DESIGN, FABRICATION, AND APPLICATIONS OF LARGE-AREA WELL-ORDERED DENSE-ARRAY THREE-DIMENSIONAL NANOSTRUCTURES

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A highly effective fabrication process combining interference lithography with deep reactive ion etching is described. This simple technique makes it possible to build well-ordered dense-array of nanostructures with good control of pattern regularity and size over a large area. The unique three-dimensional structures possible with this process can have a variety of applications in electronics and other physical sciences.

7.1 Introduction

Much of nanotechnology as we know it today is based on our ability to create objects of nanometer size scale whether chemically (typically bottom-up) or physically (typically top-down). While any fabrication technique that produces new materials or nanostructures may spur some scientific discoveries that were not possible before, engineering breakthroughs impose much more stringent criteria on the fabrication
methods, such as controllability, repeatability, and yield. In some applications, more specifically, one may need nanostructures with good regularity as well as controlled pattern, size, and shape. In some applications, furthermore, nanostructures may not be practical unless they cover a relatively large area.

While numerous nanostructures, made by many different nanoscale patterning and fabrication methods, have been reported\(^1\), we still lack the technology to achieve nanostructure formation with enough regularity and controllability of pattern, size, and shape, to enable expedient and precise scientific studies and engineering applications at the nanoscale. Although serial nano-lithographic techniques such as e-beam, ion-beam, or scanning probe lithography enable direct writing of complex nanoscale patterns, the slow speed of these patterning techniques is not suitable to cover large areas (these techniques typically cover less than 1 mm\(^2\) at a time). While the parallel method of X-ray lithography can pattern a large area, it is too expensive for most applications. On the other hand, soft lithography-based methods, such as nanoimprint lithography, replicate patterns in a parallel fashion but need a master mold which should first be manufactured by e-beam or X-ray lithography. Most non-lithographic methods, such as the use of nano templates constitut ed by self-assembled nanoparticles (e.g., block copolymers or colloidal nanospheres) or nanoporous membrane (e.g., anodic alumina membrane), lack the regularity some applications demand over a large area. For other non-lithographic methods such as the direct growth of nanostructures (e.g., carbon nanotubes or nanofibers), the controllability and regularity of the pattern size and geometry still remains an issue. Various techniques to fabricate a dense array of nanoscale posts have been developed and evaluated in reference 2.

Currently, interference lithography is considered the most efficient way to make nanoscale periodic patterns over a large area (reportedly up to \(\sim 1\) m\(^2\)) with precise control of regularity and accuracy.\(^5\) It uses simple and relatively inexpensive optics to generate uniform interference patterns such as lines and dots on a substrate. It does not use any photomask and has practically unlimited depth of focus. Because of the periodic nature of the patterns created by interference lithography, optical gratings\(^13\) or field emitter arrays\(^15\) have been fabricated efficiently. However, it should be noted that to transfer the lithographic pattern into the substrate, in particular to etch tall or high-aspect-ratio nanostructures, a thin photoresist (PR) (typically tens of nanometers thick) needs to be replaced by a hard etch mask, such as a metal\(^3\) or an oxide\(^4\), before the subsequent deep etching step. The added mask steps make the process more complex and degrade the pattern resolution possible.

Greatly simplifying the process and improving the accuracy of the pattern transfer, we have recently developed a new means of coupling the interference lithography directly with deep reactive ion etching (DRIE)\(^9\). Noting that DRIE has a very high etch selectivity for silicon over PR (e.g., \(\sim 75:1\))\(^20\), our approach is to utilize the thin PR layer patterned by the interference lithography directly as an etch mask layer in DRIE, while retaining the traits of both techniques. Well-ordered (post and gate) dense-array (230 nm in pitch) silicon nanostructures with less than 10% deviation in size and shape could be achieved over a large sample area (\(2 \times 2\) cm\(^2\)). The new combination of DRIE with interference lithography enabled even high-aspect-ratio (higher than 10:1) tall nanostructures (over 1 \(\mu\)m) in one process flow. Commonly used to etch deep trenches with vertical sidewalls in Micro Electro Mechanical Systems (MEMS) fabrication, a Bosch DRIE process (as opposed to a cryogenic process\(^16\)) has rarely been used to construct nanostructures because the well-known effect of sidewall rippling, so-called 'scalloping', is too prominent on the nanoscale. However, recently we have shown that by properly regulating etching parameters in the process recipe, the nanoscopic scalloping problem can be not only controlled but also utilized to realize three-dimensional (3D) nanostructures with sophisticated sidewall profiles\(^9\). In that work, it was further demonstrated that the tip sharpness can also be controlled by a simple additional process of thermal oxidation and the subsequent removal of the oxide. The well-defined nanostructures over a large area with designable sidewall profiles and tip shapes open new application possibilities in areas beyond electronics and photonics. In this chapter, we will revisit the new nanofabrication technique\(^9\), explaining the design and fabrication of 3D nanostructures followed by their applications.

7.2 Design and Fabrication

7.2.1 Materials and methods

Figure 7.1 shows the overall fabrication process for large-area well-
ordered dense-array 3D silicon nanostructures using interference lithography followed by DRIE. A polished silicon substrate (~ 2 x 2 cm²) is cleaned with a Piranha solution (H₂SO₄:H₂O₂, 3:1 by volume) and dehydrated for 10 minutes at 150°C. The SPR3001 photoresist (Shipley Company, Marlborough, MA) is then spin-coated at 5000 rpm for 1 minute, which gives ~50 nm film thickness. After the spin-coating, a soft-bake is done at 95°C for 1 minute on a hot plate. The substrate is then exposed under an interference lithography setup of a HeCd laser emitting at a wavelength of 325 nm (Fig 7.2). While the pattern periodicity or pitch, p, is tunable by rotating the sample stage (i.e., changing the angle, θ), we specifically set θ equal to 45°, which produces p = 230 nm. Two different regular patterns have been created: nanogate structures using a pattern of parallel lines and nanopost structures using a pattern of a dot array. Such PR dots in a grid array are obtained by two successive exposures with the substrate rotated by 90° in its plane between the exposures. After the exposures, the substrate is developed with MF701 developer (Shipley Company) for 20 seconds, rinsed with de-ionized water, blown dry with N₂ gas, and hard-baked for 1 minute at 110°C on a hot plate.

![Fabrication process of 3D nanostructures with sidewall profile and tip sharpness control](image)

**Fig 7.1** Fabrication process of 3D nanostructures with sidewall profile and tip sharpness control. PR pattern created by interference lithography is used as a direct etch mask in DRIE. DRIE etching step involves the design of etching parameters for 3D nanostructure fabrication, e.g., sidewall control for either re-entrant (left column) or positively-tapered (right column) profile. Nanostructures with positively-tapered, smooth sidewall profile can further be sharpened by thermal oxidation and the removal of the oxide.

\[ \rho \text{ (period)} = \frac{\lambda}{2\sin \theta} \]

**Fig 7.2** Schematic of Lloyds-mirror configuration of laser interference lithography system. A HeCd laser beam with a wavelength of \( \lambda = 325 \text{ nm} \) is expanded and spatially filtered through a pinhole in order to render it coherent. The coherent beam is collimated and aligned toward a mirror and a substrate holder forming a 90° dihedral angle. It inscribes a periodic line pattern of interfered light intensity on a PR-coated substrate. A line pitch \( p \) is determined by \( p = \frac{\lambda}{2(2\sin \theta)} \), where \( \theta \) is one half of the angle between the directly incoming and the mirror-reflected lights.

The substrate is then etched by DRIE using the patterned PR as an etch mask. For the DRIE etching, we use PlasmaTherm SLR770 ICP etcher (Unaxis Corporation, St. Petersburg, FL). The etching procedures and parameters for the cyclic steps of the Bosch process are shown in Fig 7.3 and summarized in Table 7.1, respectively. One etch cycle consists of two consecutive etch steps of ‘Etch A’ and ‘Etch B’ and one ‘Deposition’ step. Although several parameters in DRIE, such as pressure, RF power, and gas mixture influence the sidewall profile, the relative duration of etching time (e.g., Etch B time) versus deposition time in the cyclic Bosch process is easier to control with good reproducibility and is thus mostly utilized for the control of scalloping effect and the fabrication of 3D nanostructures. Two means are shown in Fig 7.1 to obtain 3D nanostructures with various sidewall profiles: one with a re-entrant profile on top and the other with a positively-tapered profile. After the DRIE, the remaining PR is removed by O₂ plasma ashing and the sample is cleaned by the Piranha solution. For further modification, such as needle-like sharp-tip nanostructures, the tips of nanostructures with the positive slope are sharpened by the oxidation of silicon and the subsequent removal of silicon dioxide.
right near the top but positive on the rest of the nanoposts below). The degree of the re-entrance was controlled by the scalloping size through the first cycle of the Bosch process. The Etch B time of only the first cycle was increased from 4 seconds to 6, 8, and 10 seconds, while the Etch B time of the subsequent cycles was fixed at 2 seconds. As the Etch B time of the first cycle increased, the scalloping at the beginning (i.e., tip of the nanostructures) became more pronounced and produced a re-entrant (i.e., negative) profile. Below the tip region, the sidewall profile made by the etch cycles using a shorter Etch B time (2 seconds) became smooth and positively-tapered.

### 7.2.2 Design and fabrication of “candlestick-like” nanostructures

Although the nano-scalloping effect inherent in the Bosch DRIE is undesirable in typical applications, an intricate sidewall profile for 3D nanostructures can be achieved by planning the degree of the nano-scalloping effect along the sidewall. For example, Fig 7.4 shows sidewall profiles programmed to be re-entrant or “candlestick-like” (i.e., negative
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(i.e., Etch B time) against the deposition time, but also by the total number of etch cycles. Although the regulation of Etch B time makes the creation of 3D nanostructures practicable, it is not easy to independently control the local (i.e., at a given depth) sidewall profile and the overall sidewall slope simultaneously. In addition to the Etch B time, the modulation of the other parameters such as RF power, pressure, and gas mixture is also desired for the independent control of the local sidewall profile and the overall sidewall slope. For example, Fig 7.5 shows nanostructures with overall sidewall slope was designed to be all positive but whose local sidewall profiles vary independently. The different degrees of nano-scalloping formation along the sidewall, while maintaining the overall positive-slope of the sidewall, was enabled by modulating several etch parameters concurrently. This result, as clearly shown in Figs 7.5(c) and 7.5(d), suggests that independent control of the lower-order (smaller) nano-scalloping formation along the surface of the higher-order (larger) nanostructure will enable a multidimensional “hierarchical” nanostructure. This result further supports the idea that the well-programmed nano-scalloping effect by modulating the etch parameters in Bosch DRIE can be a simple but useful tool to tailor the sidewall profile of 3D micro and nanostructures.

Fig 7.6 SEM images of silicon nanostructures with sharp tips. Tips of nanostructures with positively-tapered, smooth sidewall profiles were sharpened by thermal oxidation followed by oxide etching, measuring less than 5 nm in tip apex radius of curvature. (a)-(b) Nanorod structures with needle-like sharp tips (a: 114 ± 1 nm in height and 11 ± 1° in cone angle), (c)-(d) Nanotube structures with blade-like sharp tips (c: 180 ± 10 nm in height and 12 ± 1° in cone angle. d: 600 ± 18 nm in height and 4 ± 1° in cone angle).

7.2.4 Design and fabrication of “sharp-tip” nanostructures

As proposed in Fig 7.1, sharp-tip nanostructures can be developed from nanostructures with a positively-tapered, smooth sidewall profile. For example, Fig 7.6 shows sharp-tip nanostructures of varying heights. While the size (i.e., height or aspect ratio) of the sharp-tip nanostructures is initially determined in DRIE, it can also be modulated further in the timed oxidation step. The cone angle of the sharp-tip nanostructures is
also designable with the sidewall slope control in the DRIE step, while the subsequent thermal oxidation and wet oxide etch do not change the cone angle significantly since they are isotropic processes. The tip apex radius of curvature of the sharp-tip nanostructures shown in Fig 7.6 is less than 5 nm, regardless of the size and shape; all were measured by the image analysis of cross-sectional SEM images.

7.3 Applications

To create 3D structures with conventional fabrication techniques, multiple lithography steps with precise alignment or multi-layer resists (or multi-step post processes) within a single lithography step would be required. In this regard, the simple but efficient fabrication method of 3D nanostructures presented here, directly achievable in just one process flow in Bosch DRIE, is much more suitable for various practical applications. For example, 3D nanostructures are desirable in several applications such as T-gates for microwave transistors, wave modulators for nano-optics, and various nanoelectromechanical systems (NEMS). For a given void fraction under the surface, nanostructures with a re-entrant profile provide less open and more flat area on the surface than simple profiles do. One use of such a re-entrant profile would be to produce monolithic nanochannels by scaling the top of the nanogate structures with a thin-film coating. The well-ordered sharp-tip nanopost structures covering a large pattern area are commonly of interest in such electronic applications as field emission structures. The simple way outlined here to fabricate sharp-tip nanostructures will also facilitate the design and fabrication of high-aspect-ratio scanning probe tips. Well-ordered densely-populated nanostructures over a large sample area could also be useful for non-electronic applications as described below.

7.3.1 Low-friction superhydrophobic surface

One novel non-electronic application of sharp-tip nanostructures is to reduce friction of liquid flows. After a hydrophobic surface treatment, sharp-tip nanostructures make the surface superhydrophobic because the liquid is levitated over the air layers sustained among the non-wetting nanostructures (Fig 7.7). In this way, the liquid has minimal contact with the solid surface (i.e., contacting only the tips of the nanostructures), and is expected to flow with significantly reduced skin friction (i.e., significantly increased slip flow). Although the basic concept has been known from nature and tested for years, there has not been a deliberate effort to design and fabricate a surface to produce a meaningful reduction in friction under practical conditions (e.g., highly pressurized flows frequently encountered in engineering practice). Three new features are critical for the design and fabrication of low-friction superhydrophobic surface. First, the nanostructures should be populated with submicron density, which keeps the surface dry even under pressurized liquid. Similar surface structures with micron-scale density would be filled with liquid under a nominal pressure (e.g., > 1 atm) and lose its functionality. Second, the nanostructures should be tall and slender, providing a thick air layer below the liquid. Without enough air to lubricate, the flow friction is not reduced enough to be meaningful. Third, the sharpness of the nanostructures should minimize the liquid-solid contact. The well-controlled, high-order sharp-tip nanostructures have a dense pitch on the nanoscale enabling a detailed study of the effect of nanostructure geometries on superhydrophobicity. Such structures also show great promise in practical flow applications by tolerating highly pressurized flows without losing superhydrophobicity. Although the superhydrophobic surface is commonly thought of as conducive to help reduce pressure drops for microchannel flows, its
utility is much wider. For instance, the large slip flow at walls can help flatten the velocity profiles within microchannels, which could then be utilized to reduce the dispersion in microfluidic separation systems.

7.3.2 Novel substrate for nanobiotechnology and nanobiotechnology

The well-regulated nano-topographical properties of our nanostructures will also provide a unique testbed enabling a number of detailed studies in nanobiotechnology and nanobiotechnology. For example, cell-matrix adhesion in vivo is a 3D phenomenon that differs from the adhesion on two-dimensional (2D) substrates in vitro33. Within the extracellular matrix, cells interact with nanoscale topographical projections and depressions that vary in composition, size and periodicity34. The matrix topography is important for proper adhesion and the activation of desired intracellular pathways, affecting cell behavior in terms of morphology, cytoskeletal arrangement, migration, proliferation, surface antigen display, and gene expression35,36. Although several cell behaviors over various surface topographies had been studied with micro- and nanostructured surfaces35,36, the inability to independently control nanodimensionality and nanoperiodicity in the nanoscale range has to date precluded a systematic study of the 3D effects of nanoscale features on cell behaviors. As shown in Fig 7.8, our well-defined nanostructured surfaces provide a unique opportunity to elucidate many aspects of the nanobiology of the cell, including the 3D effect of the surface nanotopography on cell behaviors, whose understanding can further be utilized for cell and tissue engineering applications37.

For example, the lateral tip size of our sharp-tip nanostructures (less than 10 nm in tip apex radius of curvature), comparable to that of a single integrin molecule (8-12 nm) in a cell membrane, can provide unique capability to examine integrin activation and focal adhesion on 3D nanotopographies, which is essential for adhesion-mediated signaling. Our sharp-tip nanotopographies capable of excellent control of nanodimensionality and nanoperiodicity will also enable the investigation of relative contributions and interactions between nanotopographical three-dimensionality and periodicity on integrin clustering and activation. Fewer cell populations with the retardation of cell growth observed on the sharp-tip tall nanopost structures suggest that the needle-like sharp-tip nanostructures should be useful for a biological low adhesive surface, i.e., anti-adhesion or anti-fouling surface. The control of bio-adhesion or bio-fouling only through control of the surface nanotopographies, as opposed to chemical modification, will provide many advantages in the design of biomaterials such as biomedical implant surfaces. Another advantage of the needle-like sharp-tip nanostructures is that they can be used as drug delivery or biochemical manipulation systems. The needle-like sharp-tip nanoposts can be inserted into viable cells, by pressing for instance, and transport chemicals pretreated on the sharp-tip surfaces across cell membranes. Furthermore, they can be utilized as an intracellular interface for monitoring and controlling subcellular and molecular phenomena in the way of in vivo biosensors and actuators. The significant alignment with elongation of the nanograte topographies (see Fig 7.8b) also suggests the possibility of controlling the cells' orientation or structure by using directional nanostructures, which may be desirable in tissue engineering applications. For instance, nanotopography may be exploited to create cell sheets with specified cell-alignment patterns, and then layers of nanoengineered cell sheets can be stacked to create 3D tissue constructs for tissue regeneration applications.

Fig 7.8 SEM images of human foreskin fibroblast cells cultured on sharp-tip nanostructure surfaces (a: nanopost, b: nanograte)37. Each inset is a magnified image of the filopodia of cells interacting with the surface37. Human foreskin fibroblasts exhibited significantly smaller cell size and lower proliferation on nanoposts, and enhanced elongation with alignment on nanogrates. These phenomena became more pronounced as the nano-topographical three-dimensionality (structural height) increased. The nanopost and nanograte architectures provided the distinct contact guidance for both filopodia extension and the formation of adhesion molecules complex, which was believed to lead to the unique cell behaviors observed.
7.4 Conclusion

A simple and effective fabrication method for building well-ordered dense-array of nanostructures with good control of pattern regularity and size over a large area was achieved by combining interference lithography with DRIE in one process flow. The nanoscale scalloping effect in Bosch DRIE was controlled and utilized for creating novel 3D nanostructures with various sidewall profiles and tip shapes. Affordable surfaces with well-controlled nanostructures over a large area open new applications not only in electronics but also in the physical world through their unique properties originating from their nanoscale geometry. We envision that various 3D nanostructures, from not only silicon but also other materials such as metal, glass, and polymers, can be designed and fabricated for further novel applications; incorporating the current techniques in the process.

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References


