until $\lambda_o < 500$. In contrast, the experimental data confirm the existence of only two of eight $s$-polarized SPP-wave modes. Both of these modes are identified by $n = -1$ in Figure 3-4f. Both theory and experiment indicate that $s$-polarized SPP-wave modes are excited weakly in comparison to the $p$-polarized SPP-wave modes in the structure of Figure 3-1d. This suggests that this structure is not very efficient in using incident $s$-polarized light to excite SPP-wave modes. This conclusion holds even when the number of periods of the PC is increased from two to three, as can be seen by comparing the density plots in Figure 3-4b,c,e,f (two periods) with their counterparts in Figure 3-5 (three periods).

### 3.3.3 Differentiating p- and s-Polarized SPP Modes from Waveguide Modes.

To provide greater clarity about the excitation of multiple SPP-wave modes with respect to the number of periods in the PC, experimentally measured and theoretically predicted absorptances are presented as functions of $\lambda_o$ for $\theta = 43^\circ$. These absorptances are shown for two- and three-period PCs in Figures 3-6 and 3-7, respectively. Every absorptance peak whose $\theta$-location at fixed $\lambda_o$ remains invariant with the addition of the third period of the photonic crystal definitely corresponds to the excitation of SPP-wave modes. Conversely, the peaks whose $\theta$-values are highly sensitive to the total thickness of the PC are waveguide modes. The energy of an SPP-wave mode is localized, weakly or strongly, to the metal-dielectric interface, but the energy of a waveguide mode is more evenly distributed throughout the gold film with two or three periods of the PC is presented in Figure 3-8. No invariant peaks are observed, because only waveguide modes can be excited when the grating is absent. Furthermore, the absorptance of this control sample is nearly null for both polarization states for $\lambda_o > 600$ nm, indicating that the PC or Fabry-Perot interference modes do not give rise to significant absorption of light at wavelengths
longer than the interband transitions of gold.

Inspection of Figures 3-6 and 3-7 reveals that some SPP-wave modes shift slightly with the addition of a third period to the PC. In Figure 3-6a, we observe an SPP-wave mode in the vicinity of $\lambda_o \sim 600$ nm that is not evident unless three periods of the PC are present above the metallic grating. Furthermore, in the same figure we observe a significant shift of an SPP-wave mode from $\lambda_o = 660$ nm to $\lambda_o = 648$ nm when the thickness of the PC is increased from two to three periods. These SPP-wave modes, denoted by open arrows in Figure 3-6, are weakly localized to the metal/dielectric interface and, therefore, are highly sensitive to the dielectric environment above the metallic grating. Figures 3-9a-d shows the calculated spatial profiles of the magnitudes of the components of the electric field. It is evident that the SPP-wave modes thickness of the dielectric layers. Downward arrows in Figures 3-6 and 3-7a identify five $p$-polarized SPP-wave modes for $\lambda_o > 500$ nm. The interband transitions of gold\textsuperscript{11} prevent the resolution of SPP-wave modes at wavelengths shorter than 500 nm. The broad peak at $\lambda_o = 520$ nm corresponds to the excitation of two co-propagating SPP-wave modes as Floquet harmonics of orders $n = 1$ and $n = -2$. For the purpose of comparison, the measured absorptance of a flat excited with $p$-polarized light do not contain any electric field oriented parallel to the y direction; therefore SPP waves excited with $p$-polarized light are completely $p$-polarized in nature. Although the contour plots show that the electric field strength is maximized near the corners of the metallic grating, a significant portion of the field extends into all three periods of the dielectric stack. Figure 3-9e shows the variation along the thickness direction (z-axis) of the component of the time-averaged Poynting vector in the direction of propagation, taken at a slice the number of periods of the PC is increased from two to three, consistent with their localization to the metal/PC interface. In contrast, the SPP-wave mode at $\lambda_o = 648$ nm exhibits a large shift because its Poynting vector is distributed into all three layers of the PC.
Figure 3-6. Measured optical absorptance of a gold grating (350 nm period, 80% duty cycle, 50 nm depth) coupled to a 1D PC at $\theta = 43^\circ$. (a,b) Measured absorptance as a function of $\lambda_o$ when $\theta = 43^\circ$ for incident (a) $p$-polarized light and (b) $s$-polarized light. The 1D PC has either two (solid lines) or three (dashed lines) periods. Downward arrows denote the absorptance peaks that correspond to the excitation of SPP-wave modes.
Figure 3-7. Calculated optical absorptance of a gold grating (350 nm period, 80% duty cycle, 50 nm depth) coupled to a 1D PC at $\theta = 43^\circ$. (a,b) Calculated absorptance as a function of $\lambda_0$ when $\theta = 43^\circ$ for incident (a) $p$-polarized light and (b) $s$-polarized light. The 1D PC has either two (solid lines) or three (dashed lines) periods. Downward arrows denote the absorptance peaks that correspond to the excitation of SPP-wave modes. See Figure 3 for the corresponding experimental data.
The absorptance peaks identified by downward arrows in Figures 3-6b and 3-8b indicate the excitation of two different \( s \)-polarized SPP-wave modes at \( \theta = 43^\circ \). An SPP-wave mode in Figure 3-6b at \( \lambda_o = 660 \text{ nm} \) when the PC has two periods blue-shifts to \( \lambda_o = 655 \text{ nm} \) with the addition of a third period. From Figure 3-10b, it is clear that this SPP-wave mode is completely \( s \)-polarized since its \( E_x \) and \( E_z \) components are zero. Figure 3-10c presents the variation along \( z \) of the \( x \)-directed component of the time-averaged Poynting vector of this SPP-wave mode and an SPP-wave mode at \( \lambda_o = 665 \text{ nm} \) for the three-period structure. As expected from the significant blue shift, this SPP-wave mode is weakly localized to the metal/dielectric interface. The electric field has a maximum magnitude not in the mean plane of the periodically corrugated metal/dielectric interface but in the middle of the first period of the dielectric. This characteristic is very different from that of the \( p \)-polarized SPP-wave modes in Figure 3-9c. The \( x \)-directed component of the time-averaged Poynting vector of the SPP-wave mode at \( \lambda_o = 767 \text{ nm} \) is very small because it is weakly excited. Each panel in Figure 3-4 shows that different SPP-wave modes can be excited at a single \( \lambda_o \) by light incident at different angles. For instance, when \( \lambda_o = 668 \text{ nm} \), two \( p \)- and two \( s \)-polarized SPP-wave modes are excited, as shown in Figure 3-11. Corresponding plots of calculated absorptances are shown in Figure 3-12. These SPP-wave Downward arrows denote the absorptance peaks that correspond to the excitation of SPP-wave modes.

### 3.3.4 Propagation Lengths of SPP Waves.

In the simple test structures investigated in this study, any light that is not reflected must be absorbed because the metal grating is very thick. Because the dielectric material is non-absorbing, all of the absorption therefore takes place in the gold gratings. However, in real applications in which the dielectric material absorbs light, the SPP wave propagation length is an important
a) \[ \theta = 8^\circ, s \text{ polarization} \]

b) \[ \theta = 8^\circ, p \text{ polarization} \]

c) \[ \theta = 43^\circ, s \text{ polarization} \]
Figure 3-8. Measured optical absorptance of a 1D PC on flat gold. (a,b) Absorptance as a function of $\lambda_o$ at $\theta=8^\circ$ for incident (a) $p$-polarized light and (b) $s$-polarized light. (c,d) Absorptance as a function of $\lambda_o$ at $\theta=43^\circ$ for incident (c) $p$-polarized light and (d) $s$-polarized light. The 1D PC has either two (solid lines) or three (dashed lines) periods.
a) $\theta = 43^\circ, \lambda_o = 648\,\text{nm}, \, p\, \text{pol}$

b) $\theta = 43^\circ, \lambda_o = 648\,\text{nm}, \, p\, \text{pol}$

c) $\theta = 43^\circ, \lambda_o = 648\,\text{nm}, \, p\, \text{pol}$

d) $\theta = 43^\circ, \lambda_o = 648\,\text{nm}, \, p\, \text{pol}$

e) 

- metal
- 1st period
- 2nd period
- 3rd period

- $\lambda_o=901\,\text{nm}$
- $\lambda_o=627\,\text{nm}$
- $\lambda_o=648\,\text{nm}$
Figure 3-9. Field profiles of \( p \)-polarized SPP-wave modes for a gold grating (350 nm period, 80% duty cycle, 50 nm depth) coupled to a 1D PC. (a-d) Contour plots of magnitudes of (a) the electric field, (b) the x-component of the electric field, (c) the z-component of the electric field, and (d) the y-component of the electric field, calculated as functions of \( x \) and \( z \) when \( \lambda_o = 648 \) nm, \( \theta = 43^\circ \), and an SPP-wave mode is excited by incident \( p \)-polarized light. (e) Calculated variation of the \( x \)-directed component of the time-averaged Poynting vector along the \( z \)-axis at \( x = 175 \) nm (i.e., in the \( xz \) plane bifurcating a protrusion) for \( \theta = 43^\circ \) at \( \lambda_o = 901 \) nm, 627 nm, and 648 nm when \( p \) polarized incident light excites an SPP-wave mode. The dashed lines in (e) denote either the mean metal/dielectric interface or the end of a period of the PC. All calculations were made for an incident plane wave with an electric field of amplitude 1 V/m. Modes differ in the phase speed \( v_p = c / (\frac{n \lambda_0}{L} + \sin \theta) \), where \( L \) is the period of the grating, as they are excited at different angles of incidence as Floquet modes of different orders \( n \), \( c \) being the speed of light in free space. An increase in the number of periods in the PC can cause a small increase or decrease in \( \theta \) for the excitation of a certain SPP-wave mode, but that value of \( \theta \) stabilizes after the number of periods crosses a threshold, according to theoretical data shown in a previous paper.\(^{20} \)
a) \( \theta = 43^\circ, \lambda_c = 665 \text{ nm}, \ s \text{ pol} \)

b) \( \theta = 43^\circ, \lambda_c = 665 \text{ nm}, \ s \text{ pol} \)

c) Figure 3-10. Field profiles of \( s \)-polarized SPP-wave modes for a gold grating (350 nm period, 80\% duty cycle, 50 nm depth) coupled to a 1D PC. (a-b) Contour plots of the magnitude of (a) the electric field (the \( y \)-component of the electric field) and (b) the \( x \)-component (or \( z \)-component) of the electric field. (c) Calculated variation of the \( x \)-directed component of the time-averaged Poynting vector along the \( z \)-axis at \( x = 175 \text{ nm} \) (\( i.e. \), in the \( xz \) plane bifurcating a protrusion) for \( \theta = 43^\circ \) at \( \lambda_c = 767 \text{ nm} \) and 665 nm when \( s \)-polarized incident light excites an SPP-wave mode. The dashed lines in (c) denote either the mean metal/dielectric interface or the end of a period of the PC. All calculations were made for an incident plane wave with an electric field of amplitude 1 V/m.
Figure 3-11. Measured optical absorptance of a gold grating (350 nm period, 80% duty cycle, 50 nm depth) coupled to a 1D PC at $\lambda_o = 668$ nm. (a,b) Measured absorptance as a function of $\theta$ when $\lambda_o = 668$ nm for incident (a) $p$-polarized light or (b) $s$-polarized light. The 1D PC has either two (solid lines) or three (dashed lines) periods. Downward arrows denote the absorptance peaks that correspond to the excitation of SPP-wave modes.

a)
Figure 3-12 Calculated optical absorptance of a gold grating (350 nm period, 80% duty cycle, 50 nm depth) coupled to a 1D PC at $\lambda_o = 668$ nm. (a,b) Calculated absorptance as a function of $\theta$ when $\lambda_o = 668$ nm for incident (a) $p$-polarized light and (b) $s$-polarized light. The 1D PC has either two (solid lines) or three (dashed lines) periods.
Longer propagation lengths imply that a greater fraction of trapped light will be absorbed in the absorbing dielectric layers rather than in the metal. Figure 3-13a shows the calculated propagation lengths of the multiple \( p \)- and \( s \)-polarized SPP waves excited in the structure shown in Figure 3-1d. The labeling of the SPP waves is the same as in Figure 3-4a,d to allow easy comparison of the propagation lengths of the SPP-wave modes. One of the \( p \)-polarized SPP wave-modes, denoted as \( p_2 \), has a propagation length of 1500 \( \mu m \) (1.5mm) at \( \lambda_o = 800 \) nm. Most of the other \( p \)-polarized SPP-wave modes have propagation lengths that are 100 \( \mu m \) or longer when \( \lambda_o > 600 \) nm. The SPP-wave modes on the branch \( p_1 \) have very short propagation lengths for \( \lambda_o < 600 \) nm; however, when \( \lambda_o > 600 \) nm, these modes can have propagation lengths up to \( \sim 5 \mu m \). Due to the low propagation length of the \( p_1 \) SPP mode over the entire spectral range, this SPP mode must be highly confined to the metal/dielectric interface.

Two of the \( s \)-polarized SPP modes, denoted as \( s_1 \) and \( s_2 \), have propagation lengths of 80 \( \mu m \) or longer when \( \lambda_o > 600 \) nm. The other \( s \)-polarized SPP mode denoted as \( s_3 \) in Figure 3-13a is excited below \( \lambda_o < 490 \) nm; the propagation length of this mode is short (\( \sim 4.8 \mu m \)) because of strong absorption of light by gold in the region of the interband transitions. Figure 3-13b shows that the propagation lengths of all the SPP-wave modes converge to 2-5 \( \mu m \) for \( \lambda_o < 500 \) nm because of this effect; an expanded view of this region is shown in Figure 3-13b. Figure 3-13c shows the propagation lengths for a structure in which the PC is replaced by a uniform slab of silicon oxide or silicon nitride. In this case, the propagation lengths are shorter than 100 \( \mu m \) across the entire spectral range of interest. The important conclusion is that multiple SPP modes generated in the PC can propagate farther because light is not, in general, as strongly localized to the metal-dielectric interface as it is in uniform dielectric structures.
3.3.5 Excitation of s- and p-Polarized SPP Waves in Deep 1D Grating Structures.

The experimental and theoretical results described heretofore establish the broadband excitation of multiple SPP-wave modes using both p- and s-polarized light, but the latter modes are quite weak and are therefore of limited utility for light trapping in the dielectric layers. In order to improve the excitation efficiency of the s-polarized SPP-wave modes, we redesigned the gold grating to have 93 nm depth and 50% duty cycle, keeping the grating period $L$ still fixed at 350 nm (Figure 3-1c). When the PC was deposited on this grating, the dielectric layers conformed to the grating’s corrugations, as shown in Figure 3-1e for a three-period PC.

The redesigned grating yields stronger excitation of both s- and p-polarized SPP-wave modes and waveguide modes, according to the density plots shown in Figure 3-14 for two- and three-period structures. SPP-wave modes of either polarization state that are excited as Floquet harmonics with $n > 0$ are now excited with higher efficiency than in Figure 3-4, even in the spectral regime of high background absorption due to the interband transitions of gold. Modes that are excited at $\lambda_o < 600$ nm as Floquet harmonic of the order $n=-1$ are overestimated by 5% -15% when $\theta> 40^\circ$ due to non-specular reflection (Figure 3-15). The optical response of this structure is very sensitive to the dielectric profile above the metallic grating. Reliable comparisons with theoretical predictions from the rigorous coupled-wave approach could not be accomplished for the deeper grating structure because the calculations are sensitive to several inputs: (i) the curves describing the shape of each conformal dielectric layer, (ii) variations in the thickness and the composition of each dielectric layer from one unit cell to another, and (iii) the aperiodicity of the corrugations of the metallic grating. A more realistic model would require several unit cells of the structure to be treated as one unit cell, but then computations could not be made within a reasonable period of time. These difficulties notwithstanding, theoretical contour plots for samples with two periods of the PC, calculated on the basis of the simple unit cell, are presented in Figure 3-16.
Figure 3-13. Calculated propagation lengths of SPP waves. (a) Calculated propagation lengths of $p$- and $s$-polarized SPP waves excited at the interface of a shallow 1D gold grating (350 nm period, 80% duty cycle, 50 nm depth) and a 1D PC. Inset shows an expanded view of the boxed region. (b) Expanded view of (a) showing the propagation lengths of SPP-wave modes for $\lambda_0 < 500$ nm. (c) Propagation lengths of SPP-wave modes when the PC layers are replaced by a uniform slab of silicon nitride or silicon dioxide.
Figure 3-17 shows the measured absorptances $A_p$ and $A_s$ as functions of $\lambda_o$ for $\theta = 8^\circ$ and $\theta = 43^\circ$ for two- and three-period PC structures. Similar plots, but as functions of $\theta$ for $\lambda_o = 670$ nm and $\lambda_o = 720$ nm, are provided in Figure 3-18. Four $p$-polarized SPP-wave modes and five $s$-polarized SPP-wave modes are excited at $\theta = 8^\circ$; likewise, five $p$-polarized and three $s$-polarized SPP-wave modes are excited at $\theta = 43^\circ$. More $p$-polarized SPP-wave modes are excited at higher $\theta$, but more $s$-polarized SPP modes are excited at lower $\theta$.

Figure 3-18 shows that two $p$- and two $s$-polarized SPP-wave modes are excited at $\lambda_o = 670$ nm, but only one SPP-wave mode of each polarization state is excited at $\lambda_o = 720$ nm. The excitation efficiencies of the $s$-polarized SPP-wave modes are higher at lower $\lambda_o$. Importantly, while the excitation efficiencies of the $s$-polarized SPP-wave modes are not as high as those of the $p$-polarized SPP-wave modes, they are clearly much higher than those of the $s$-polarized SPP-wave modes in the shallow grating structure shown in Figure 3-1d. Indeed, we conclude from Figures 3-14, 3-17, and 3-18 that the excitation efficiencies of $s$-polarized SPP-wave modes in the deeper grating structure of Figure 3-1-1e can approach 100% (i.e., $A_s \approx 1.0$). It is also likely that the redesigned structure supports more SPP-wave modes than identified in these figures. The weakly bound SPP-wave modes that are not invariant with the PC thickness require more accurate theoretical modeling to confirm their existence.
Figure 3-14. Measured optical absorptance of a gold grating (350 nm period, 50% duty cycle, 93 nm depth) coupled to a 1D PC. (a,b) Density plots of measured absorptance as a function of $\lambda_o$ and $\lambda_i$ for incident $p$-polarized light when the 1D PC has either (a) two or (b) three periods. (c,d) Density plots of measured absorptance as a function of $\theta$ and $\lambda_o$ for incident $s$-polarized light when the 1D PC has either (c) two or (d) three periods.
Figure 3-15. Non-specular reflectance of order $n = -1$ of unpolarized incident light from a gold grating (350 nm period, 50% duty cycle, 93 nm depth) coupled to a three-period thick PC when $\theta = 40^\circ$ and $45^\circ$. For $\theta \leq 35^\circ$, the maximum reflectance of the -1 order peak was less than 5%. 
Figure 3-16. Calculated optical absorptance of a gold grating (350 nm period, 50% duty cycle, 93 nm depth) coupled to a 1D PC. (a) Density plots of absorptance as a function of $\theta$ and $\lambda_o$ for incident $p$-polarized light obtained by theory. (b) Density plots of absorptance as a function of $\theta$ and $\lambda_o$ for incident $s$-polarized light obtained by theory. The PC has two periods. The calculated data should be taken as indicative but not exact for reasons explained in the text.
a) \(\theta = 8^\circ, p\) polarization

- \(2\) periods
- \(3\) periods

b) \(\theta = 43^\circ, p\) polarization

- \(2\) periods
- \(3\) periods

c) \(\theta = 8^\circ, s\) polarization

- \(2\) periods
- \(3\) periods

d) \(\theta = 43^\circ, s\) polarization

- \(2\) periods
- \(3\) periods
**Figure 3-17** Measured optical absorptance of a gold grating (350 nm period, 50% duty cycle, 93 nm depth) coupled to a 1D PC. (a,b) Measured absorptance as a function of $\lambda_o$ for incident $p$-polarized light, when $\theta$ is either (a) 8° or (b) 43°. (c,d) Measured absorptance as a function of $\lambda_o$ for incident $s$-polarized light, when $\theta$ is either (c) 8° or (d) 43°. The 1D PC has either two (solid lines) or three (dashed lines) periods. Downward arrows denote the absorptance peaks that correspond to the excitation of SPP-wave modes.
**Figure 3-18** Optical absorptance of a gold grating (350 nm period, 50% duty cycle, 93 nm depth) coupled to a 1D PC. (a,b) Measured absorptance as a function of $\lambda_o$ and $\theta$ when $\lambda_o = 670$ nm and the incident light is either (a) $p$ or (a) $s$ polarized. (c,d) Measured absorptance as a function of $\lambda_o$ when $\lambda_o = 720$ nm and the incident light is either (c) $p$ or (d) $s$ polarized. The 1D PC has either two (solid lines) or three (dashed lines) periods. Downward arrows denote the absorptance peaks that are likely to correspond to the excitation of SPP-wave modes.
3.4 Conclusions

We have theoretically modeled and experimentally demonstrated a new approach for broadband trapping of light as SPP-wave modes: an appropriately designed metallic-grating-backed periodic dielectric multilayer supports the existence of multiple SPP-wave modes of both $p$- and $s$-polarization states over a wide spectrum of free-space wavelengths. Significantly, we have successfully demonstrated that with proper design, $s$-polarized SPP-wave modes can be excited with high efficiency.

Solution of the time-harmonic Maxwell equations indicates that the fields of several SPP-wave modes are weakly localized to the periodically corrugated metal/dielectric interface. The weakness of the localization implies that the incident light energy can be more evenly distributed in a light-absorbing PC that is the active component of a sensor or solar cell. The long propagation lengths of many of the multiple SPP waves also indicate that less energy is dissipated in the metallic layer relative to structures with uniform dielectrics. Theory shows that the relationship between the number of SPP-wave modes that can be excited in a given spectral regime and the period of the PC is somewhat complicated.\textsuperscript{24} In this initial experimental study, we found that multiple SPP-wave modes are excited in a range of free-space wavelengths $\lambda_o$ comparable to the period of the PC. This effect remains to be explored and optimized for specific applications.

The materials used in this study are commonplace in nanotechnology. Given the broad interest in plasmonic nanostructures and photonic crystals, which can be fabricated from many different materials, the synergy that arises from their combination should be useful in many future optical applications.
References


Chapter 4 Effect of grating period on the excitation of multiple surface plasmon polariton waves guided by the interface of a metal grating and photonic crystal

4.1 Introduction

A surface plasmon-polariton (SPP) wave is an evanescent surface wave whose propagation is guided by the interface of a metal and a dielectric material.\(^1\) SPP waves have been studied intensively in recent years for a wide range of potential and actual applications such as chemical sensors,\(^2\) biological sensors,\(^3\) photovoltaics,\(^4\)\(^-\)\(^7\) photo-electrochemical cells,\(^8\) solar fuel production,\(^9\) and solar thermal photovoltaics.\(^10\)

Both the metal and the dielectric material are conventionally taken to be homogeneous. SPP waves can only be excited by \(p\)-polarized light when light is incident parallel to the grating vector of a one-dimensional (1D) metallic grating.\(^1\) Furthermore, only a single SPP-wave mode can be excited at a specific free-space wavelength \(\lambda_0\). The excitation of only a single \(p\)-polarized SPP-wave mode seriously limits this technique from being a viable choice for enhancement of light harvesting in solar cells, because incident \(s\)-polarized light is inefficiently used. Our recent theoretical\(^11\) and experimental\(^12\) studies have shown that multiple SPP-wave modes of both linear polarization states can be excited at the interface of a 1D gold grating and a 1D photonic crystal. Gold gratings with a fixed period but different depths and duty cycles were used to excite multiple SPP-wave modes. As expected, the absorptance of the metal-grating/photonic-crystal structure is highly sensitive to the grating profile. We present here the results of our investigations on the effect of grating period on the excitation of multiple SPP-wave modes.
4.2 Materials and Methods

4.2.1 Fabrication metallo-dielectric structures

Gold gratings were fabricated as described in detail elsewhere. In brief, ZEP520A photoresist (Zeon, Tokyo) was spin cast onto a silicon wafer at 4000 rpm. The silicon wafer was then patterned by electron-beam lithography at 100 keV on ZEP520A photoresist and developed in N-amyl acetate for 180 s, followed by immersion in a solution of isopropanol: methyl isobutyl ketone (8:1) and then rinsing with water. After development, the photoresist yielded the inverse pattern of the desired gold grating. The pattern in the photoresist was transferred to a silicon wafer by inductively coupled reactive ion etching on a Versalock 700 (Plasma-Therm, St. Petersburg, FL) with pure chlorine gas flowing at a rate of 40 sccm for 60 s. The photoresist was then dissolved in nanostrp, a commercially available resist stripper. Gold was thermally evaporated onto the patterned silicon wafer at 1 A/s deposition rate. A drop of EpoTek 377 epoxy (Epoxy Technology, Billerica, MA) was placed on the patterned gold film. A glass slide was placed on top of the epoxy resin drop. The epoxy resin was cured in the oven for 1 h at 125 °C. The patterned gold film was released from the silicon wafer with a razor blade, thereby yielding a gold grating glued to a glass slide. Line scans on an atomic force microscope (AFM) of two gratings are presented in Fig. 4-1.

Silicon oxynitride layers were grown by plasma-enhanced chemical vapor deposition on a Cluster Tool (Applied Materials, Santa Clara, CA) at 220 °C directly onto gold gratings. Ammonia, silane, and nitrous oxide were used in varying ratios to deposit the layers with specific refractive indexes. The cross-sectional image on transmission electron microscope (TEM) of a three-period-thick photonic crystal backed by a gold grating is shown in Fig. 4-2. The AFM line scans were collected on a Digital Instruments 3100 AFM (Digital Instruments, Tonowanda, NY),
Figure 4-1. AFM line scans of gold gratings with a period of (a) ~300 nm and (b) ~350 nm.

Figure 4-2. TEM image of a cross-section of a three-period-thick photonic crystal backed by a gold grating with a period of ~300 nm. The thickness of each dielectric layer in the photonic crystal is ~52 nm except for the ninth layer in each period, which is ~80 nm in thickness.
and the TEM image was collected on a Phillips 420 TEM (Phillips, Amsterdam, The Netherlands).

### 4.2.2 Characterization of metallo-dielectric structures

The refractive index of every layer, whether dielectric or metallic, was measured with an RC2 spectroscopic ellipsometer (Woollam, Lincoln, NE) as a function of $\lambda_0$. For that purpose, a layer of the specific material was deposited on either a glass slide or a polished silicon wafer. The measured relative permittivities of all nine dielectric layers present in the photonic crystal are presented in Fig. 4-3(a), and that of gold in Fig. 4-3(b).

Reflectance measurements were performed on a Lambda 950 UV-Vis (Perkin Elmer, Waltham, MA) with a Universal Reflectance Accessory. Measurements were performed in steps of 1 nm for $\lambda_0$ and 1º for the angle of incidence $\theta$.

### 4.3 Results and Discussion

The specular reflectance $R_{0p}$ and the total reflectance $R_p$ of a photonic crystal backed by a gold grating were calculated for $p$-polarized incident light using the rigorous coupled wave approach (RCWA), when the period of the grating was 308 nm. The number of terms in the expansion of field phasors in terms of Floquet harmonics and that of the permittivity as a Fourier series was taken to be 31. The protuberances of the grating were taken to be of sinusoidal shape. According to the calculations, the non-specular components of the total reflectance in the considered spectral regime were very small and the metal grating was thick enough to prevent transmission across itself; therefore, the absorptance $A_p = 1 - R_{0p}$. As previous work has shown that the gratings with protuberance near 50 nm in height (as is the case in this work) do not assist
Figure 4.3. (a) Relative permittivity as a function of $\lambda_0$ of all dielectric layers; the label (1) denotes the layer closest to the metal grating, the label (9) denotes the layer farthest away from the gold within a given period, and the intermediate layers are numbered in the order in which they appear between layers labeled (1) and (9). (b) Real and imaginary parts of the relative permittivity of an optically thick gold film as a function of $\lambda_0$. 
in the excitation of $s$-polarized SPP-wave modes, calculations were not made for $s$-polarized incident light. The measured absorptance $A_p$ is plotted in Fig. 4-4 as a function of the angle of incidence $\theta$, when the period of the grating is either $\sim 300$ nm or $\sim 350$ nm, and $\lambda_o = 850$ nm. As the peak at $\theta \approx 35^\circ$ in Fig. 4-4a is independent of the thickness of the photonic crystal, it represents the excitation of a $p$-polarized SPP-wave mode. However, no waveguide modes or SPP-wave modes are excited when the period of the grating is 300 nm because no absorptance peaks are present in Fig. 4-4b.

The measured absorptance $A_p$ as a function of $\theta$ is plotted in Fig. 4-5 when $\lambda_o = 650$ nm and the period of the grating is either $\sim 300$ nm or $\sim 350$ nm. When the grating period is 350 nm, two peaks at $\theta = 17^\circ$ and $23^\circ$ are present in Fig. 4-5a, whether the photonic crystal has two periods or three. These peaks must be due to the excitation of $p$-polarized SPP-wave modes. When the period of the grating is $\sim 300$ nm, only one SPP-wave mode (at $\theta = 41^\circ$) is excited. Let us note the fairly good match between the calculated and measured absorptance in Fig. 4-5b except that the sharp peaks present in the calculated-absorptance plot were absent in the measured absorptance plot, and the peak at $\theta = 41^\circ$ in measured-absorptance plot is slightly shifted to a higher value in the calculated-absorptance plot. These differences between experimental and theoretical data are expected because RCWA assumes a periodic variation along the direction of propagation of SPP waves; however, the actual fabricated grating is somewhat different in each period.

Figure 4-6 shows the plot of measured absorptance $A_p$ in relation to the angle of incidence $\theta$ for a three-period thick photonic crystal backed by a grating with a period of either 350 nm or 300 nm, when $\lambda_o = 575$ nm. Multiple peaks show that multiple guided modes (either SPP or waveguide) were excited in both samples. However, the grating with the smaller period leads to greater absorptance at shorter wavelengths.
Figure 4.4. Measured absorptance $A_p$ as a function of the angle of incidence $\theta$ of two- and three-period-thick photonic crystals each backed by a gold grating with a period of (a) 350 nm and (b) 300 nm, when $\lambda_o = 850$ nm.
Figure 4-5. Measured and calculated absorptance as functions of $\theta$ of two- and three-periods thick photonic crystals backed by a gold grating with a period of (a) 350 nm and (b) 300 nm, when $\lambda_o = 650$ nm. Vertical black arrows identify the peaks that represent the excitation of SPP-wave modes.
Figure 4-6. Measured absorptance $A_p$ as a function of the angle of incidence $\theta$ of a three-period-thick photonic crystal backed by a gold grating with a period of either ~300 nm or ~350 nm, when $\lambda_o = 575$ nm.
No absorptance peaks are observed at infrared wavelengths when the grating period is smaller (Figure 4-4), but absorptance peaks appear at shorter wavelengths (Figures 4-5 and 4-6). The grating with the larger period (350 nm) exhibits more absorptance peaks at the same wavelengths. This shows that the decrease in the period of the grating shifts the SPP-wave modes to shorter wavelengths; however, the decrease in the period also results in higher efficiency of excitation.

4.3 Conclusion

One-dimensional photonic crystals backed by gold gratings of different periods were used to study the effect of the period of the grating on the excitation of $p$-polarized SPP-wave modes. Multiple SPP-wave modes with distinct characteristics were excited using two different gratings; however, the grating with the smaller period supports multiple SPP-wave modes that are shifted to smaller wavelengths relative to the grating with the larger period. Multiple SPP-wave modes are expected to provide a route to enhance the efficiency of photovoltaics if incorporated into a thin-film solar cell or planar concentrator system.

References


Chapter 5 Wafer-scale fabrication of plasmonic crystals from patterned silicon templates prepared by nanosphere lithography

5.1 Introduction

The fabrication of plasmonic nanostructures such as metallic gratings has recently garnered much attention due the ability of such structures to concentrate and guide light. Sub-wavelength confinement of light leads to enhanced absorption by semiconductors or by light-absorbing molecules that are positioned near the metal surface; this resonant phenomenon has motivated the exploration of metallic nanostructures for applications in thin film photovoltaics, photo-electrochemical cells, and bio-sensors.

The excitation of surface plasmon-polariton (SPP) waves at a flat metal/dielectric interface is forbidden due to the momentum mismatch between the incoming light and the SPP wave. Prism or grating coupling is typically used to provide the momentum balance needed to launch an SPP wave. Sub-wavelength scale grating couplers are traditionally made by direct-writing methods such as electron beam lithography or focused ion beam milling. The drawback of these techniques is that sample sizes typically range from hundreds of microns to a few square millimeters, and much larger structures are too costly or time-consuming to fabricate. Techniques such as nano-imprint, nano-stencil lithography, Moiré nanolithography, and soft lithography are useful alternatives for generating larger pattern sizes, but they require direct-writing techniques for fabrication of the master with which the pattern is produced. Nanosphere lithography has also been used to create plasmonic nanostructures through direct assembly of metal nanoparticles, or through lift off or direct etching of metals with polymer nanosphere masks. However, for these techniques the templates cannot be reused because the spheres that are deposited serve as a sacrificial mask. Template stripping, a technique that uses a single patterned silicon template to prepare hundreds of metallic replicas, has recently emerged as a high
throughput method for preparing ultrasmooth plasmonic nanostructures.\textsuperscript{19-20} This technique has mainly been used for fabricating grating couplers from silicon masters patterned by electron beam lithography, focused ion beam milling and optical lithography. Plasmonic nanostructures fabricated by such techniques require a large initial investment for the tools and masks with which to generate wafer-scale patterns. There have been several reports of combining nanosphere lithography and template stripping for fabricating periodic triangle nanoparticle arrays\textsuperscript{21-26} nano-dome arrays\textsuperscript{27}, and nano-pyramid arrays\textsuperscript{28}. However these papers have not demonstrated the ability to control depth, filling fraction and profile in metallic gratings fabricated from a polystyrene mask of a fixed periodicity. Our recent work on the optimization of metallic gratings for thin film solar cells has shown that the depth (usually 50 nm or deeper) and profile of the metallic gratings are important in enhancing the absorption of light.\textsuperscript{29} The preparation of periodic and ultra-smooth grating couplers on a large scale, at low cost with precise control over periodicity, profile, filling fraction and depth is quite challenging by using existing techniques. In this Letter we demonstrate a simple technique that allows one to fabricate hexagonal plasmonic gratings at low cost, and without the use of direct writing methods, on the wafer scale with precise control over grating periodicity, profile, filling fraction and depth.

\section*{5.2 Materials and Methods}

\subsection*{5.2.1 Fabrication of patterned silicon templates}

To create plasmonic nanostructures over large areas, we have combined template stripping with colloidal lithography to fabricate metallic nano-pillar and nano-well arrays. A schematic of this process is shown in Figure 5-1. Close-packed monolayers of 510 nm diameter carboxylate-modified polystyrene spheres (Thermoscientific, W050CA) were deposited on two-
inch silicon wafers by shadow nanosphere lithography as described elsewhere.\textsuperscript{30-31} The silicon substrate with the polystyrene sphere monolayer was annealed on a hot plate for 30 s at 105°C to promote the adhesion of the spheres to the substrate. The diameter of the polystyrene spheres was reduced by reactive ion etching (Plasmatherm Versalock ICP-RIE 700) in an oxygen plasma (45 sccm, 90W) as shown in Figure 5-2. The diameter of the polystyrene beads can be controlled by adjusting the oxygen plasma etching time. It is important to note that if the PS beads are etched to smaller than 50% of their original size they become porous and non-circular. For fabrication of metallic nano-pillar arrays, a 30 nm thick alumina film was then grown by electron beam evaporation (Semicore Evaporator) over the oxygen plasma-etched polystyrene films at 1 Å/s. The polystyrene was removed by bath sonication in water for 15 min. The pattern was defined into the silicon wafer by reactive ion etching in a chlorine plasma (45 sccm) at a power of 100W. Aluminum oxide was chosen as the mask material for this step because it does not etch in pure chlorine plasmas, and this allows one to etch deeply into the silicon wafer if desired.\textsuperscript{32} The alumina was then removed by placing the substrate in a bath of concentrated phosphoric acid at 50°C for 1 h.

For the fabrication of metal nano-well arrays, the oxygen plasma-etched polystyrene nanosphere monolayer was used directly as a mask to define the pattern in the silicon wafer. SF\textsubscript{6}/Ar (10 sccm:40 sccm) was chosen to etch the silicon wafer anisotropically because this gas mixture provides good selectivity between silicon and the polystyrene mask. The depth of the silicon master template can be controlled in this step by controlling the SF\textsubscript{6}/Ar etch time. In this step is it important not to use chlorine gas for etching due to low selectivity between silicon and polystyrene; the use of chlorine leads to structures with roughened edges. The polystyrene spheres were removed from the substrate by bath sonication in water for 15 min.
5.2.1 Fabrication of replicated gold gratings

Periodically patterned metallic structures were fabricated by electron beam evaporation of gold over the patterned silicon templates. Degassed Norland Optical Epoxy #71 was drop cast over the metal film and a clean glass slide was placed on top. The epoxy resin was cured by UV irradiation for 30min and peeled off the silicon template by sliding a razor blade between the slide and silicon wafer. In order to shift the surface plasmon polariton resonance wavelength of the patterned structures into visible range, 100 nm of silica was electron beam evaporated over the templates at 1Å/s. In numerical simulations of the optical properties of these structures (see below) the silica was assumed to be conformal to the gold nano-wells. The patterned silicon templates can be cleaned and reused many times without pattern degradation.19 Figure 5-3 shows the silicon master template and a wafer-size replica prepared by this technique.

5.3 Results and Discussion

5.3.1 Characterization of replicated gold gratings

The profile of the features can be controlled by adjusting the etching parameters during sample preparation. As shown in Figure 5-4 a-b, the filling fraction can be controlled by adjusting the diameter of the polystyrene nanospheres during the oxygen reactive ion etching step. Longer etching times yielded wells with smaller diameters, while shorter etching times yielded larger well diameters. In addition, the depth of the gratings can be adjusted by increasing the silicon etching time with SF6/Ar or Cl2 to achieve the desired depth. Figures 5-4a-b show electron micrographs of gold nano-well gratings with different filling fractions, and Figures 5-4c-d show electron micrographs of gold nano-pillar gratings. Figure 5-5 shows AFM height scans and line scans. The data indicate that the patterned gold surface is ultra-smooth. The RMS
Figure 5-1. Schematic of the process flow for fabricating metallic nano-pillar and nano-well gratings by assembly of a polystyrene sphere monolayer and template stripping.
**Figure 5-2.** Ordered polystyrene (PS) monolayers on 2 inch silicon substrates. a) Photograph of PS films on a silicon wafer. b) SEM image of a PS film. c) cross sectional SEM image of PS film. d) SEM image of oxygen-etched PS.

**Figure 5-3.** Wafer scale silicon grating is shown on the right. A wafer scale gold replica is shown on the left.
Figure 5-4. Periodically patterned nanostructures: Gold nano-well grating with a) large filling fraction and 50 nm depth; b) small filling fraction and 70 nm depth. a,b) insets show 3D AFM images. SEM c) top-down image of gold nano-pillar grating d) cross sectional image of the gold nanopillar array shown in (c). e) a 200nm deep patterned silicon nano-well master template used to fabricate the gold nano-pillar gratings shown in (c,d).
Figure 5-5. AFM height scans of a) gold nano-well with small filling fraction. b) gold nano-well with large filling fraction. AFM line scans of c) gold nano-well with small filling fraction. d) gold nano-well with large filling fraction. The AFM line scans clearly indicate that the patterned gold possess ultrasmooth surfaces.
roughness varied between 0.2 - 0.8 nm for both samples when measured at various points along the bottom or top of the gold nano-well arrays. The patterned metal films made by this technique are derived from polycrystalline 2-D colloidal crystals with grain sizes up to a few millimeters, and the metal replicas retain the degree of crystalline order of the template.

5.3.2 Optical characterization of replicated gold gratings

To test the quality of these metallic films, we measured their specular reflectance with a Perkin Elmer UV-Vis spectrophotometer. Finite Difference Time Domain (FDTD) electromagnetic simulations were performed with Lumerical Solutions FDTD software (Vancouver, Canada) to compare to the reflectance data. In the numerical simulations, Bloch boundary conditions were used in the x direction, periodic boundary conditions in the y direction, and perfectly matched layers in the z direction. The optical constants of silica were taken from the literature. The optical constants of gold was measured by spectroscopic ellipsometry (Woollam RC2 Spectroscopic Ellipsometer) on a planar film and fitted with the appropriate models. A plane-wave source with 45 degree polarization angle (unpolarized light) and 8 degree angle of incidence were used. Reflection and transmission were calculated by placing (in the simulation) power monitors 500 nm above and below the structure. Transmission in this structure was found to be negligible, consistent with the optically thick (>100nm) gold layers. Field distributions were calculated by placing field-profile monitors along specific planes within the unit cell.

The simulated and experimental reflectance of the silica-coated nano-well array imaged in Figure 5-4b is shown in Figure 5-6. The resonant wavelengths in the simulated and experimental spectra match well. The sample exhibits multiple resonance peaks. The two most efficiently coupled resonances, at 658 nm and 683 nm, have coupling efficiencies of ca. 70% and
60%, respectively. The multiple peaks observed in this structure are caused by Fabry-Perot interference effects between reflected SPP waves within the nano-well.\textsuperscript{34} The peaks in the experimental data are less intense and broader due to some randomization induced by the defects and grain boundaries of the polycrystalline colloidal template and resulting replica pattern.\textsuperscript{35} Figure 5-7 show the calculated electric field profile of a cross section that passes through the center of the middle of the ZY plane of the unit cell, at $\lambda_o = 658$ nm and $\lambda_o = 683$ nm. The sharp points of the nano-well display the largest field enhancements in the structure. An interference pattern caused by a partially reflected SPP waves is observed at the bottom of the well. The evanescent decay of the field intensity away from the metal surface provides further evidence that the reflectance dips are caused by the excitation of SPP waves.\textsuperscript{1}

### 5.4 Conclusion

In summary, we have demonstrated a scalable, high throughput method for preparing two-dimensional metallic grating couplers for plasmonic applications. The technique combines elements of both nanosphere lithography and template stripping, which together provide a means of producing masters and replica plasmonic nanostructures inexpensively and on the wafer scale. It should be possible to trap light in different wavelength ranges by changing the size of the PS beads that define the period of the grating. Nagpal et al. have shown that such silicon templates can be used many times without noticeable degradation in the metal replicas.\textsuperscript{19} We investigated the plasmonic properties of a test structure and successfully demonstrated that metallic gratings fabricated by this technique exhibit interesting plasmonic reflectance properties that are consistent with FDTD simulations. Gratings fabricated by this method may be useful for enhancing the efficiency of photovoltaics and in other applications where large-area, inexpensive light-trapping structures are needed.
Figure 5-6. Experimental and simulated reflectivity of a gold nano-well grating with a 100 nm silica overlayer. The inset shows a schematic of the unit cell used in the FDTD simulation.

Figure 5-7. Calculated electric field intensity in middle of the unit cell through the ZY Plane a nano-well array at a) $\lambda_o=658\text{nm}$ B) $\lambda_o=683\text{nm}$. These diagrams are not plotted to scale.
References


Chapter 6 Microporous Brookite-Phase Titania Made by Replication of a Metal-Organic Framework

6.1 Introduction

A variety of templating strategies using surfactants,\textsuperscript{1-4} block copolymers,\textsuperscript{5-7} colloidal crystals,\textsuperscript{8-11} mesoporous silica\textsuperscript{12,13}, and zeolites\textsuperscript{14-16} have been developed for the synthesis of porous materials with controlled pore dimensions. These techniques generally rely on infiltration of porous solids\textsuperscript{7-15} or solution-phase co-assembly of soft templates with precursor reagents;\textsuperscript{1-6} the template is removed by chemical etching or calcination if the sample is a hard or soft template, respectively. These methods have provided a means of controlling the pore wall thickness, pore periodicity, pore diameter and pore connectivity in thin films and nano-particulate materials.

Porous metal oxides are now the subject of intense interest because of their uses in photocatalysis,\textsuperscript{17-20} electrochemical energy storage,\textsuperscript{21,22} and heterojunction photovoltaics,\textsuperscript{23-25} High surface area and crystallinity are vital to the performance of oxides in these applications.\textsuperscript{20-26} While high surface area crystalline metal oxides can be prepared with ordered mesopores, it is still a significant challenge to make crystalline metal oxide particles that contain ordered micropores.\textsuperscript{17} Nanocomposites of amorphous metal oxides and microporous or mesoporous organic templates can be synthesized quite easily; however, the high temperatures needed to crystallize the amorphous oxide and remove the soft template result in collapse and sealing of the micropores, because degradation of the template and grain growth occur simultaneously.\textsuperscript{17} Metal oxides prepared by these templating methods have pore diameters that range from 0.48 to 50 nm.\textsuperscript{3,27-29} However, the micropores in these replicated materials in general do not have any ordering derived from the template.\textsuperscript{40-45}
Metal-organic frameworks (MOFs) or porous coordination polymers are solids that offer control of pore size and geometry by selecting the appropriate molecular building units. Recently there have been several reports of using MOFs as precursor materials to high surface area graphitic carbon, which is made by infiltration with a carbon precursor followed by calcination or by direct decomposition of the MOF. In neither case do the carbon replicas show evidence of pore ordering that is derived from the MOF template. There have also been many reports of the synthesis of non-porous metal and metal oxide nanoclusters and nanoparticles within the pores of zeolites and MOFs. More recently, there have been some reports of porous metal oxides made by direct calcination of MOFs that contain the metal of interest from the framework; again the sizes and connectivity of pores in these oxides are not derived directly from the pore structure of the MOFs.

In this paper we report the synthesis of a crystalline metal oxide with a micro-meso binary pore system from a MOF template. The micropores in this material are derived from MOF and are partially ordered. The mesopores are generated by incomplete filling of the template. For this initial study we chose titania as a model system. Interestingly, phase pure brookite, a rare titania polymorph that is otherwise difficult to prepare in pure form, results from replication of the copper-based MOF, HKUST-1.

6.2 Materials and Methods

6.2.1 Synthesis of titania replicas

Porous titania replicas of HKUST-1 were prepared by liquid-phase impregnation under vacuum as illustrated in Figure 6-1. HKUST-1 was prepared as described elsewhere with minor modifications. In a typical procedure, 2.0 g of the MOF template was heated overnight at 200
°C in vacuum in a Schlenk flask. After cooling the flask to room temperature, 10 mL of titanium (IV) isopropoxide, Ti(O-iPr)$_4$ (96% Sigma Aldrich), was injected directly over the powder. This represents a large excess; preliminary experiments with 400 µL Ti(O-iPr)$_4$ per gram of HKUST-1 gave hollow pyramidal structures. The Schlenk flask was kept under dynamic vacuum for 30 min after injection of Ti(O-iPr)$_4$. The MOF was kept immersed in the liquid Ti(O-iPr)$_4$ for a minimum of 24 h under static vacuum to allow the precursor molecules to infiltrate into the pores. The sample was then removed from the Schlenk flask, washed and centrifuged with ethanol three times to remove excess Ti(O-iPr)$_4$. The powder was redispersed in ethanol and filtered, and washed with additional ethanol. The washing step with ethanol is critical for removing Ti(O-iPr)$_4$ from the surface of the MOF particles. The dried powder was suspended in 10mL of a mixture of ethanol and water (1:1 by volume), placed in a 23mL Teflon-lined stainless steel autoclave, and heated for 20 h at 200 °C. After this hydrothermal treatment, the sample was filtered. The resulting powder was placed in 1M HCl to etch the HKUST-1 template, then filtered and washed with water. The powder was then subjected to a second etch with 5 wt% H$_2$O$_2$. Finally the solution was filtered and washed with water and ethanol resulting in a porous crystalline titania powder. The titania replica derived from HKUST-1 is denoted as MT1. Without the hydrothermal treatment step, we obtained only amorphous titania.

### 6.3 Results and Discussion

#### 6.3.1 Metrology of titania/MOF composites and replicated titania

Figure 6-2a and 6-2b show scanning electron microscopy (SEM) images of the HKUST-1 template and of HKUST-1/titania composite particles after hydrothermal treatment (henceforth
Figure 6-1. Schematic illustration of the synthesis of microporous brookite from a MOF template.
denoted as the composite) that retain the square bipyramidal shape of the HKUST-1 crystals. Many of the composite particles consist of fractured pieces derived from the template. Although these fractured particles do not show the macroscale morphology of the MOF crystals, they do contain the same nanostructured porosity. Figure 6-2c show a SEM image of porous titania (MT1) obtained after HKUST-1 template removal. Some of the MT1 particles retain the square bipyramidal shape of the HKUST-1 crystals. SEM images at higher magnification (Figure 6-3) show that the pyramidal MT1 particles consist of smaller particles that appear fibrous and porous on their surface. Figure 6-2d shows a high resolution TEM image of MT1. Disordered micropores with uniform spacing are evident in the sample. A fast Fourier transform (FFT) of the boxed region in Figure 6-2d indicates that the average spacing of the pores is 1.0 nm. Lattice fringes with 0.33 nm spacing, attributed to the brookite phase of titania, are also seen in the image and the FFT.

### 6.3.2 Composition of replicated titania

The Ti/Cu molar ratio measured by atomic absorption spectroscopy was 9.6, indicating that the etched sample consists predominantly of titanium dioxide. Figure 6-4 shows high resolution X-ray photoelectron spectra (XPS) of MT1, HKUST-1, and the composite. HKUST-1 contains Cu$^{2+}$ (Figure 6-4a) as indicated by the position of the Cu 2p$_{1/2}$, Cu 2p$_{3/2}$ and Cu$^{2+}$ satellite peaks. XPS shows the presence of residual Cu$^{+}$-O bonds in MT1, indicated by the Cu
Figure 6-2. FESEM images showing (a) bi-pyramidal crystals of the HKUST-1 template, and (b) the composite after the hydrothermal treatment but before etching. The white dotted lines highlight particles that retain the morphology of the HKUST-1 crystals. (c) Porous titania (MT1) after removal of the HKUST-1 template. (d) High-resolution TEM image of MT1. The inset shows a fast Fourier transform (FFT) of the image. The rings in the inset correspond to the average pore spacing (1.0 nm) and the brookite (111) and (120) lattice spacings of 0.33 nm.
Figure 6-3. a,b) High magnification FESEM images of the MT1 fragmented particles shown in Figure 2C. c,d) Images of other MT1 particles showing that some particles retain the microscale morphology of the parent template.

Figure 6-4. High resolution XPS scans of MT1, HKUST-1 template and the composite after crystallization. (a) Normalized copper spectra. (b) Normalized oxygen spectra.
2p\textsubscript{3/2} peak at 932 eV and the Cu 2p\textsubscript{3/2} peak at 952 eV (Figure 6-4a).\textsuperscript{58} These data can be interpreted as a change in oxidation state from Cu\textsuperscript{2+} to Cu\textsuperscript{1+} after the removal of the template. Interestingly, Figure 6-4a indicates that the composite contains both Cu\textsuperscript{2+} and Cu\textsuperscript{+}; this indicates that hydrothermal crystallization partially reduces copper in the template. It is likely that the copper impurity present in the sample is amorphous Cu\textsubscript{2}O, which is formed by reduction of Cu\textsuperscript{2+}.

The XPS spectra in Figure 6-5 show Ti 2p\textsubscript{1/2} and Ti 2p\textsubscript{3/2} peaks centered at ~465 and ~459 eV, respectively, indicating that both samples contain the Ti\textsuperscript{4+}-O bonds of TiO\textsubscript{2}.\textsuperscript{58} The O 1s XPS spectrum of HKUST-1 in Figure 6-4b shows a major peak at a binding energy of ~532 eV and a small shoulder at ~534 eV, which confirm the presence of carboxyl and ester groups, respectively.\textsuperscript{59} The O 1s XPS spectrum of the composite shows peaks at ~532 eV, ~534 eV and 530.01 eV which indicate that the sample contains carboxyl, ester and Ti-O bonds. The XPS spectrum of MT1 shows a major peak at a binding energy of ~530.5 eV, which indicates the presence of Ti-O bonds.\textsuperscript{58-59} After etching, the peak corresponding to the Ti-O bond shifts slightly to 530.5 eV, suggesting that template removal causes a change in the bonding environment of Ti. The peaks corresponding to ester and carboxyl groups are not present in MT1, confirming that the HKUST-1 template is completely removed. The carbon species present in the sample could not be identified because the carbon signal from MT1 could not be differentiated from background adventitious carbon.

6.3.3 Crystallographic characterization

X-ray diffraction (XRD) patterns were recorded to follow the progression of crystalline phases formed in the reaction (Figure 6-6). The composite showed an identical XRD pattern to that of the original HKUST-1 template, indicating that the composites are well ordered before template
Figure 6-5. High resolution titanium XPS scans of MT1 and the composite after hydrothermal treatment.
removal. The low angle region of the XRD pattern of MT1 shows a large, broad peak centered at \(2\theta = 8.4^\circ\), which corresponds to a distribution of pore spacings centered at 1.06 nm ± 0.4 nm.

The pore spacing of MT1 determined by XRD is consistent with the results shown in Figure 6-2d. The TEM image shows lattice planes with ~0.33 nm periodicity corresponding to the (111) and (120) lattice planes of brookite phase titania. A simulated pattern of the HKUST-1 template shows three sharp diffraction peaks between \(2\theta = 5-12^\circ\), which correspond to the 200, 220, and 222 reflections. This suggests that pore ordering of MT-1 is derived from the HKUST-1 template, albeit with greater disorder. Figure 6-6 also shows XRD data collected after MT1 was ground with a mortar and pestle. The disappearance of the low angle peak indicates the loss of pore order with grinding. The diffraction peaks of MT1 at higher angles, which can be attributed to nanocrystalline brookite, are not affected by grinding. We investigated the effect of solvents and temperature during the crystallization step; XRD patterns confirmed that phase pure brookite was formed under a range of different conditions (Figure 6-7). Under the hydrothermal conditions used in this study, the anatase or rutile phase titania are most typically formed. The formation of phase pure brookite in the case of the HKUST-1 template most likely arises from the presence of Cu\(^{2+}\) ions as noted in previous reports.\(^{54}\)

### 6.3.4 Porosity measurements by nitrogen gas sorption

The dehydrated HKUST-1 template contains square-shaped pores of ~1.0 nm diameter.\(^{55,60}\) This is comparable to the van der Waals diameter of the flexible Ti(O-iPr)\(_4\) molecule which was estimated using ChemDraw as 0.99 nm. The average micropore diameter of the titania replica is smaller than the value expected from replication of the MOF framework. The smaller dimensions can be attributed to volume shrinkage of the infiltrated titania upon condensation and crystallization. The porosity of the samples was analyzed by nitrogen gas adsorption-desorption
**Figure 6-6.** X-ray powder diffraction (XRD) patterns of porous titania (MT1) (black), MT1 after grinding in a mortar and pestle (red), HKUST-1 simulation (blue), and brookite phase titania (green).

**Figure 6-7.** XRD patterns showing titania phases obtained under different reaction conditions. Hydrothermal condition are shown in Table 6-1.
Table 6-1. Hydrothermal reaction conditions

<table>
<thead>
<tr>
<th>Name</th>
<th>Temperature (ºC)</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT2</td>
<td>220</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>MT3</td>
<td>200</td>
<td>H$_2$O/EtOH (1:1 vol)</td>
</tr>
</tbody>
</table>
isotherms at 77 K (Figure 6-8). The adsorption-desorption isotherms of MT1 show typical type IV behavior.\textsuperscript{61} The steep uptake at low relative pressure indicates the presence of micropores. The micropore volume and isosteric heat of adsorption derived from N\textsubscript{2} adsorption by Dubinin-Radushkevich (DR) analysis\textsuperscript{62} are 0.090 ml/g and 10.8 kJ/mol, respectively. The Horvath-Kawazoe (HK) method\textsuperscript{63} was used to fit the adsorption isotherm and obtain the micropore size distribution. The graph in Figure 6-9b shows that MT1 (HCl etched only) has a relatively broad distribution of micropore diameters with a maximum frequency near 0.52 nm. Figure 6-10a shows that after H\textsubscript{2}O\textsubscript{2} etching the micropore distribution of MT1 becomes more uniform, and additionally the maximum frequency of the micropore diameter increases to 0.60 nm.

A hysteresis loop in the adsorption-desorption isotherm was observed at higher pressures indicating the presence of mesopores (Figure 6-8 and 6-9a). The mesopore volume was calculated as 0.23 mL/g from the micropore volume and total pore volume near P/P\textsubscript{0} = 1. To measure the mesopore distribution, Barrett-Joyner-Halenda (BJH) theory\textsuperscript{64} was applied to the desorption branch of the isotherm. This analysis indicates that the mesopore diameter in MT1 is centered around 6 nm. The Brunauer-Emmett-Teller (BET) surface area\textsuperscript{65} of MT1 was in the range 180 – 190 m\textsuperscript{2}/g after HCl etching but before H\textsubscript{2}O\textsubscript{2} etching. After H\textsubscript{2}O\textsubscript{2} etching the surface area increased to 265–270 m\textsuperscript{2}/g.

The broad distribution of both micro- and mesopores is likely caused by incomplete filling of the HKUST-1 template with titania. The volume shrinkage during crystallization and solvent elimination during hydrolysis make it difficult to completely fill the small pores with titania. Based on the N\textsubscript{2} adsorption experiment, we measured a micropore volume of 0.49 mL/g for the HKUST-1 template. From the pore volume of HKUST-1 and the brookite density (4.1 g/cm\textsuperscript{3}), we can estimate that a completely filled composite should have a Ti/Cu ratio of 5.3. The Ti/Cu ratio of the composite was found to be 1.4 by XPS, indicating only partial pore filling. A
Figure 6-8. Nitrogen adsorption desorption isotherm of MT1 at 77 K after HCl and H$_2$O$_2$ etching.

Figure 6-9. (a) Nitrogen adsorption desorption isotherm of MT1 at 77 K after HCl etching. (b) HK micropore size distribution calculated from the adsorption isotherm shown in (a) for MT1 and the HKUST-1 template, and (c) BJH mesopore size distribution of MT1 calculated from the adsorption isotherm shown in (a).
Figure 6-10. (a) HK micropore size distribution calculated from the N\textsubscript{2} adsorption isotherm for MT1 shown in Figure 6-8. (b) BJH mesopore size distribution of MT1 calculated from N\textsubscript{2} adsorption isotherm shown in figure 6-8.
N₂ adsorption experiment on the composite (Figure 6-11) gave a micropore volume of 0.23 mL/g, which is almost the half that of HKUST-1. This is also consistent with only partial filling of the pores in the composite by titania. From the framework volume of HKUST-1 and the density of brookite, a perfect titania replica should have a micropore volume of 0.36 mL/g. This is close to the total pore volume (0.09 micropore + 0.23 mesopore = 0.32 mL/g) we observe in the replica. This suggests that partial collapse of micropores in the imperfect replica gives rise to an equivalent mesopore volume.

### 6.3 Conclusions

In summary, we have demonstrated a simple method of synthesizing high surface area micro/mesoporous brookite phase titania with surface areas up to 270 m²/g by using HKUST-1 as a template. The porous particles have micropore diameters and pore spacings that are derived from the MOF template. The mesopores appear to arise from incomplete filling of the pores of the template by Ti(O-iPr)₄. Because many metal oxides can be crystallized hydrothermally from metal alkoxide precursors, it is likely that other microporous oxides can be synthesized by the same technique. Further work is underway to determine the range of compositions and stability of porous oxides that can be made by replication of MOFs.
**Figure 6-11.** Nitrogen adsorption desorption isotherm of HKUST-1 filled with crystalline titania.

**Table 6-2.** Effect of etching on surface area and pore volume of MT1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Micropore volume (ml/g)</th>
<th>Mesopore volume (ml/g)</th>
<th>Total pore volume (ml/g)</th>
<th>BET surface area (m²/g)</th>
<th>Isosteric heat of adsorption q_{st} (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT1 HCl etched</td>
<td>0.063</td>
<td>0.17</td>
<td>0.23</td>
<td>186</td>
<td>10.3</td>
</tr>
<tr>
<td>MT1 HCl+H₂O₂ etched</td>
<td>0.090</td>
<td>0.23</td>
<td>0.32</td>
<td>270</td>
<td>10.8</td>
</tr>
</tbody>
</table>
References


47. Muller, M.; Lebedev, O. I.; Fischer, R. A. Gas-phase loading of [Zn(4)O(btb)(2)] (MOF-177) with organometallic CVD-precurors: inclusion compounds of the type [L(n)M](a)@MOF-177 and the formation of Cu and Pd nanoparticles inside MOF-177, *J Mater Chem* **2008**, *18*, (43), 5274-5281.


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