Atomic Layer Deposition for Membranes, Metamaterials, and Mechanisms

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Scaling and Moore’s law have guided the miniaturization of transistors for 50 years: device dimensions are decreased proportionally such that the electric field \( \varepsilon \) remains constant. The most challenging scaling dimension is the gate oxide thickness \( t \), and atomically thin deposition (ALD) was invented as a means to create nanometer-thick gate oxides with excellent dielectric properties. The analogous scaling parameter for a thin flexible mechanical system is the strain field \( \varepsilon \), with the same challenge of making nanometer-thick, high-quality layers.

We show that ALD is an ideal approach for scaling mechanical systems to micrometer-scale dimensions. In particular, the cycle-by-cycle thickness control and low defect density offered by ALD enables precise and reproducible design of mechanical systems while retaining integration with standard microfabrication considerations. These features of the ALD process are especially important at the nanometer scale, where films produced by other methods such as sputtering and evaporation are discontinuous, rough, or islanded. Our work demonstrates that free-standing ALD films with nanometer dimensions can be produced at high yield, be released from their substrate with mechanical integrity, and be shaped into micromechanical devices.

Bending and folding techniques such as origami and kirigami enable the scale-invariant design of 3D structures, metamaterials, and robots from 2D starting materials. These design principles are especially valuable for small systems because most micro- and nanofabrication involves lithographic patterning of planar materials. Ultrathin films of inorganic materials serve as an ideal substrate for the fabrication of flexible microsystems because they possess high intrinsic strength, are not susceptible to plasticity, and are easily integrated into microfabrication processes. Here, atomic layer deposition (ALD) is employed to synthesize films down to 2 nm thickness to create membranes, metamaterials, and machines with micrometer-scale dimensions. Two materials are studied as model systems: ultrathin SiO\(_2\) and Pt. In this thickness limit, ALD films of these materials behave elastically and can be fabricated with sub-f\( \lambda \)-scale bending stiffnesses. Further, ALD membranes are utilized to design micrometer-scale mechanical metamaterials and magnetically actuated 3D devices. These results establish thin ALD films as a scalable basis for micrometer-scale actuators and robotics.

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The bending stiffness is related to the Young’s modulus \( Y \) and Poisson’s ratio \( \nu \) of the material through \( \kappa = \frac{Yf^4}{12(1-\nu^2)} \). We fit this equation to the stiffness of each hinge as a function of thickness in Figure 2g. Scaling the thickness from 2 to 8 nm results in nearly two orders of magnitude change in the bending stiffness. Power-law stiffness scaling and angstrom-scale thickness precision of ALD enable precise bending stiffness engineering. We extract the Young’s modulus of SiO_2 from the fit in Figure 2g, finding \( Y = 90 \pm 10 \) GPa. This value is comparable to values for bulk material (70–80 GPa), indicating that even at 2 nm thickness, the films behave mechanically similar to macroscopic counterparts. We operate these hinges

Ferromagnets with a saturated in-plane moment \( \mu_s \) are deflected when we apply an out-of-plane magnetic field \( B \). The bending moment on a hinge with dimensions \( L \times W \) is given by \( \tau_{\text{hinge}} = \kappa(\theta/L) \). This must equal the magnetic torque \( \tau_{\text{mag}} = \mu \times B = \mu_s B \cos \theta \), yielding: \( \theta/\cos \theta = \mu/B/\kappa(W/L) \). We test this relationship by fabricating hinges schematically drawn in Figure 2e. A 1 µm thick panel is patterned on top of the magnet which serves a dual purpose of managing residual thin-film stress in the magnet layer and as a spacer layer to control magnetic interactions between different parts of the device. The magnetic moment and coercivity of the magnetic film were measured by vibrating sample magnetometry (Figure S4, Supporting Information). Figure 2f shows the measured hinge deflection angles for ALD films of two different thicknesses, 5 and 8 nm, as a function of the magnetic field \( B \). (Initial deflections of the hinge are taken into account in the term \( \theta_0 \).) The hinge is deflected reversibly with no observable hysteresis (Figure 2f). Similar data were obtained for a 2 nm SiO_2 film, which is presented in Figure S1 in the Supporting Information. The behavior agrees well with the predicted magnetic moment/torque relation.

This experiment is repeated on 65 hinges with three different film thicknesses (2, 5, and 8 nm) to infer the bending stiffness. The bending stiffness is related to the Young’s modulus \( Y \) and Poisson’s ratio \( \nu \) of the material through \( \kappa = \frac{Yf^4}{12(1-\nu^2)} \). We fit this equation to the stiffness of each hinge as a function of thickness in Figure 2g. Scaling the thickness from 2 to 8 nm results in nearly two orders of magnitude change in the bending stiffness. Power-law stiffness scaling and angstrom-scale thickness precision of ALD enable precise bending stiffness engineering. We extract the Young’s modulus of SiO_2 from the fit in Figure 2g, finding \( Y = 90 \pm 10 \) GPa. This value is comparable to values for bulk material (70–80 GPa), indicating that even at 2 nm thickness, the films behave mechanically similar to macroscopic counterparts. We operate these hinges

One may speculate about the relationship between the stiffness and the bending moment of the hinge, which is presented in Figure S1 in the Supporting Information. The behavior agrees well with the predicted magnetic moment/torque relation.
thousands of times without observation of failure (Video S1, Supporting Information) because extreme deformations are possible at low bending strain.

ALD membranes can readily be made into mechanical metamaterials through in-plane and out-of-plane patterning. Figure 3 presents several example metamaterials that utilize lithography to engineer their properties. The sheet can become almost a thousand-fold stiffer than the perpendicular regions when entire unit cells buckle out of the device plane. Corrugated membrane metamaterials can also be created by patterning the substrate prior to ALD growth, as shown in Figure 3d–f. Corrugations parallel to the loading direction increase the bending stiffness while corrugations perpendicular to the loading direction remain flexible[12,24] effecting anisotropic mechanical properties within a sheet. The alternating pattern of 75 nm deep parallel and perpendicular corrugations shown in Figure 3d allows the sheet to flex only where the corrugations are perpendicular; the parallel sections are nearly a thousand-fold stiffer than the perpendicular regions (see the Experimental Section). When the sheet is compressed (Figure 3e), it adopts an accordion-like buckled configuration. Periodic perforations in the sheet serve as a contrast agent making possible a 3D reconstruction of the buckled sheet (Figure 3f). Corrugated ALD membranes such as these can be used to create micrometer-scale origami devices with corrugated folds and panels that collapse into a desired final shape under compression or exhibit bistable behavior.[25–27]

These ultrathin materials can also be used for micrometer-scale actuators and machines that function with exquisitely small forces and torques. To demonstrate this concept, we present three classes of magnetically actuated systems in Figure 4. The first class consists of devices inspired by pop-up kirigami (Figure 4a,b). By placing magnets on any panel that we wish to be vertical, we can create pop-up 3D structures such as the staircase in Figure 4a. To control the magnetization direction, we initially saturate the magnets in the same direction with a large external field and subsequently manipulate the structures with sub-coercive fields. Figure 4b shows a related device, but with an additional magnet on the base of the structure. Continuous rotation of the external magnetic field can fold the structure over on top of itself at which point it forms a latch with the bottom magnet.

The devices shown in Figure 4c–e are magnetic actuators that contract to bear loads. The free end of a magnetically actuated cantilever bears a weight fabricated from platinum. If the restoring force of the cantilever exceeds the weight of the load, it lifts the weight off the substrate as in Figure 4c. On the other hand, if the weight exceeds the restoring force of the cantilever, it is dragged along the substrate (Figure 4d). Each weight panel exerts ≈2.4 pN of force on the end of the cantilever. We vary the number of weights on a cantilever of fixed geometry, measure its deflection, and calculate its mean curvature to produce a force–distance curve for the device. Despite the extreme deformations, this structure is still accurately described as a singly clamped cantilever with its boundary

![Figure 2. Mechanical properties of ALD membranes. a) Schematic drawing of the radiation-pressure force–distance measurement. b) Transmission optical microscopy image of polymer-decorated cantilevers. The beam profile can be reconstructed from the positions of the dots. c) Force–distance curve for a cantilever with W = 10 μm, L = 100 μm, and t = 5 nm. The weight of the pad keeps the cantilever from deflecting for small applied forces. d) Compilation of spring constants as a function of cantilever geometry, showing consistency with a single bending stiffness for SiO2 films of 2, 5, and 8 nm thickness. e) Schematic of the applied and restoring torques for a magnetically actuated hinge. f) Forward and backward field sweeps for two magnetically actuated hinges fabricated from 5 and 8 nm films. Square markers are forward sweeps and circular markers are reverse sweeps. g) Measured hinge stiffness for SiO2 films of 2, 5, and 8 nm thickness.](image-url)
condition set by the magnetic panel. For a cantilever with dimensions $10 \, \mu m \times 27 \, \mu m$, we calculate a spring constant $k = (9.5 \pm 0.1) \times 10^{-7}$ N m$^{-1}$, which is plotted in Figure 2d to show consistency with the other measurements. A related device is shown in Figure 4e, where magnetic panels are attached to linear springs. Upon application of an external field, the panels rotate out of the plane and move laterally closer to each other while applying a load on the springs in an analogous fashion to a muscle.

Finally, a gripper device is shown in Figure 4f. The gripper has magnets along the folding panels patterned as isosceles triangles to force the magnetization to spontaneously align along the median of the triangle. Application of a magnetic field forces the device to orient its panels along the field axis, producing a gripping motion.

The magnetically actuated structures and devices presented here demonstrate functional components of micrometer-scale machinery. Many envisioned applications of small machines involve deployment in inaccessible locations, such as within organisms. Magnetic fields provide a useful external control mechanism as magnetic fields are not screened by tissue. Our ALD-derived devices exploit the utility of magnetic control while opening the possibility for further scaling at shorter length scales. Furthermore, local control over the magnetic order within an elastic sheet enables shape-transforming soft robotics at the macroscale. ALD sheets with magnetic panels with patterned magnetization enable realization of similar magnetic soft robots at the micrometer scale.

The mechanical properties and fabrication protocols for ALD membranes and metamaterials facilitate their potential application in very sophisticated micromechanical systems. For example, the low processing temperatures and fabrication compatibility enable ALD actuators to be added to silicon-based integrated circuits for smart microsystems and machinery. In addition, the diverse materials palate offered by ALD enables bimorph actuators of dissimilar materials while still maintaining a low bending stiffness for the film stack. These actuators can be leveraged to create self-assembled and environmentally responsive 3D structures and actuators. An additional benefit of ultrathin versions of bulk materials is that the surface chemistry of many ALD films is well-studied. This enables chemical functionalization and patterning, enabling the coupling between chemical sensitivity and mechanical responsivity. Combination of these capabilities may be used for sensors, self-assembled devices, optical devices, and microscale robotic systems.

**Experimental Section**

Device Fabrication: The devices presented in this paper were fabricated on piranha-cleaned Borofloat glass wafers. First, a layer of aluminum or 1% silicon in aluminum was deposited with thermal evaporation (Al) or DC sputtering with a radio frequency backsputter (Al/Si alloy) to a thickness of 300 nm to serve as a release layer for the ALD devices. Photolithography and reactive ion etching defined alignment markers in the aluminum which were used for all future process steps. Photolithography and BCl3-based inductively coupled reactive ion etching defined trenches in the aluminum release layer for corrugated devices. The sidewall angle was $85^\circ$–$88^\circ$ as determined from scanning electron microscope. After these first two layers of lithography, wafers were cleaned in organic solvents and oxygen plasma to remove residues prior to ALD. The ALD was carried out in either an Oxford FlexAL plasma-assisted reactor at 200 °C (for metal oxides) or in an Arradiance thermal reactor at 250 °C (for platinum). Prior to growth of the ALD film of interest, 20 cycles of aluminum oxide were grown as a buffer layer to ensure a
from the probe to the grid. The sample was further thinned with a low-energy ion beam at grazing incidence. STEM and EELS were performed in an FEI Titan Themis STEM at 120 keV. The beam convergence angle was 30 mrad, with a probe current of ~15 pA. The EELS spectrum and images were acquired with an energy dispersion of 0.25 eV per channel using a Gatan Quefina dual-EELS spectrometer. A linear combination of power laws was used to fit and subtract the background. The EELS false color composition map was created by integrating the silicon L$_{2,3}$ edge, the aluminum L$_{2,3}$ edge, and the carbon K edge. All of the EELS analyses were done with open source Cornell Spectrum Image software. Images are included in Materials and Methods in the Supporting Information.

Mechanical Measurements of ALD Bending Stiffness: Forces applied to cantilevers using the radiation pressure were calculated by

$$F = \beta \frac{A}{C} (A + 2R)$$

(1)

where $A$ is the absorption of the metal tag, $R$ is the reflectivity of the metal tag, and $\beta$ is an experimentally determined factor that accounts for the fraction of total applied power $P$ that is incident on the tag. As the power was increased, the focal plane of the tag was tracked with a piezo-controlled microscope objective (60X, NA = 0.7). The fitted linear slope of the force–distance plot yielded the spring constant for the device. The factor $\beta$ was determined ex situ by focusing the laser through pinholes of varying diameters while measuring the transmitted power. The metal tags studied in these experiments were fabricated from 10 nm Ti/50 nm Au. The reflectivity was measured to be 0.97 at 1064 nm with broadband spectral reflectance (Filmetrics F40-UV, 140-1100 nm). The high reflectivity at this wavelength allowed to neglect the absorption term when calculating the applied radiation force.

Stiffening of a Corrugated Sheet: The stiffness of a plate was proportional to the moment of inertia of the plate’s cross-section. For a plate of width $W$ and thickness $t$, the moment of inertia is $I_z = W t^2 / 12$. For a plate with a trench with depth $z$ and trench width $d$ such that $W = 2d$, the moment of inertia is

$$I_z = \frac{(d - 2t)^3}{3} + \frac{2z t^3}{12} + \frac{(d + 2t)^3}{12} + (d + 2t)(z + \frac{1}{2}) - A C_y$$

(2)

where $A = 2zt + (d - 2t) t$

(3)

and

$$C_y = \frac{2z t^2 + (d - 2t) t}{22d - 2(d - 2t)(z - t)}$$

(4)

For this system, $t = 5$ nm, $z = 75$ nm, and $d = 4 \mu$m, giving a relative stiffening $I_z / I_{z0} = 950$.

3D Reconstruction of Corrugated Materials: Corrugated ALD membranes were fabricated with a pattern of perforations that serve a dual purpose of facilitating device release and providing bright spots in transmission microscopy to localize the sheet in the z-axis. A piezo-controlled microscope objective (PiezoSystem jena, 60x, NA 0.7) was used to scan through focus while recording the piezo displacement. The image sequence was intensity-thresholded frame-by-frame and the piezo displacement was used to reconstruct the 3D rendering.

Supporting Information

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

The authors declare no conflict of interest.

Keywords

atomic layer deposition, kirigami, metamaterials, nanofabrication, NEMS

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