Supporting Information for:

Bidirectional Self-Folding with Atomic Layer Deposition Nanofilms for Microscale Origami

Baris Bircan†, Marc Z. Miskin§, †, Robert J. Lang∥, Michael C. Cao†, Kyle J. Dorsey†, Muhammad G. Salim†, Wei Wang§, David A. Muller†, †, Paul L. McEuen§, †, Itai Cohen*, §, †

†School of Applied and Engineering Physics, 271 Clark Hall, Cornell University, Ithaca, New York 14853, United States
§Laboratory of Atomic and Solid State Physics, 511 Clark Hall, Cornell University, Ithaca, New York 14853, United States
∥Kavli Institute at Cornell for Nanoscale Science, 420 Physical Sciences Building, Cornell University, Ithaca, New York 14853, United States
*Robert J. Lang Origami, Alamo, California 94507, United States
⊥Cornell Center for Materials Research, 627 Clark Hall, Cornell University, Ithaca, New York 14853, United States

Contents:

1) Sample Fabrication Details
2) ALD Bilayer Characterization
3) Finite Element Modeling
4) Supporting Video Description
1) Sample Fabrication Details

We thermally evaporate a 300 nm thick aluminum release layer onto a clean, 430 μm thick, double side polished sapphire wafer. We then perform plasma enhanced atomic layer deposition (PEALD) in an Oxford ALD FlexAL system to deposit 20 cycles of silicon dioxide at 200 °C followed by 120 cycles of silicon nitride at 350 °C. The number of cycles for both processes correspond to an approximate deposited film thickness of 2 nm. Tris[dimethylamino]Silane (3DMAS) and oxygen plasma are used for silicon dioxide growth. 3DMAS and argon-nitrogen plasma are used for silicon nitride growth. Next, we thermally evaporate a 150 nm thick layer of aluminum on top of the ALD stack to act as an etch mask in subsequent steps. We spin coat the wafer with P20 primer and Shipley 1813 photoresist (5000 rpm, 2000 acceleration, 30s) and soft bake for 90 seconds at 115 °C. We use contact photolithography to expose the photoresist and develop to define the mountain (downward) fold regions of each origami device. We then hard bake the photoresist at 115 °C for 5 minutes. We transfer the photoresist pattern into the aluminum etch mask (with BCl₃/Cl₂ plasma etching), and then the ALD film stack (with CF₄ plasma etching). We strip the photoresist by soaking the wafer in MICROPOSIT Remover 1165 and rinsing in isopropanol and DI water. We then oxygen plasma clean our sample and perform PEALD in inverted order, depositing 120 cycles of silicon nitride at 350 °C followed by 20 cycles of silicon dioxide at 200 °C. The conformality of the ALD process ensures that the entire wafer, including the previously patterned features, is covered by the grown films. We again spin coat P20 primer and Shipley 1813 photoresist (5000 rpm, 2000 acceleration, 30s) and soft bake for 90 seconds at 115 °C. We use contact photolithography to expose the photoresist and develop to define the valley (upward) fold regions as well as the areas the flat panels will be bonded to. We then use CF₄ plasma etching to transfer this pattern into the inverted ALD stack. During this step, the aluminum etch mask protects the previously patterned mountain (downward) fold regions from the CF₄ plasma. We leave a 3 to 5
μm overlap between the two photoresist patterns to ensure the resulting ALD sheets making up each device will be continuous after etching. We strip the photoresist by soaking in MICROPPOSIT Remover 1165, and rinsing in isopropanol and DI water. Next, we spin coat the wafer with SU-8 2002 photoresist (4000 rpm, 1000 acceleration, 30s) and soft bake for 1 minute at 65 °C followed by 1 minute at 95 °C. Using contact photolithography, we expose the photoresist and define panels that will make up the flat panels on each origami structure. Next, we post exposure bake the resist for 1 minute at 65 °C, followed by 2 minutes at 95 °C. We develop in SU-8 Developer for 1 minute and rinse in isopropanol. We then anneal the panels on a hot plate by heating the wafer from 95 °C to 150 °C, holding for 5 minutes, and cooling the hot plate to room temperature. Finally, we leave the samples in hydrochloric acid solution with added surfactant (sodium dodecylbenzenesulfonate). This dissolves the aluminum release layer and etch mask and releases the origami devices into solution where they can fold. All device layers are designed to have aligned holes exposing the release layer so that undercut time during the release process is reduced.

2) ALD Bilayer Characterization

Bilayer Curvature Characterization

To measure the intrinsic curvature of the ALD bilayers, we fabricate the SiNx (bottom layer) - SiO2 (top layer) cantilevers shown in Figure S1A. We observe that these cantilevers bend upwards when released, and measure the resulting curvature as 0.1 μm\(^{-1}\) (Figure S1A, lower panel). We use this fixed curvature value to design and fabricate the hinge shown in figure 2 of the main text. The magnitude of the fold angle is given by the ratio of the ALD hinge width between rigid SU-8 panels to the fixed 10 μm radius of curvature produced by the bilayer. This device folds upwards to 90° as designed, confirming the feasibility of our approach to creating a fold.
Since the substrate would prevent hinges with the inverted bilayer stack from bending down, we fabricate tethered devices that consist of one upward and one downward folding hinge with equal width between rigid SU-8 panels (Fig. S1B). Since the larger SU-8 panel is observed to be horizontal after release, we conclude that the magnitude of the two fold angles are equal, which indicates that the bilayer curvature is the same in both directions. This characterization is sufficient to design and fabricate any fold with angles ranging from -180° to +180°. When creating the lithography mask designs for the shapes shown in figure 4 of the main text, we again use the fixed value for the bilayer curvature to decide the ALD hinge width for each fold, regardless of direction. The direction for each fold is determined by the bilayer stack order at the fold location. The correct assembly of these geometries demonstrates that our approach can reliably create folds in both directions, even when complex elastic effects due to the coupling of folding hinges are present.

**Figure S1.** ALD Bilayer Curvature Characterization. (A) Optical micrographs of a row of five SiNₓ - SiO₂ cantilevers before (upper panel) and after (lower panel) release. We observe that these cantilevers bend upwards when released, and we measure the resulting curvature as 0.1 µm⁻¹. (B) Schematic (upper panel) and optical micrograph (lower panel) of a tethered device that consists of one upward and one downward folding hinge with equal width between rigid SU-8 panels. Since the large SU-8 panel remains horizontal after release, we conclude that the bilayer curvature is the same for folding in both directions.
Cross Sectional STEM Imaging

Samples for cross-sectional scanning transmission electron microscope (STEM) imaging were prepared by focused ion beam (FIB) milling and lift-out. A 500 μm thick, single side polished silicon wafer with 100 nm of thermally grown oxide was cleaned using a Piranha solution. PEALD was performed on the wafer to deposit a 10 nm thick film of aluminum oxide (at 200 °C, using trimethylaluminum and oxygen plasma), followed by 120 cycles of silicon nitride at 350 °C, and 20 cycles of silicon dioxide at 200 °C. The wafer was then cleaved along primary axes and capped with a thin layer of amorphous carbon for protection during the FIB process. Capped samples were loaded into a Thermo-Fischer Helios G4 FIB system for processing.

The FIB uses a semi-automated routine to mill out a lamella for attachment to a TEM grid. The routine begins with ion-beam assisted deposition of platinum in the area of interest, followed by patterning fiduciary marks for alignment of subsequent features. Bulk material is removed around the sample area at a beam voltage of 30 kV to produce a lamella structure for lift-out. A micromanipulator probe is inserted into the chamber and the lamella structure is attached to the probe. The probe brings the lamella to a TEM grid, attaches the lamella to the grid, and detaches the probe from the lamella. Once attached, the lamella is further thinned in a series of grazing-angle sequences while decreasing both the beam voltage and beam current. Initial thinning begins at 30 kV with a current of 0.45 nA, decreases to 16 kV and 0.12 nA, decreases further to 5 kV and 41 pA, and concludes at 2 kV and 21 pA. After thinning, the sample is removed from the FIB and stored in a vacuum desiccator. This procedure limits beam-induced sample damage and produces suitably thin samples for electron imaging and spectroscopy.

Imaging was performed on a probe-corrected Thermo Fisher Titan Themis Cryo S/TEM at 120 kV in STEM mode with a 21.4 mrad probe aperture semi-angle. The electron energy loss spectra
(EELS) were collected using a Gatan Quefina dual-EELS spectrometer from 50 eV to 562 eV at 0.25 eV per channel. This energy range covers the relevant Si-L_{2,3}, O-K, N-K, C-K, and Al-L_{2,3} edges.

**X-Ray Photoelectron Spectroscopy**

ALD bilayer samples were analyzed using a Scienta Omicron ESCA-2SR XPS with operating pressure ca. 1x10^{-9} mBar. Monochromatic Al Kα X-rays (1486.6 eV) were generated at 300W (15kV; 20mA). Analysis spot size was 2 mm in diameter with a 0° photoemission angle and a source to analyzer angle of 54.7°. A hemispherical analyzer determined electron kinetic energy, using a pass energy of 50 eV for high resolution scans. Samples were charge neutralized using a low energy electron flood gun.

**3) Finite Element Modeling**

The finite element models of the origami devices were constructed using the finite element analysis software ABAQUS. Model dimensions were matched to the device designs used in experiments. Since the material thicknesses are significantly smaller than the in-plane dimensions, shell elements were used in modeling. The ALD sheets were modeled as composite sections consisting of silicon dioxide and silicon nitride, and the SU-8 panels were modeled as homogenous sections. All materials were assumed to be linear elastic and isotropic. In order to ensure the modeled structures would have smooth deformation fields, material was removed from the models at the vertices of the ALD sheets. Folding was simulated by prescribing isotropic expansion to the silicon nitride layer and dynamic effects were neglected. Displacement boundary conditions were applied to fix the position of a single panel in each device in the simulations.
Since the finite element models are built without material at their vertices and are subjected to simple boundary conditions that simplify computation, they are not an exact match to the experimentally realized devices. We construct these models to highlight the overall 3D shapes of our devices by visualizing the self-folding ALD sheets, which are not visible in the device micrographs.

4) Supporting Video Description

Supporting Video 1: The footage, taken using an optical microscope, shows a hinge made with an ALD SiNₓ (bottom) - SiO₂ (top) bilayer and a flat SU-8 panel. When released, the hinge folds upward at a 90° angle. A micromanipulator probe is used to apply force to the hinge and deform it into its open position. Once the probe is removed, the hinge fully recovers to its original folded position, demonstrating elastic operation.