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3D LITHOGRAPHY

Atomic gold-enabled three-dimensional lithography for silicon mesostructures

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Three-dimensional (3D) mesostructured semiconductors show promising properties and applications; however, to date, few methods exist to synthesize or fabricate such materials. Metal can diffuse along semiconductor surfaces, and even trace amounts can change the surface behavior. We exploited the phenomena for 3D mesoscale lithography, by showing one example where iterated deposition-diffusion-incorporation of gold over silicon nanowires forms etchant-resistant patterns. This process is facet-selective, producing mesostructured silicon spicules with skeletonlike morphology, 3D tectonic motifs, and reduced symmetries. Atom-probe tomography, coupled with other quantitative measurements, indicates the existence and the role of individual gold atoms in forming 3D lithographic resists. Compared to other more uniform silicon structures, the anisotropic spicule requires greater force for detachment from collagen hydrogels, suggesting enhanced interfacial interactions at the mesoscale.

Semiconductors with three-dimensional (3D) mesoscale features (1–5) are an emerging class of materials, with promising applications from stretchable bioelectronics (3) to alternative plasmonics and metamaterials (6). However, progress in this area has been impeded by challenges in chemical synthesis (4) and limitations in 3D fabrication methods (1, 2, 4, 7). As a result, this area would benefit from new synthetic concepts or new components in lithography. One place to look for such inspiration is in biomaterials-based processes, which routinely assemble mesostructured materials. In the growth of natural hard biomaterials, trace amounts of interfacial organic species are important components (8), yielding unusual 3D biomaterial shapes and properties. The application of trace organic molecules as components (e.g., an etching resist) in semiconductor-based lithography is hard to achieve, given that a semiconductor processing typically involves either high-temperature gas-phase or harsh solution-phase preparations. However, inorganic species are much more stable and can be introduced as trace components into various semiconductors, as either impurities in the bulk volume (9–11) or as diffused species near the surface (12–16), with the latter holding great potential in 3D semiconductor lithography, given that surface diffusion is versatile and more controllable.

Here we focus on 3D mesoscale lithography of silicon (Si) nanowires with diffused gold (Au) (13, 14, 17), where Au originates from the nanoparticle catalyst used for nanowire nucleation and elongation (Fig. 1, supplementary materials (18), and fig. S1). Because Au diffusion over Si surfaces is pressure-dependent (16), we first adopted periodic pressure modulation during Au-catalyzed Si nanowire synthesis to develop Au diffusion–induced patterns along nanowire sidewalls (Figs. S1 to S3), where silane (SiH4) and diborane (B2H6) were used as a Si precursor and a p-type dopant, respectively. Next, we revealed the Au-based patterns with anisotropic wet chemical etching in KOH solutions [materials and methods (18) and fig. S4]. The as-grown Si structures have rather uniform diameters except for periodic swells at the evacuation locations (Figs. S2 and S3). After etching, we identified two Si mesostructures from the same growth batch: a type I spicule with platelike nodes and a type II spicule with triangle-shaped nodes (Fig. 1, A and B). Portions of the nanowire surfaces remained after etching, suggesting that the diffused Au acted as an etching resist. Both spicule structures show gradient, curved, and anisotropic surface textures. These formations are reminiscent of other complex nanowire morphologies (19–24) but are also similar to some naturally occurring hard materials, such as skeletons (9). Transmission electron microscopy (TEM) images of p-type Si spicules (Fig. 1, C to F, and fig. S5) show that type I and type II structures grow along the <111> and <112> directions, respectively. Although type I is a single crystal, the type II spicule has a {111} twin plane (II), which separates subunits α and β (Fig. 1F, TB marks the twin boundary), as determined by the two sets of diffraction spots (Fig. 1F, magenta/white and blue/white dashed circles) in the selected area electron diffraction (SAED) pattern.

We used scanning TEM (STEM) for tomograms of mesostructured Si spicules (19) (Fig. 2, A and B, and fig. S6). In addition to the expected structural gradient and anisotropy, we revealed convex and
curved anisotropic shells (magenta lines) and \{111\} facets-based polyhedron cores (type I: octahedron; type II: trigonal bipyramid, blue and green lines) as the coupled two principal “tectonic” motifs for individual nodes (Fig. 2, A and B, and fig. S7).

Fig. 1. Electron microscope images of type I (A, C, and D) and type II (B, E, and F) skeletonlike Si spicules. (A) and (B) SEM images. The right-hand columns are zoomed-in views of individual segments shown in the lefthand columns. (C) to (F) TEM and SAED patterns of type I and type II structures, viewed from \([111]\) (C), \([110]\) (D), \([111]\) (E), and \([\overline{1}10]_a/\overline{1}10_b\) (F) zone axes. The numbers in SAED patterns are diffraction spots, which reveal \([111]\) and \([112]_b/\overline{1}11]_b\) growth orientations for type I and II structures. Magenta and blue in (E) and (F) highlight information from twinning subunits \(\alpha\) and \(\beta\), respectively. Scale bars, 200 nm.

Fig. 2. Mesostructured Si spicules show defined motifs, pronounced curvature, anisotropy, and gradient. (A and B) STEM tomography of type I (A) and II (B) spicules, with polyhedron-curved shell models shown on the right. The blue and brown arrows in the STEM tomography mark two different concave features. The magenta and green arrows in the models suggest “morphogenesis” orientations for the two “tectonic” motifs. (C to F) Isosurfaces [(C) and (D), \(110\), \(112\), \(111\), \(011\) (110)] and quantitative analysis of \(S_{(110)/S_{(112)}}\) in type I [(C) and (E)] and II [(D) and (F)] spicules. The segment indices are identical to those in (A) and (B). The numerical values in each segment were obtained using Amira 5.5 (FEI Visualization Sciences Group). Green and magenta in (C) mark the inside and outside surfaces, respectively. SSA, specific surface area. Scale bars in (A) and (B), 200 nm.
We analyzed the surfaces (18) and mean curvatures (the average of the two principal curvatures) of individual segments (Fig. 2, C and D). We confirmed that there were two groups of concave and highly curved patches in a type I spicule segment (segment IV, Fig. 2C, left)—lower (brown arrows) and higher (blue arrows) sets—consistent with the octahedron model (fig. S8). They are arranged with a threefold symmetry and were formed from selective etching of the left (Fig. 2A, brown arrow) and right (Fig. 2A, blue arrow) domains about the central plate, respectively (fig. S8). In contrast, a type II spicule segment (segment VI, Fig. 2D, left) is capped with (111) planes, and only one (110) mirror plane is observed. 3D mean curvature maps (segment I, Fig. 2, C and D, right) confirm the concave (blue) and convex (red) surfaces and show that large mean curvatures concentrate at the coupling regions between lateral shells and polyhedron cores (Fig. 2, A and B).

The individual segment volumes and specific surface areas (i.e., surface area/volume) generally increase and decrease, respectively, from segment I to VII in both structures (Fig. 2, E and F, left). These facts suggest that etching of Si and the corresponding porosity are more significant near the Au catalyst. The segment cross-sectional areas (Fig. 2, C and F, right; and fig. S9), (112) and (110) planes in the type I spicule, and (110) and (111) planes in the type II spicule, all generally increase from segment I to VII, suggesting a gradient in the pattern of etching resistance. The ratios of the two cross-sectional areas also change in different segments (Fig. 2, E and F, right), indicating non-uniform radial evolution of segment geometry.

To understand the pattern formation mechanism, we used x-ray photoelectron spectroscopy (XPS) to characterize Si surfaces before wet chemical etching (Fig. 3A). Deconvolution of Au 4f lines indicates the presence of two principal Au components in the detectable regime (<10 nm): metallic Au and intermetallic silicide-like Au (Fig. 3A, upper panel). For example, an Au 4f 7/2 peak at 84.0 eV with a full width at half maximum (FWHM) of 1.9 eV indicates metallic Au, whereas the one at 85.3 eV with a FWHM of 2.1 eV suggests the intermetallic Au species (25). The fact that intermetallic Au yields a notable XPS signal area ratio: intermetallic/metallic ~ 1.068) suggests significant Au diffusion and subsequent incorporation into Si subsurface regions. To decouple the role of metallic Au from the intermetallic one in establishing the sculpted structure, we removed metallic Au with a standard gold etchant, as confirmed from XPS (Fig. 3A, lower panel). The primary sculpted structures are maintained after wet chemical etching (fig. S10), suggesting that intermetallic Au in the Si subsurface plays a major role as an etching resist.

Using laser-assisted local electrode atom-probe tomography (APT), we studied Au together with...
other elements with subnanometer spatial resolution (figs. S1I to S15). A proximity histogram (Fig. 3B and fig. SI3) (38, 26), plotted along the spicule radial direction and collected from an etching-resistive portion (fig. S1I), indicates an Au-enriched region localized at the Si/silica interface (the Si sidewall). The width of this region is ~7 nm. The Au peak concentration is ~370 atomic parts per million (ppm), which is less than that of boron (B) (~1370 atomic ppm in Si) but is substantially greater than the equilibrium Au concentration in bulk Si (27) and Si nanowires (37). The enhanced concentration of Au in the Si subsurface may be due to the kinetic trapping (9) of Au by radically deposited Si upon SiH4 decomposition. A 3D, atom-by-atom chemical reconstruction from a 30 nm × 30 nm × 20 nm region (Fig. 3C) reveals that Au exists mostly as isolated atoms, instead of continuous Au films, which are routinely used as etch masks for Si. The incorporation of Au atoms in a Si matrix also explains the intermetallic Au feature in XPS (Fig. 3A).

Si wet chemical etching involves electron transfer at the solid/liquid interface (28). To answer how Au atoms induce an etch resist effect, we performed three-electrode electrochemical measurements (Fig. 3D) using pressure-modulated (black) and conventional nonmodulated (red) p-type Si nanowires as the working electrodes (Fig. 3D, inset), where bulk metallic Au (Au that is not incorporated in Si) was removed with a gold etchant. Representative current–versus-voltage scans recorded in 5% (weight by volume) KOH at room temperature (Fig. 3D) demonstrate that the open circuit potential (the potential difference between working and reference electrodes at the open-circuit state, $V_{oc}$) shifted anodically (from ~1.199 to ~1.081 V) when pressure-induced Au diffusion was applied, suggesting more difficult etching. A passivation potential, ~0.595V, appears in both pressure-modulated and nonmodulated samples and can be attributed to formation of a blocking oxide layer (29). However, in the conventional Si nanowire sample (red), we identified a shoulder peak centered around ~0.785 V, which is not apparent in the Au-incorporated Si sample (black) and can be ascribed to an electrochemical process at Au-free Si nanowire surfaces. Because Au atoms are known to form recombination centers in Si, the random Au-based carrier traps effectively retard adjacent electron-based reactions (28, 29) over the Au-incorporated nanowire shell region. This etching resistant effect involves a shallow chemical reaction through individual atoms and is different from that in traditional silicon nitride ($\text{Si}_3\text{N}_4$) or Au film–based etching masks, where physical blockage by chemically inert materials plays a key role.

We studied the effect of a p-type dopant, B$_2$H$_6$, on the spicule morphologies. Results collected in <112> Si spicules (Fig. 3E) demonstrate that as B$_2$H$_6$ feeding increases from 1:4000 to 1:1000 (B:Si), the areas of Au-atom–decorated shells (enclosed in dashed yellow lines, Fig. 3E, inset) and the widths along the midline on the remaining (111) facets (dashed red lines, Fig. 3E, inset) increase. Additionally, the midline width versus segment plot (Fig. 3E) exhibits typically zero values in the segments closer to Au catalysts (phase I), followed by a linear increase (phase II, see linear fittings, Fig. 3E), and finally a plateau regime (phase III). The initial absence of Au-protected (111) facets suggests that in <112> Si spicules, (113) facets are the major Au deposition zones, whereas (111) facets are primarily used for Au diffusion and incorporation, which initiate at a later stage (figs. S16). The linear advance of the interface (i.e., $L \propto t$ or $L \propto n$, where $n$ is the segment index) in phase II suggests that the patterned resist formation is a Au/Si reaction–limited process (28), because a diffusive one is usually described by nonlinear power laws ($L \propto t^a$, $a > 0.5$) (22). The plateau indicates the merging of Au-incorporated patterns from adjacent segments, after which interconnection is achieved. The higher feeding ratio of B:Si, 1:1000 (red) versus 1: 4000 (blue), yields a larger slope (i.e., 37.6 nm per segment versus 28.7 nm per segment) and an earlier onset (segment 5 versus 9) for the linear regions, suggesting that B$_2$H$_6$ can promote Au deposition, diffusion, and incorporation. A similar behavior was observed in <111> Si spicules, and we note that (112) facets are primary Au deposition zones (fig. S17).

We tested the effect of an n-type dopant, phosphine (PH$_3$) (Fig. 3F and fig. S18). STEM tomography (Fig. 3F) displayed a mesostructure with less gradient. To achieve optimal growth, we identified an ~15°C higher growth temperature than when B$_2$H$_6$ was used, consistent with the fact that PH$_3$ and B$_2$H$_6$ can inhibit and enhance SiH$_4$ decomposition (30), respectively. Additionally, we needed to use an ~5 times longer evacuation time to promote Au coverage, suggesting that PH$_3$ is less effective than B$_2$H$_6$ in enabling the spreading of Au on Si surfaces (figs. S2 and S3) and that such spreading is critical for both efficient Au deposition and diffusion. Finally, if neither B$_2$H$_6$ nor PH$_3$ was added (i.e., intrinsic Si), we observed a larger number of isolated Au nanoparticles on the Si sidewalls (fig. S3), which yielded less-defined mesostructures upon etching (figs. S19 and S20).

We propose a modular deposition-diffusion-incorporation mechanism for patterned-interface (Figs. 1 to 3 and fig. S15) formation. Initially, the Si structure follows vapor-liquid-solid axial growth (Fig. 3G, 1). Upon evacuation, the growth stops (Fig. 3G, 2), and catalyst instability at a low pressure (~0.2 Torr) initiates Au deposition (Fig. 3G, III, graded orange band) and subsequent diffusion (Fig. 3G, II, graded pink band). During SiH$_4$ pressure recovery in the ramp period, the Au deposition and diffusion cease (I3), while the Si growth rate increases (Fig. 3G, I, graded blue band) to form a new segment (Fig. 3G, 3). Decomposition of SiH$_4$ on the Si sidewalls assists robust incorporation of Au atoms into the Si substrate. Iteration of this process (Fig. 3G, 4 to 6) generates the anisotropic and graded Au/Si interfaces, which...

**Fig. 4. Si spicules interact strongly with collagen hydrogel.** (A) Representative F-D curves collected using an individual Si spicule as a probe. Insets displace the spicule-based AFM probe at different magnifications. More traces are shown in fig. S26. (B and C) Box-and-whisker plots of forces (B) and work (C) required to detach Si spicules (black), un-etched Si nanowires (red), diameter-modulated Si nanowires (blue), and nanoporous Si nanowires (purple). Half of the data points are within the box, and 80% are within the whiskers. Solid and dashed lines mark the median and mean, respectively. The dots represent maximum and minimum values. The means of detachment force are 4.16 nN (mesostructured spicule), 0.455 nN (un-etched nanowire), 1.03 nN (modulated nanowire), and 0.827 nN (nanoporous nanowire). The means of detachment work are 20.0 fJ (mesostructured spicule), 1.39 fJ (un-etched nanowire), 2.86 fJ (modulated nanowire), and 2.15 fJ (nanoporous nanowire). $n = 50$ F-D curves per probe, and numbers above bars indicate the P value of the Mann-Whitney test.
still shows decent resist quality after 10 months of storage in air (fig. S21). This proposed mechanism is further corroborated by the fact that (i) B-doped nanowires grown without pressure modulation only yielded uniform etching structures (fig. S22) (18, 19); (ii) intentional gold diffusion only at the end of p-type nanowire synthesis also yielded etch resist (fig. S23); (iii) diffused Au did not recruit B (figs. S14 and S15), which is known to affect Si etching; and (iv) possible B incorpo-ration directly from the gas phase is along the specular radial direction, which is orthogonal to the direction for resist formation. Overall, we showed that dopant incorporation or nanowire initial morphology itself cannot yield the observed complex structures. The curvatures of the final spicules are defined by the shapes of patterned resists, curved catalyst/Si interfaces, crystallographic orientations, and etching conditions (fig. S24). The isolated isolated Au nanoparticles play multiple roles, such as catalyzing Si growth, defining edge curvature, and supplying diffused Au atoms and clusters (fig. S25). Finally, we note that since metal diffusion along semiconductor surfaces is general, as in GaP-Au (15), GaAs-Au (15), and Si-In/Sn (10) systems, such a patterned and lithography approach may be applied in other semiconductors.

The anisotropic mesoscale texture of Si spicules suggests that they may have different interactions with surrounding matrices such as hydrogels or biological tissues, as compared to other more isotropic Si structures such as diameter-modulated nanowires (18, 19). To test this possibility, we first mounted single mesostructured Si spicules (<120>–oriented, p-type) onto atomic force microscopy (AFM) cantilever tips with a f-ocussed ion-beam system (fig. 4A, inset). Next, by approaching/retracting the spicules to/from the colla-\l
gen type I hydrogel [materials and methods in (18) and fig. S26], we were able to monitor the force and work of the spicule-matrix interactions in both the forward and reverse directions. For each recording, we chose a fresh location over the hydrogel surface. To study the effects of probe ge-ometry and surface, we performed control measurements (figs. S26 and S27) with an un-etched Si nanowire, a uniform diameter-modulated Si nano-\l
gire (18, 19), and a nanoporous Si nanowire (18). A representative force-distance (F-D) curve recorded from the Si spicule probe exhibits a detachment force of ~3.9 nN and a detachment work of ~15.6 fJ (fig. 4A). Statistical analyses of F-D measure-\l
ts with the single Si spicule and different Si nanowire probes (fig. 4, B and C; n ~ 50 F-D curves per probe) demonstrates that the anisotropic mesostructure, rather than surface area or nano-scale roughness, yields a major enhancement in detachment force and detachment work (figs. S26 and S27). The observation that the aniso-tropic spicule requires the largest detachment force from collagen is reminiscent of natural sys-\l
tems, such as a bee's stinger, which can become rooted in skin. This suggests the potential of adopting mesostructured Si spicules for building tight junctions with other soft materials, such as in tissue-interfacing adhesives or bioelectronics.

REFERENCES AND NOTES

18. See the supplementary materials on Science Online.

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SUPPLEMENTARY MATERIALS

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Direct observation of an abrupt insulator-to-metal transition in dense liquid deuterium

Eighty years ago, it was proposed that solid hydrogen would become metallic at sufficiently high density. Despite numerous investigations, this transition has not yet been experimentally observed. More recently, there has been much interest in the analog of this predicted metallic transition in the dense liquid, due to its relevance to planetary science. Here, we show direct observation of an abrupt insulator-to-metal transition in dense liquid deuterium. Experimental determination of the location of this transition provides a much-needed benchmark for theory and may constrain the region of hydrogen-helium immiscibility and the boundary-pressure in standard models of the internal structure of gas-giant planets.

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HIGH-PRESSURE PHYSICS

I n 1935, Wigner and Huntington (1) were the first to predict that when squeezed to sufficiently high density (p) and pressure (P), hydrogen would undergo a density-driven transition from an insulating, molecular solid to a conducting, atomic solid. Subsequently, this fundamental question of precisely how and at what P hydrogen metallizes at low temperature (T) has become one of the longest-standing open questions of high-pressure physics (2). More recently, there has been much interest in the analogous molecular insulator to atomic metal transition in the liquid at low T just above the melt line, largely due to its relevance to planetary science (3, 4). A metallization transition in this region could provide a constraint for the