

Nanopatterned Surfaces Based on Template-Assisted Multilayer Electrodeposition

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Nanopatterned surfaces are useful in various scientific investigations (such as surface plasmon enhanced Raman scattering,^[1] guided biological cell growth,^[2] and dry adhesion^[3]) as well as being used in subsequent nanofabrication technologies (e.g., soft lithography,^[4] nanoimprinting^[5] and nanotransfer printing^[6]). In general, the realization of these surfaces relies on the arbitrary pattern generation capability of electron-beam lithography (EBL), typically on planar surfaces. To reduce the fabrication cost, and/or facilitate the realization of surfaces with complex, three-dimensional nanoscale features while retain much of the flexibility of EBL, much effort has been devoted to unconventional nanofabrication approaches based on controlled organization of small nanostructures such as wrinkles,^[7] colloids,^[8] block copolymers.^[9] and thin films.^[10-14] We report on a new route to nanopatterned surfaces based on the selective, isotropic growth of an electrodeposited multilaver structure comprised of alternating, heterogeneous materials of controlled nanoscale thicknesses.

In general, post-processing of fabricated multilayer structures can be regarded as a non-lithographic route to nanostructures. By cutting and/or polishing multilayer structures that have been formed using various methods (e.g. molecular beam epitaxy,^[10,11] chemical vapor deposition,^[12] electrodeposition,^[13] and sequential sputtering and anodization^[14]) and subsequently selectively etching a material from the revealed superlattice structures, nanoscale surface relief gratings are achieved in which feature sizes are controlled by the deposition parameters. These structures can be translated into nanoscale planar features using pattern transfer techniques,^[10,11] yielding sub-50 nm pitch nanowire structures that are useful in many applications (e.g., nanomechanical resonators,^[10] chemical sensors,^[15] and ring oscillators^[16]). Although the achievable size scale and pattern density of

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these approaches are comparable to that of electron-beam lithography (EBL), the achievable structures are usually limited by the simple geometry of the polished multilayer superlattice, i.e., one-dimensional, straight features distributed within a narrow, planar surface defined by the total thickness of the deposited multilayer (which is typically only a few tens of micrometers).

In this study, we show that the achievable structural diversity of the multilayer-based approaches can be greatly improved by adopting selective, isotropic growth of an electrodeposited multilayer from the predefined area of a template. Electrodeposition is selected as the multilayer deposition method primarily because its deposition reaction is highly selective to electrically conductive surfaces, and also controllable to form relatively thick (>100 μ m) multilayers with nanoscale individual layers of designed thicknesses at room temperature without employing vacuum tools. This process, which is referred to as a template-assisted multilayer electrodeposition (TAME), leads to the realization of the patterned surfaces with multidimensional, multiscale (10 nm–10 μ m) topography that is defined by both deposition control and template geometry design.

The TAME process begins with a template fabrication process based on conventional projection lithography (Figure 1a-d). A sacrificial silicon dioxide layer is deposited on a silicon substrate which may possess predefined topography as depicted in Figure 1b, and a conductive seed layer, typically copper (Figure 1a,b,d) or nickel (Figure 1c), is defined on the oxide layer. The seed layer is an electricallyconnected group of meshes with evenly spaced, uniform micrometer-scale openings. Depending on how a seed layer is defined on the substrate, the templates are categorized into two types. The seed layer of a Type 1 template is patterned either by wet chemical etching (Figure 1a,b) or a throughmold electrodeposition (Figure 1c). The seed layer of a Type 2 template is defined by patterning an additional sacrificial photoresist layer on the copper layer (Figure 1d), thereby masking portions of the copper layer with nonconductive photoresist.

Following the template fabrication, an electrodeposited nickel/copper multilayer is selectively grown from the seed layer while its isotropic, conformal growth is topographically guided by the insulating surface of the template (Figure 1e–h). In order to validate the TAME process, it is important to employ a deposition technique that can achieve multilayer structures with arbitrary individual layer thicknesses at reasonable process throughput. In particular, the







Figure 1. Nanopatterned surface realization based on the template-assisted multilayer deposition (TAME) process. Fabrication of a) a planar Type 1 template, b) non-planar Type 1 templates with patterned seed layers defined by chemical etching or c) through-mold electrodeposition, and d) a Type 2 template. Note that only a small portion of the meshed seed layer is depicted in each figure; the conducting paths between the seemingly isolated copper patterns illustrated in (a) and (b) are not shown. e–h) Multilayer electrodeposition. i–l) Sacrificial layer removal. The schematics are turned upside down. The sacrificial photoresist layer of the Type 2 template is removed after the oxide and the seed layers are sequentially removed. m) Selective copper etching.

technique should be able to rapidly produce nickel/copper multilayers with wide-ranging 1) periodicities (e.g., from tens-of-nanometers to over a micron) and 2) material thickness ratios (e.g., 99:1, nickel to copper, or vice versa), while 3) achieving superior compositional contrast between nickel and copper. It is possible to deposit multilayers from an appropriately-configured single bath by periodically changing deposition potential to deposit alternating layers of respective metals.^[17,18] However, a dual-bath approach with its independent cathodic depositions (Figure S1, Supporting Information) was considered the most appropriate technique to preserve the maximum process window for TAME structures.^[18,19]

The thicknesses of the individual layers formed within each deposition sequence are controllable both by deposition time and deposition current density; in this work, the deposition current was held constant and the layer thickness was determined by deposition time. The increasing conductive surface area of a growing multilayer may decrease the current density, and therefore, the growth rate, correspondingly. However, this has been suppressed to a negligible level (5–7%) by proper layout design of patterned seed layers. Alternatively, a continuously adjustable current that maintains constant current density could be utilized. The deposition is continued at least until the insulating surfaces exposed within the meshed portion of the seed layer are concealed under the deposited multilayer structure.

The sacrificial layers are selectively removed to reveal the bottom surface of the seed layer as well as the multilayer superlattice comprised of the "growth rings" of the electrodeposited layers (Figure 1i-l). The sacrificial oxide layer is removed by a hydrofluoric acid etch (through the exposed oxide surface remaining after the electrodeposition), and the photoresist layer is removed by an acetone rinse. Since both etch processes are sufficiently selective so as to not damage the electrodeposited structure, the revealed surface is smooth $(R_a < 10 \text{ nm})$ while the topography inversely-replicated from the template is preserved. A subsequent, timed selective copper etch defines the elevation of the nickel with respect to the copper (h) (Figure 1m), thereby forming a surface relief structure. The widths of protrusions (w) and trenches (g) correspond to the individual thicknesses of nickel and copper, respectively. In general, the cross-sections of the protrusions as well as the trenches are nearly rectangular when his similar to, or smaller than w and g (Figure S2, Supporting Information). Although not emphasized in this study, we confirmed that various nickel-based alloys, such as NiFe, CoNiFe, and CoNiP, are also compatible with the process; other metal pairs can be employed as the multilayer materials as long as 1) both materials are intact in the sacrificial layer removal process, 2) a desired material can be selectively etched from the multilayer structure, and 3) the interface roughness between the neighboring layers is sufficiently smaller than the size scale of the desired nanostructures.

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Figure 2. Fabricated surface structures. a,b) Optical images of a surface relief grating (w = 200 nm, g = 300 nm, h = 75 nm). (a) Diffraction from the surface grating formed within the meshed seed layer (yellow green). Copper seed layer is observed in brown. b) Magnified view of sample shown in (a). c) An atomic force microscope (AFM) image. d–l) Scanning electron microscope (SEM) images. d–f) Surfaces from a non-planar, Type 1 template (w = 250 nm, g = 250 nm, h = 160 nm). The nanostructures (light grey) shown in the top and bottom part of (d) are oriented -30° and $+30^{\circ}$ with respect to the larger-scale topography, respectively. e,f) Magnified images of the solid and dotted regions of (d). Nickel layers (light grey) are distinguished from the etched copper layers (dark grey). The inset of (f) is an angled, magnified image of the pattern. g,h) Nanopatterned surfaces from a Type 2 template (w = 50 nm, g = 125 nm). The insets show low magnification views. j–l) Circular, high aspect-ratio nanowall arrays (w = 80 nm, g = 500 nm, h = 8 µm). k) is a magnified, topside view of (j). The inset shows a close up view. l) is a cross-sectional view of A-B shown in (k).

The TAME-based, nanopatterned surfaces can be realized in batch-scale since the multilayer structure is selectively, and simultaneously, grown from a seed layer that is distributed over an area of arbitrary size. The processing time is defined by the minimum total multilayer thickness required to laterally deposit over the desired insulating surfaces exposed through the meshed seed layer (which is typically a few tens of micrometers at maximum), regardless of the desired total nanopatterned surface area. Nanopatterned surfaces exceeding 1 cm² have been routinely produced based on a few hours of multilayer deposition. **Figure 2**a–c shows a sample die comprised of multiple surface gratings with fill-factor (i.e., the ratio between the nanopatterned surface area to the total surface area including the seed layer) as high as 83%; sixteen samples of which total nanopatterned surface area of 1.5 cm² have been co-fabricated based on a single deposition of a 20- μ m thick multilayer structure which corresponds to the multilayer deposition time of 2 hours (Figure S3, Supporting Information).

The critical advantage of the TAME process over the previous multilayer-based approaches lies in its improved achievable structural diversity. Nanopatterned surfaces with various multidimensional features that are difficult to achieve through top-down, standard nanolithography can be synthesized. Hierarchical surface structures with coexisting microand nanoscale features are achieved by using Type 1 and



Type 2 templates with three-dimensional insulating structures. Figure 2d-f shows the nanoscale features achieved based on the multilayer structures fabricated through the process depicted in Figure 1b.f.i, that are independently oriented with respect to the microscale topography inversely replicated from the template. On the contrary, Figure 2g,h shows the structures obtained through the process depicted in Figure 1d,h,l, that are inherently concentric and selfaligned to the replicated topography. For both types of hierarchical structures, nanoscale features can be defined not only on the planar surfaces, but also along the sidewalls that are rounded (Figure 2e,f) or nearly vertical (Figure 2g,h); note that the throughput of such sidewall patterning using standard focused ion beam milling is relatively limited due to its serial nature. The structural diversity could be further improved by employing various three-dimensional template structures created by established techniques (e.g., V-shaped silicon trenches formed by anisotropic, potassium hydroxide etching,^[20] thermally-reflowed photoresist structures,^[21] and angled photoresist structures achieved by grey scale photolithography^[22]). In addition, nanostructures with high vertical aspect-ratio can be formed by selectively etching copper throughout the desired volume of the deposited multilayer structure. Figure 2j-l shows vertically oriented, high aspectratio (1:100) "nanowall" arrays fabricated based on a Type 1 template with electrodeposited, thick nickel seed layer (Figure 1c.g.k). Vertical orientation of the nanostructures is achieved even for such tall structures (Figure 21) since the removed thickness of copper $(8 \ \mu m)$ is smaller than the thickness of the seed laver (10 um).

Restrictions on the TAME process include that non-conductive materials cannot be utilized as the multilayer materials, and therefore the surfaces directly achieved from this process are mostly limited to metals; however, subsequent processes could be employed to derive functional surfaces with improved material diversity. The as-fabricated surface relief structures could exhibit magneto-optic Kerr effect resulting from the dense arrangement of ferromagnetic nickel, and non-magnetic copper structures.^[23] By a single step replica molding, or nanoimprinting, the dual-scale topography of the TAME-based surfaces could be replicated into various polymeric materials; surfaces with anisotropic structural wettability^[24] could be produced in a facile manner. Based on the conformal deposition of an electrolytically active layer, or a bilayer comprised of an electrical insulator and a conductor on the nanowall structures with controlled dimensions, batteries^[25] and capacitors^[26] with designed power and/or energy densities could be realized.

The widths of the protrusions (*w*) and trenches (*g*) of the TAME-based surface structures (i.e., the widths of the nickel and copper growth rings) are in proportion to the individual layer deposition time of nickel and copper, respectively (**Figure 3**a), while the height differences between them are due to the copper etching time (Figure 3b). The growth rates of nickel and copper at the typical current densities of 10 mA cm^{-2} and 15 mA cm^{-2} are 2.58 nm s⁻¹, and 4.24 nm s⁻¹, respectively (see Supporting Information for further discussions on the deposition and selective etching processes). These are calculated based on the patterned, multiscale





Figure 3. a) Widths of the growth rings as a function of individual layer deposition time (error represents ±three standard deviations). b) Etched copper thickness as a function of etching time (error represents ±one standard deviation). c) Patterned surface with multiscale features. Nickel layers (light grey) are distinguished from the etched copper layers (dark grey). In the 1st, 2nd, 3rd phase of the multilayer deposition, nickel and copper layer deposition times are 9, 27, and 81 seconds, respectively.

structures with wide-ranging pitches (p = w+g) formed by changing the individual layer deposition time through multiple deposition phases (Figure 3c). As observed in the fabricated structures discussed so far, the growth rings formed within an opening of the meshed seed layer are geometrically similar with their centers being identical. This means the multilayer growth is nearly isotropic, and therefore, the measured rates with respect to an arbitrary axis are sufficient to represent the growth rates along all directions. Features as small as several nanometers (w = 4 nm, g = 9 nm) can be created; however, the features with sub-50 nm pitches tend to be randomly corrugated as observed in Figure 3c, due to both the grain boundaries of the polycrystalline electrodeposited materials as well as the surface roughness replicated from the surface of the sacrificial layer. The interlayer roughness resulting from the exchange reaction between the deposited nickel surface and the copper ions dissolved in the copper electrolyte could be mitigated by depositing copper under proper potentiostatic conditions (see Supporting Information, page 6).

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Figure 4. a) Pictorial depiction showing how I_n and $S(r_n)$ are defined by the deposited multilayer structure at the deposition sequence, n = 3. b,c) The modeled locus (light green), I_n , and the corresponding locus detected from the actual SEM image of fabricated nanostructures (red), A_n , for varying n (r_n [nm] = 400n). I_n is caculated using A_1 as the periphery of the seed layer (see Experimental Section). d) Schematics of a planar, Type 1 template. Site A and B indicate the samples located on the upper and lower portion of the wafer, 2.5 cm apart from each other. e) Schematic cross-sectional view of the multilayer structures being formed at respective sites. f) Average pitch of the nanostructures measured from different locations, as a function of the deposition sequence, *n*. The average pitch at *n* is calculated by measuring the total width of 5 pairs of nickel and copper growth rings formed between the (n-9)th sequence and the *n*th sequence, and dividing it by the number of pairs. The measurements are based on the actual surface structures with designed critical dimensions (w =200 nm, g = 300 nm). Ideally, the average pitch should be 500 nm along the entire deposition sequence. Error represents ±one standard deviation.



The positions and geometries of the growth rings can be mathematically modeled from a given set of initial conditions including the template geometries and full sequence of individual layer deposition time by assuming an ideal multilayer growth, i.e., perfectly uniform, isotropic growth of both nickel and copper with constant growth rates throughout the process. The projection of an arbitrary metal layer surface formed at the *n*th sequence onto the insulating surface of the template is defined as I_n (Figure 4a), and calculated as the locus of points equidistant from the periphery of the patterned seed layer by r_n , i.e., the theoretical estimation of the multilayer thickness after the *n*th sequence:

$$r_n = \sum_{i=\text{odd}}^n G_{\text{Ni}} t_i + \sum_{i=\text{even}}^n G_{\text{Cu}} t_i \tag{1}$$

where $G_{\rm Ni}$ and $G_{\rm Cu}$ are the estimated growth rates of nickel and copper, respectively, and t_i is the deposition duration of the *i*th deposition (the equation is based on the convention of nickel being the layer deposited at the first sequence). Then, a sequenced calculation of I_n would lead to the modeled multilayer superlattice. The calculation of I_n is performed based on a morphological dilation of the area defined within the patterned seed layer, by a structuring disk of radius of r_n , $S(r_n)$ (Figure 4a).^[27] The model is validated by comparing the modeled locus, I_n , and the corresponding locus detected from the actual image of fabricated structures, A_n , as shown in the figures showing the growth rings generated from the curved corner of the seed laver forming an acute angle (60°) between the deposition sequences n = 17 and n = 33 (Figure 4b), and from the three different portions of the seed layer merging into a triangular growth ring between n = 54 and n = 72 (Figure 4c). The gradual geometry and position change of the growth rings throughout the deposition can be accurately modeled, proving that the TAME-based nanopatterned surface realization is highly controllable.

The discrepancy between I_n and A_n represents the accumulation of any non-ideal, spatiotemporal aspects of the multilayer growth between the first and the *n*th sequence. In general, nanostructures with relatively larger feature sizes are observed in the samples deposited from the lower part of the substrate (i.e., those patterns immersed most deeply in the deposition bath) (Figure 4d,f), since the sample substrate is immersed while the current supplies are "on." In addition, nanostructure feature sizes may vary with respect to the changing geometry of the conductive surface of the growing multilayer structure. From the results from a single site (either site A or B depicted in Figure 4d), it is observed that the measured pitches change as the deposition sequence progresses for the nanostructures formed within the meshes, unlike the measured pitches from those sites formed at the edge of a die, which are nearly constant (Figure 4e,f). The change reflects the increasing copper deposition rate in the vicinity of the insulating template surface with respect to the decreasing gap between the approaching surfaces of the growing multilayer. This counterintuitive trend is attributed to the leveling effect of the commercially-available copper electrolyte, and will vary for seed layers with different thicknesses and/or mesh designs.





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In summary, we have presented the TAME process for a facile, controllable realization of patterned surfaces with various architectures over large areas with individual features ranging from a few tens of nanometers to several micrometers, without the need for traditional nanolithography tools. This method offers an alternative way to create patterned surfaces with dual-scale topography or nanowall electrodes that are difficult to achieve with current top-down nanofabrication technologies. The process could lead to a deterministic approach toward molecular, or atomistic scale patterning, by combining a proper selective deposition method (e.g., layer-by-layer assembly^[28]) with appropriate template materials.

Experimental Section

Materials and Fabrication: We use a pre-cleaned 4 inch, testgrade silicon wafer as a substrate. Fabrication of a pre-etched silicon substrate is based on a standard photolithography followed by an isotropic silicon etching using SF_6 chemistry via an inductively-coupled plasma etching tool. A 1 µm-thick sacrificial silicon dioxide layer is deposited by plasma enhanced chemical vapor deposition. The seed layer is a copper (500 nm) layer sandwiched by titanium (30 nm) layers formed by a DC sputter. The seed layer wet etching is performed using a predefined, 1.2 µm-thick photoresist layer (Microposit SC1813, Shipley) as an etch mask; titanium and copper are etched by diluted hydrofluoric acid (2% vol.) and a phosphoric acid-based commercial etchant (Aluminum Etchant -Type A, Transene), respectively. The electrodeposited, thick nickel seed layer used in the study is fabricated based on a conventional through-mold electrodeposition using a patterned, negative photoresist (NR 21-20000P, Futurrex) as a mold. The photoresist structures for Type 2 templates are patterned using a positive photoresist (AZ P4620, AZ Electronic Materials). The titanium layer on the copper seed layer is removed right before the multilayer electrodeposition. The nickel electrodeposition bath consists of 200 g L^{-1} NiSO₄·7H₂O, 5 g L^{-1} NiCl₂·6H₂O, 25 g L^{-1} H₃BO₃, 3 g L⁻¹ saccharin, with pH of 2.5 \pm 0.1. The copper electrodeposition is performed using a commercialized, copper sulfate-based electrolyte (Clean Earth Mirror Copper solution, Grobet USA). Both depositions are performed at room temperature, without any bath agitation. Details of the automated dual-bath deposition setup and its operation can be found in the Supporting Information. The sacrificial oxide layer is removed by immersing the sample wafer into the concentrated hydrofluoric acid (49% vol.) for 1-2 hours at room temperature. The selective copper etching is performed using an acidified thiourea solution, i.e., 1 M thiourea solution with pH adjusted to 1 with concentrated hydrochloric acid.^[29]

Characterization: Optical images are acquired using Keyence VHX-600 digital microscope. Veeco Dimension 3100 AFM is used to measure surface morphology. Hitachi S-4700 and JEOL 7500F are used for SEM imaging and growth ring widths measurement. Trench depths are measured through angled SEM imaging, AFM scanning, focused ion beam etching using FEI Strata DB235 FIB, and sample cleaving. The sample is cleaved by a wafer dicing machine with a nickel blade (50-µm thick) after the sample is potted in epoxy (Figure 2I).

Image Processing: Grey scale images of two-dimensional, periodic nanostructures are taken by SEM. After the original image is processed through a proper set of contrast adjustments and lowpass filtering, a binary image of the same size is created in which boundaries of the seed layer as well as the multilayer superlattice are selectively detected and plotted based on the Canny edge detection method. The detected boundaries are referred to as A_n . The area of the patterned seed layer is defined as D_0 . Then, I_n of interest is obtained from the periphery of a newly defined area D_n , which results from the binary dilation of D_0 by a structuring disk of radius of r_n , $S(r_n)$, or $D_n = D_0 \oplus S(r_n)$; in other words, D_n is the locus of the points covered by $S(r_n)$ when the center of $S(r_n)$ moves inside D_0 . The desired I_n , and A_n are overlapped on the oringinal SEM image to produce images shown in Figure 4b,c. Codes are generated based on MATLAB.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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