Nanostructured Films

Surface-Templated Nanostructured Films with Two-Dimensional Ordered Arrays of Voids**

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Template-induced syntheses have been broadly applied to the creation of structured materials with unique properties that are difficult to produce by other procedures.[1–10] Self-assembled colloidal crystals are ideal templates for creating three-dimensional (3D) highly ordered macroporous materials and photonic crystals.[6,7,11–16] In this approach, the voids between colloidal spheres are infiltrated with another material and subsequent removal of the template by either wet etching or thermal decomposition leads to the formation of 3D ordered air cavities inside the structure-filling materials. Nanosphere lithography (NSL), on the other hand, uses monolayer or double-layer colloidal crystals as either an etching or deposition mask to define a two-dimensional (2D) ordered mosaic array of microcolumnar structures inside the voids of colloids.[17–20] Surfaces of 2D arrays of submicron spheres have also been demonstrated as templates in the creation of metallic half-shells.[21,22] Here we report a different method that uses the periodic surfaces of 3D ordered colloidal crystals as templates for the production of 2D ordered surface gratings.

Surface gratings with 2D regular arrays of voids are of considerable technological importance and great scientific interest. Periodic metallic subwavelength hole arrays exhibit unusual optical transmission,[23] which offers the potential for developing new microoptical devices.[24] Surface gratings with submicron periodicity have been used in fabricating distributed feedback lasers,[25] broadband waveguide polarizers,[26] selective optical absorbers,[27] and surface-enhanced Raman scattering (SERS) substrates,[28] as well as in improving the extraction efficiency of organic light-emitting diodes (OLEDs).[29] Such arrays of voids can also be used as picoliter beakers for chemical and biochemical microanalysis.[30,31] The fabrication of surface gratings with submicron periodicity typically involves lithography (photolithography for >300 nm features and electron-beam lithography for <300 nm features) and etching.[23] These processes are costly and tend to be limited by either low resolution or low throughput. In contrast, the surface-template approach described in this paper provides a much simpler and cheaper nonlithographic alternative for the mass fabrication of surface gratings from a diverse range of materials.

Naturally, one could use monolayer colloidal crystals in templating 2D surface gratings. However, the fabrication of large 2D colloidal single crystals is problematic.[32] By contrast, convective self-assembly[13,33,34] and the recently developed spin-coating technique[35] provide us with simple methods for making large 3D colloidal crystals by using microspheres of 100–2000 nm. Therefore, we use 3D colloidal crystals as templates for making 2D surface gratings, provided that subsequent material deposition only occurs on the colloidal crystal surface.

A schematic outline of the procedures for producing free-standing, 2D ordered surface gratings by using convectively assembled colloidal crystals as templates is shown in Figure 1. We first grow a multilayer silica or polystyrene colloidal single crystal on a glass slide by using the convective self-assembly method.[33] The typical thickness of the final crystal is 20 layers and the diameters of the colloids range from 100–500 nm. Although there are defects in the resultant colloidal crystal, such as point vacancies and vertical cracks, the single crystalline domain extends over the whole sample area of several centimeters square.[33] A thin layer (300–1000 nm) of material is then deposited on the top surface of the colloidal crystal by conventional physical vapor deposition (PVD) techniques, including RF and DC-magnetron sputtering deposition (Perkin–Elmer 8200) and electron-beam evaporation (Denton DV-502A E-beam evaporator). In sharp contrast with chemical vapor deposition (CVD), which has been widely used in filling all available interstitial voids of 3D colloidal crystals,[11,13] PVD only forms conformal half-shells on the crystal surface, thereby obstructing penetration of materials into the inner voids.[21,22] For hydrofluoric acid resistant materials, such as Au, Ag, Pt, and Cr, silica colloidal

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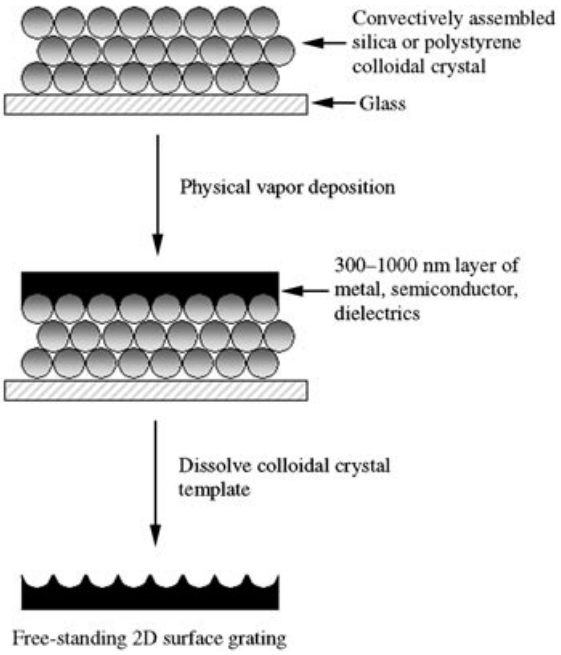

Figure 1. Experimental procedures for making free-standing, 2D surface gratings by using convectively self-assembled colloidal crystals as templates.

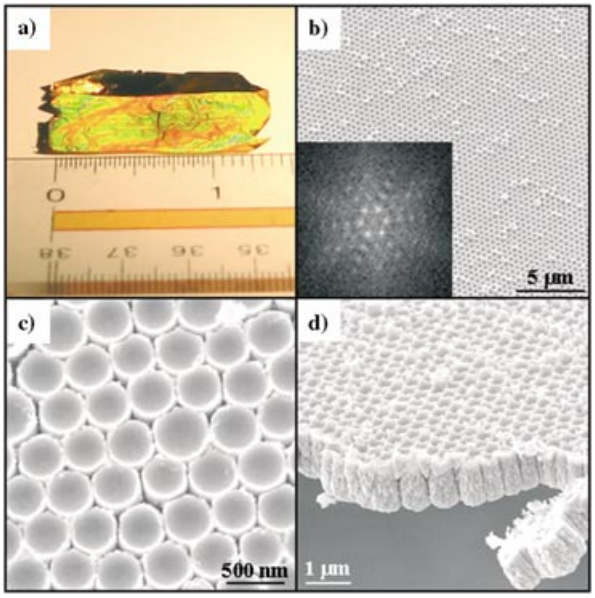

Figure 2. Self-standing surface gratings. a) Photo of a self-standing gold surface grating replicated from silica colloids of 410 nm diameter. The units marked on the top of the ruler are inches (≈2.5 cm). b) Top-view SEM image and its fast Fourier transform (FFT) image (inset) of the sample shown in (a). c) Higher-magnification SEM image of the same sample that shows the partially connected shells. d) Cross-sectional view of the same sample. Gold was deposited by using a Perkin–Elmer 8200 RF sputtering system.

crystals are used as templates; otherwise, for Ti, Al, Si, Ge, indium tin oxide (ITO), and SiO_2, polystyrene templates are used. The silica or polystyrene colloidal templates can then be etched away by a 2% HF or toluene rinse to leave behind a free-standing, iridescent film, as shown by the photo of a gold film of 410 nm periodicity in Figure 2a. The iridescent colors of the film are caused by Bragg diffraction of visible light by the 2D ordered arrays of submicron voids.[36]

Figure 2b shows a typical SEM image of a flexible gold surface grating with 2D periodic arrays of voids with 410 nm diameters. The voids match the size of the template spheres and retain their single-crystal close-packed ordering over an area of several centimeters square. The long-range hexagonal ordering of the voids is further confirmed by the FFT image shown in the inset of Figure 2b. A higher-magnification image (Figure 2c) reveals that the shell-like voids are only partially connected. This is more apparent from the cross-sectional micrograph of the film (Figure 2d); microcolumnar pillars maintain the original arrangement of template colloids. This appears to be caused by the rapid deposition rate ($>5\ nm\,s^{-1}$) and large grain size (>20 nm) of the RF sputtering deposition used for making the sample. The rapidly accumulated large grains prevent subsequently deposited material from penetrating into the small interstices (≈ 100 nm) between colloids on the surface. Other PVD techniques with much slower deposition rates ($<1\ nm\,s^{-1}$) and smaller cluster sizes (<1 nm), such as electron-beam and thermal evaporation, allow homogeneous material deposition over the sample surface, thereby resulting in the formation of continuous films (see Figure 4).

Although the above approach with convectively assembled colloidal crystals as sacrificial templates is favorable for low-volume, laboratory-scale production, it has several drawbacks that limit its use for the mass fabrication of surface gratings with submicron periodicity. First, the convective self-assembly method is a tedious process from the viewpoint of large-scale fabrication. It takes days to make a centimeter-square-size crystal.[33] Second, it is problematic to make high-quality colloidal crystals larger than several centimeters square, due to the gravitational sedimentation of colloids and solvent evaporation.[13,33,34] Third, the final surface gratings have many protrusion defects (Figure 2b) caused by unwanted material deposition in the inner interstices of the 3D templates.

To overcome these drawbacks, we adapted our recently developed shear-induced spin-coating technique for making colloidal crystal templates.[35] Planar crystals as large as 81 cm^2 (on a 10 cm diameter wafer), can be routinely made within 10 minutes. The resultant polymer-embedded colloidal crystals exhibit highly ordered surface modulation and can be directly used as templates for creating 2D gratings (Figure 3). The same PVD processes as described above are used to coat a thin layer of material on the top surface of the spin-coated colloidal crystals. Protrusion defects can be completely avoided as the inner voids are filled with polymer and PVD material deposition can only occur on the colloidal crystal surface. Another great advantage of the new approach is that, for metals with weak adhesion to the templates, such as Au, Ag, Pt, and Pd, the resultant surface gratings can be easily peeled off from the template surface. No wet etching is required and the original templates can be reused in making new surface gratings.

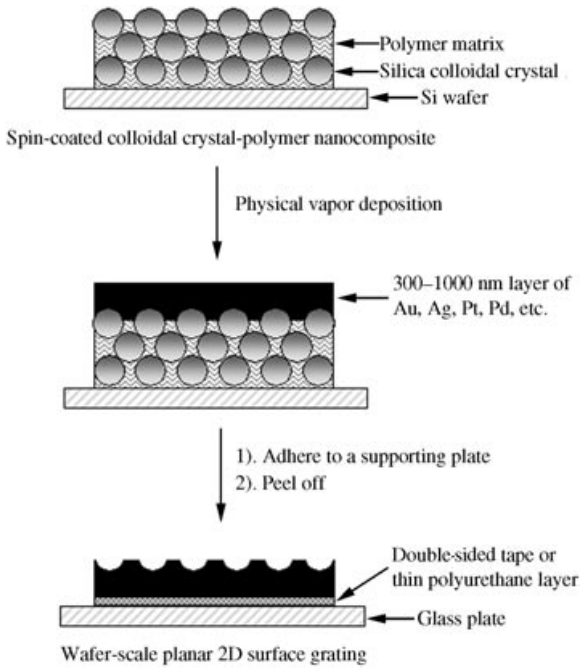

Figure 3. Experimental procedures for making wafer-scale, 2D surface gratings by using spin-coated colloidal crystals as templates.

Figure 4a shows a 10 cm diameter (81 cm^2) platinum surface grating templated from a spin-coated silica colloidal crystal (320 nm diameter). A thin polyurethane layer is used to adhere the platinum film to a supporting glass plate. Under white-light illumination, a striking six-arm diffraction star is apparent. The adjacent arms of the diffraction star form exact 60° angles, a result indicating the formation of 2D hexagonally close-packed void arrays over the whole sample surface.[37,38] The multiple reflected colors are caused by different incident angles of the illuminating white light.[36,37] The long-range hexagonal ordering of the void array is evident from the SEM image and its FFT image shown in Figure 4b. The higher-magnification SEM image in Figure 4c reveals that the voids are well separated from each other. This occurs for two reasons: first, silica colloids in the original colloidal crystal are separated from each other by about 1.4 times the sphere diameter;[35] second, the surface protrusion height of silica spheres in the original template is less than the radius of spheres. By using a simple geometrical calculation, the depth of the final voids (h) can be related to the radius of the template colloid (r) and the radius of the voids (a) as $h = r-\sqrt{r^2-a^2}$. The calculated void depth of the sample in Figure 4c is $\approx$58 nm, which is about one-third of the radius of the template silica sphere (160 nm) and is in good agreement with the measured depth from the cross-sectional SEM image shown in Figure 4d. To make deeper voids, homogeneous oxygen reactive-ion etching (RIE) can be used to remove the surface polymer layer to release silica spheres with various depths.

Besides PVD, other procedures such as poly(dimethylsiloxane) casting can also be applied in making highly ordered, wafer-scale surface-relief structures, which can then be used as molds for soft lithography[39,40] and nanoimprint lithography[41] to fabricate periodic submicron dot and hole arrays from a large variety of functional materials.

In summary, we have developed a nonlithographic approach to the fabrication of large-area surface gratings with 2D ordered arrays of submicron voids. 3D ordered colloidal crystals, made by convective self-assembly and spin-coating, are used as templates to create 2D surface gratings, provided the material deposition only occurs on the periodic surfaces of the templates. The technique allows the production of surface gratings from a large variety of functional materials, such as metals, semiconductors, and dielectrics; these gratings may find important technological applications in areas ranging from subwavelength optics to biological microanalysis.

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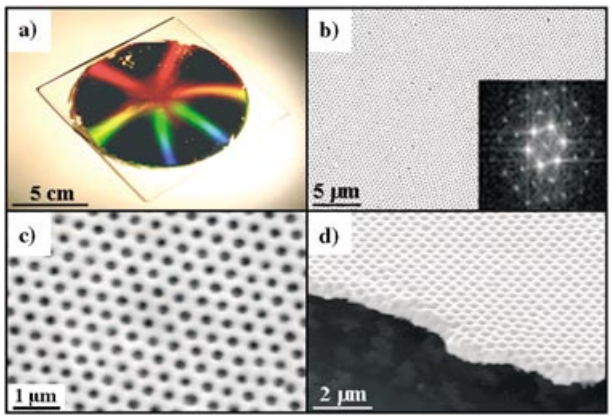

Figure 4. Wafer-scale surface gratings. a) Photo of a 10 cm diameter platinum surface grating templated from a spin-coated silica (320 nm diameter) colloidal crystal. b) Top-view SEM image and its FFT image (inset) of the sample shown in (a). c) Higher-magnification SEM image of the same sample. d) Cross-sectional view of the same sample. Platinum was deposited by using a Denton DV-502A E-beam evaporator.

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