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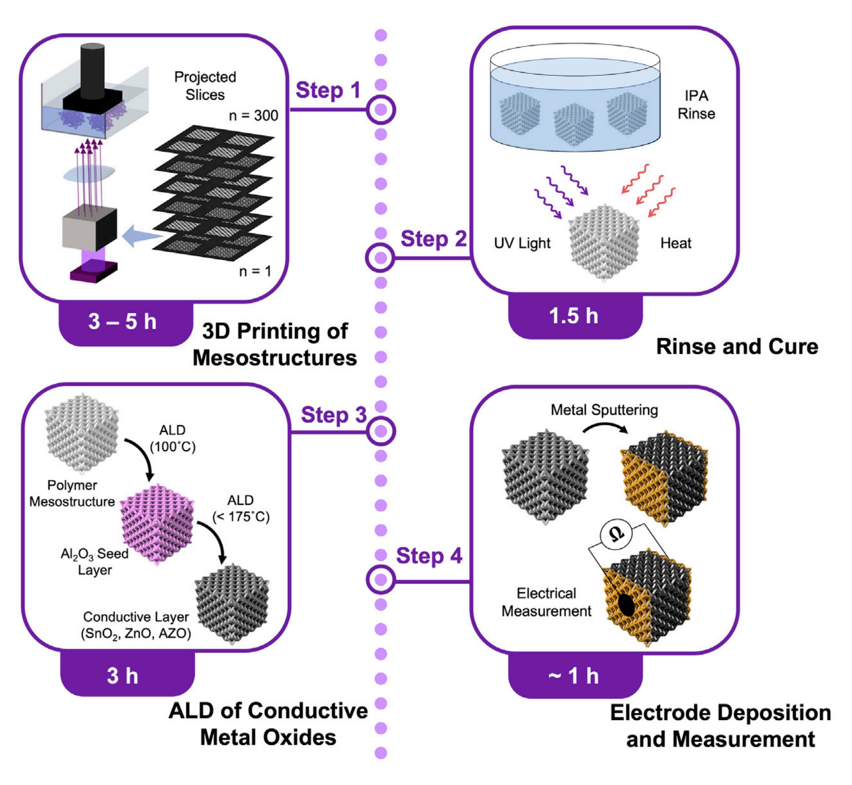
Protocol for deposition of conductive oxides onto 3D-printed materials for electronic device applications



Additively manufactured (AM) three-dimensional (3D) mesostructures can be designed to enhance mechanical, thermal, or optical properties, driving future device applications at the micron to millimeter scale. We present a protocol for transforming AM mesostructures into 3D electronics by growing nanoscale conducting films on 3D-printed polymers. In this generalizable approach, we describe steps to utilize precision thermal atomic layer deposition (ALD) of conducting, semiconducting, and dielectric metal oxides. This can be applied to ultrasmooth, customizable photopolymer lattices printed by high-resolution microstereolithography.

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Highlights

Atomic layer deposition of ultrathin conductive oxides on 3D-printed polymers

Microstereolithography process for fabrication of mesoscale 3D-printed structures

Protocol is amenable to coating a variety of 3D-printed polymers with conductive oxides

Electrical characterization of 3D-printed sensors enabled by sputtered electrodes

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Protocol for deposition of conductive oxides onto 3D-printed materials for electronic device applications

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SUMMARY

Additively manufactured (AM) three-dimensional (3D) mesostructures can be designed to enhance mechanical, thermal, or optical properties, driving future device applications at the micron to millimeter scale. We present a protocol for transforming AM mesostructures into 3D electronics by growing nanoscale conducting films on 3D-printed polymers. In this generalizable approach, we describe steps to utilize precision thermal atomic layer deposition (ALD) of conducting, semiconducting, and dielectric metal oxides. This can be applied to ultrasmooth, customizable photopolymer lattices printed by high-resolution microstereolithography.

For complete details on the use and execution of this protocol, please refer to Huddy et al. (2022).

BEFORE YOU BEGIN

Additive manufacturing (AM) can be accomplished through a variety of fabrication methods. This protocol uses microstereolithography (μSLA) to print AM mesostructures that serve as polymer templates for deposition of nanoscale conductive materials by thermal atomic layer deposition (ALD). ALD is a common method used for deposition of ultrathin oxide materials. Here we focus on the deposition of nanoscale Al_2O_3, SnO_2, ZnO, and aluminum doped (5 wt.%) zinc oxide (AZO). The insulating Al_2O_3 film can be used as a dielectric or a seed layer for other material growths. As a seed layer, the Al_2O_3 allows for deposition of conductive (SnO_2) and/or semiconductive (ZnO, AZO) materials. Without this seed layer, ALD growth of conducting/semiconducting materials is inhibited on photopolymer materials. This process can be expanded to other photopolymer materials and ALD oxide coatings beyond those employed here (including structures printed with other 3D printers, see Huddy et al., 2022 for details), allowing conversion of AM mesostructures into devices with potential applications in energy storage, sensing, and microrobotics.

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
3DSR UHR Resin	Kudo3D	https://www.kudo3d.com/shop/3dsr-uhr-resin/
BMF HTL resin (yellow)	BMF	https://bmf3d.com/micro-3d-printing-materials/
Tetrakis(dimethylamino)tin(IV), 99% (99.99%-Sn)	STREM	CAS: 1066-77-9
Trimethylaluminum, min. 98%	STREM	CAS: 75-24-1

(*Continued on next page*)

Continued

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Diethylzinc, min. 95%	STREM	CAS: 557-20-0
Software and algorithms		
Kudo3D Print Job Software	Kudo3D	https://www.kudo3d.com/shop/kudo3d-print-job-preparation-software/
Kudo3D Printer Communication Software	Kudo3D	N/A
Other		
Micro 15 μSLA printer	Kudo3D	https://www.kudo3d.com/micro/
UV Cure System	ELEGOO Mercury Plus	2 in 1 3D Printing Washing and Curing Station
Oven	M-Triangel	M1-Max 14″
Thermal ALD System	Anric Technologies	AT410
Kapton Tape	MYJOR	31201500
Gold sputterer	Hummer	N/A
Probe station	Alessi	N/A
Source Measurement Unit (SMU)	Keysight Technologies	B2902A
Ozone generator	Anric Technologies	AT-OZONE

Alternatives: In this protocol we use a source measurement unit and a semiconductor probe station with micromanipulators to electrically measure the current voltage characteristics of the 3D samples, however, larger probes similar to those commonly found on multimeters may be used as long as they can be secured in place during measurement and make good contact with the sample electrodes. Good contact can be quantified by taking multiple measurements of the same sample. If repeated measurements of the same sample exhibit low variability (coefficient of variance or COV < 2%), the contact between the sample and the measurement probes is good and measurements will be reliable.

Additionally, other metal organic precursors (e.g., $TiCl_4$, $HfCl_4$, tris (dimethylamino) silane (TDMAS)) could be used for this process as long as the thermal ALD process can be performed at temperatures below the glass transition (T_g) of the 3D-printed polymer. We provide a reference to Gordon (2014), which lists a variety of ALD precursor chemistries that would satisfy these constraints.

Instead of gold electrodes, it is also possible to sputter other metals (e.g., Cu, Ag, Pt) to use as contacts, as long as the resistance across the electrode matches the values mentioned in this process.

STEP-BY-STEP METHOD DETAILS

3D printing of mesostructures

Timing: 3–5 h

Microstereolithography (μSLA) is a high-resolution 3D printing process that allows for fabrication of mesoscale structures with beam sizes in the range of 10 μm–1 mm, shown in Figure 1A. Details on the mechanics of the process can be found in the references (Han et al., 2019; Ge et al., 2020). The following steps outline the process for creating a structure with this process.

1. Create an .stl file of the part to be printed based on a CAD model.
2. Import the .stl file of the part into the Kudo3D software.
3. Add supports to the part via the support mode feature. Supports are features that provide additional structure to a part in order to ensure that a print is successful and remains attached to the print plate throughout the build.

Note: Parameters for the support structures used to print the lattice structures in this protocol are listed in the chart below. These support parameters would be effective for structures with

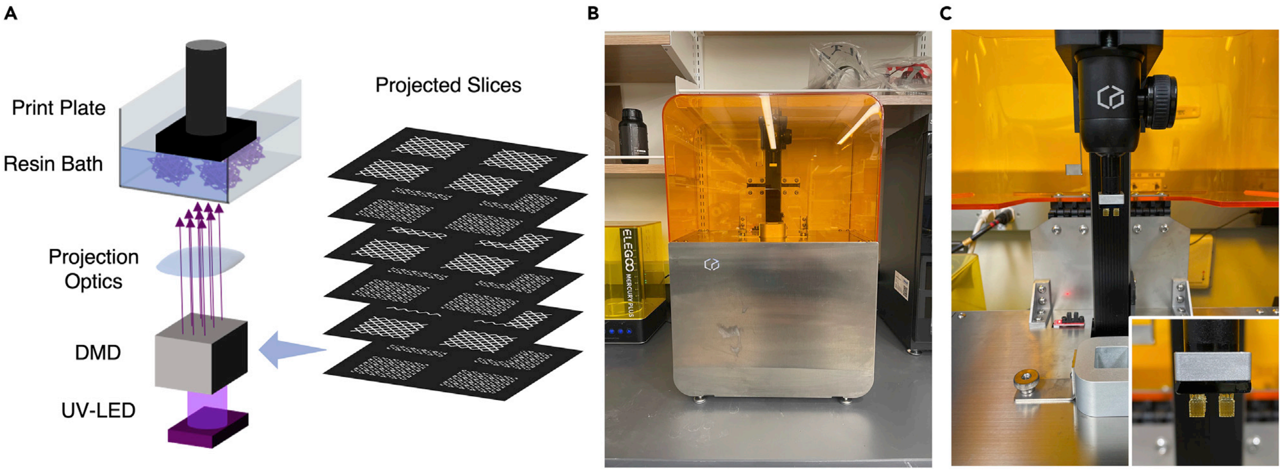

Figure 1. Microstereolithography (μSLA) process for 3D printing of mesostructures

(A) Schematic of μSLA process showing example slice files, which are projections of a small fraction of the resulting part.

(B) Kudo3D Micro μSLA printer used for printing of 3D mesostructures.

(C) A completed print using the Kudo3D Micro μSLA printer with inset highlighting the prints still attached to the print plate. Prints will appear yellow until fully rinsed and crosslinked.

features of similar size (50 μm). As the feature size increases or decreases the size of the supports should be adjusted to match.

Support parameters

Parameter	Value
Support density	125%
Tip diameter	0.20 mm
Critical build angle	30.0°
Sampling strategy	Creases and surfaces
Surface sampling	Random points
Strategy	Single supports only
Pole Diameter	1.0 mm
Pole widening factor	1.5
Place above base at	4.0 mm
Internal supports	Enabled
Height of the foot	1.0 mm
Diameter at the top of the foot	1.0 mm
Diameter at the bottom of the foot	1.5 mm

Note: Printing parts without supports is possible if the part is strong enough to support itself during the print. Small features connecting larger features may be failure points, so using supports provides extra strength to ensure print success. Additionally, using supports decreases the chances of damaging a part when removing it from the build plate. However, these conditions may not be the most appropriate supports for a part (see troubleshooting section) and can be adjusted as necessary.

4. Slice the part using the slice function. This produces images projected by the Digital Micromirror Device (DMD) as shown in Figure 1A.
   a. Choose a location to save the sliced file.

   b. Choose a "Material and print profile" of 10 μm. This is the thickness of each exposed layer. If thicker layers are desired or lower resolution is okay, 15 or 20 μm can be chosen instead.
   c. Check "Zip slice export" so that the software also produces a .zip file when slicing. If this is forgotten, simply compress the folder produced during slicing into a .zip file.
5. Set the print parameters for the part using the .csv file provided in Table S1. Sample parameters are provided in the table below.
   a. "fromlay" refers to the starting layer for the given parameters and should be one more than the ending layer for the previous step.
   b. "tolay" refers to the last layer that will use the given parameters and can be the same as the starting layer if the print parameters are only meant for one layer.
   c. "expos" refers to the exposure time and is measured in seconds.
   d. "lift" refers to the height the print plate moves away from the resin bath after an exposure and is measured in mm.
   e. "ups" refers to the lift speed of the print plate as it moves away from the resin bath after exposure and is measured in mm/s.
   f. "downs" refers to the lift speed of the print plate as it moves towards the resin bath after the delay and is measured in mm/s.
   g. "delay" refers to the amount of time spent waiting once the print plate reaches lift height and is measured in seconds.
   h. Other parameters in the .csv file not mentioned in the chart below represent other print parameters. In the file, 0.01 is the slice thickness in mm (this should be changed if a different slice thickness was chosen in step 4) and 450 refers to the current being supplied to the LED (this should not be changed).

Fromlay	Tolay	Expos	Lift	Ups	Downs	Delay
1	1	8	4	15	150	1
2	2	4	4	20	150	1
3	5	3	4	20	150	1
6	10	2	3	20	150	1
11	15	1.2	3	25	150	1
16	30	1	3	15	150	1
31	100	0.8	3	15	150	1
101	200	0.8	2.5	15	150	1
201	700	0.8	2	15	150	1

⚠ CRITICAL: Make sure the total number of layers in the .csv file matches the number of slices made by the Kudo3D software. The number of slices is shown when slicing the .stl file and can be verified by checking the number of .png files in the folder produced by slicing the .stl file.

6. Upload the .zip file and the .csv file to the print software.
7. Confirm that the number of slices in the .zip file matches the number of slices the printer is going to perform by checking the number next to "Total Layers" in the print software and then checking the last number in the "To Layer" column on the print page of the software. If these two numbers match, continue on. If not, see the troubleshooting section.
8. Prepare the printer, shown in Figure 1B, for fabrication.
   a. Remove the resin bath from the printer.

⚠ CRITICAL: Make sure not to scratch the membrane forming the base of the resin bath, since this is the window through which the light engine images the part. Rest the resin bath on clean, low particle wipes if it is set down. Also make sure that there are no particles in between the printer and the resin bath. Particles that get stuck between the machine and the resin bath will block UV exposure and inhibit printing.

b. Remove all resin in the resin bath.
c. Refill resin bath with 3–5 mL of unused resin, more resin is required for prints with a larger build volume.

Note: It is not required to rinse the resin bath between prints. If rinsed between prints, there is a higher risk of scratching the membrane or introducing solvents into the resin, both of which would negatively impact the success of the print. Additionally, unused resin does not require degassing before filling the resin bath.

d. Return the resin bath to the printer and secure in place.

Note: It is possible to use the same resin for multiple prints, but do not exceed three prints without refreshing the resin, as it will start to become sticky and more viscous. Resin used multiple times without refreshment should be discarded, however, resin used once or more with refreshment may be recycled back into the container after use and does not need to be thrown away. If resin is recycled, make sure to stir the resin in the container to mix the fresh resin with the used resin.

9. Move the print plate to the zero position.
10. Begin print. The printer will then complete the part through a series of exposures, or slices, with a 385 nm UV LED.

Note: Make sure printer is not bumped or vibrated during printing, as this will impact the resolution of the prints.

11. Wait for the print to complete – when finished, the part will rise out of the resin bath as shown in Figure 1C.

Rinse and cure of 3D-printed mesostructures

Timing: 1.5 h

Rinsing excess resin and curing of 3D-printed parts completes the polymer scaffold fabrication process. This step cross-links the resin, hardening the printed part and allowing for later deposition of conductive materials.

12. Rinse the part in isopropyl alcohol (IPA) as shown in Figure 2A to wash away excess resin from within the part.
    a. Submerge the part in IPA while it is still connected to the print plate, being careful not to submerge the entire build platform to avoid damaging it. Let the part sit for 5 min or until resin flow away from part has subsided.
    b. Remove the part from the IPA bath, submerge in a second IPA bath, and let it sit for 3 min or until resin flow has ceased (Figure 2B).
    c. Remove the part from the second IPA bath.

Note: Stirring or sonicating the print during the rinse may speed up rinsing by facilitating the flow of IPA into smaller openings/pores of a part.

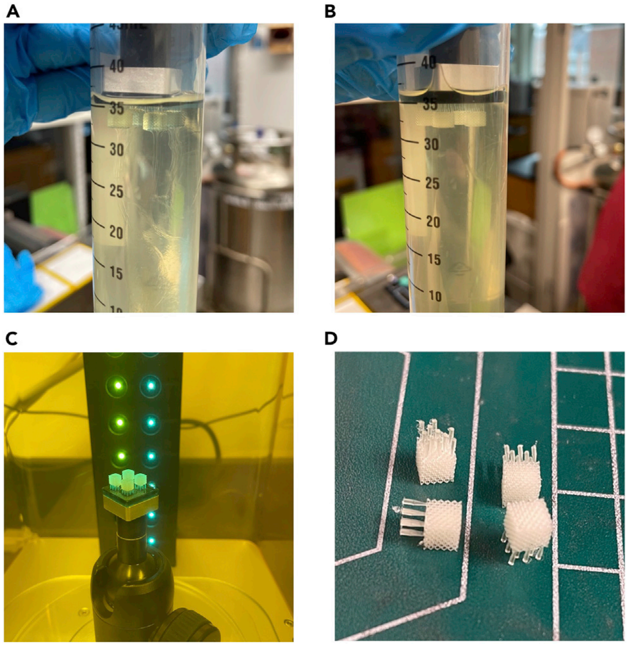

Figure 2. Rising and curing of 3D-printed mesostructures

(A–C) μSLA printed structures on the print plate (A) while submerged in IPA showing resin flowing off the printed sample, (B) while submerged in IPA showing no resin flow off the printed part, and (C) during UV curing.
(D) 3D-printed mesostructures after UV curing and heat curing, showing supports used during the print.

13. UV cure the printed part for 20 min using a 405 nm light source to further crosslink the polymer and solidify the part for use (Figure 2C).
14. Remove the parts from the build plate using a razor, careful not to cut or damage the parts (Figure 2D).
15. Heat cure parts in an oven under ambient conditions for one hour at 60°C.

Note: Cure timing can be extended to improve crosslinking, however, if growing conductive materials with ALD, additional curing will take place during the thermal ALD process. The heat cure step can also be completed in a vacuum oven if preferred.

Optional: Let part dry after IPA baths and before UV cure. This drying step, if desired, can be completed in air, an oven, or a vacuum oven. It is also optional to remove parts from the build plate prior to the UV cure instead of after.

Thermal atomic layer deposition of conductive metal oxide coatings

Timing: 3 h

Thermal atomic layer deposition allows for growth of conductive materials on the external and internal facets of a given 3D-printed structure (Figure 3A). ALD of thin oxides on polymers has been explored for both planar substrates (Bihari et al., 2020) and nanoscale AM structures fabricated by two photon lithography (Jang et al., 2013; Kestilä et al., 2018), but has been limited to deposition of insulating materials. The following steps outline the process we have developed for deposition of conductive materials on AM 3D polymer structures that can be printed by lower cost, high throughput stereolithography processes. The tailored thickness of an ALD film allows precise control of the electrical properties of these coatings.

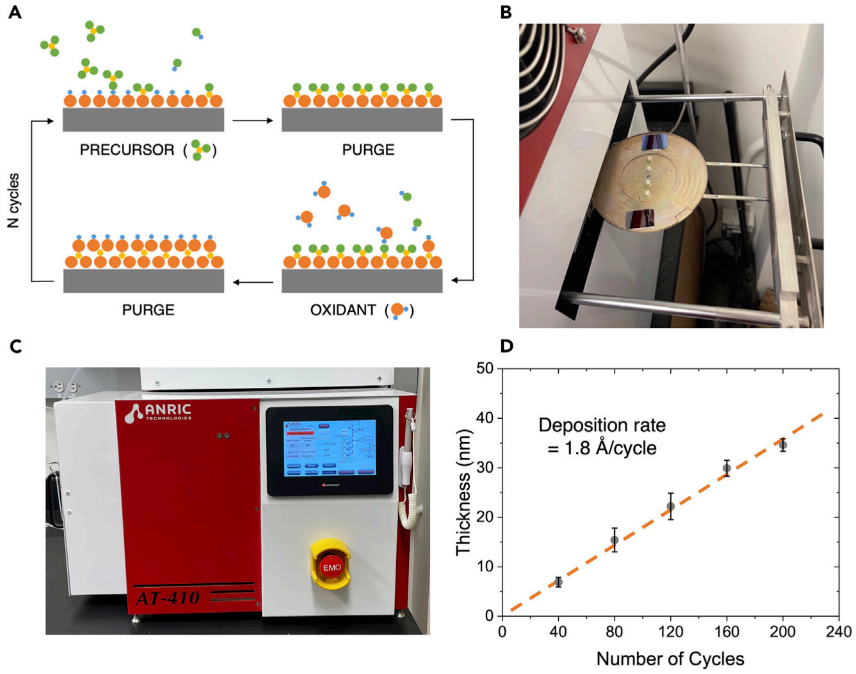

Figure 3. Thermal atomic layer deposition (ALD) of metal oxide thin films on 3D-printed mesostructures

(A) Schematic showing ALD process.

(B) 3D-printed samples and control Si and SiO_2 wafer pieces on the ALD platten prior to deposition.

(C) Anric atomic layer deposition system used for ALD of metal oxides in this process.

(D) Thickness of AZO films deposited on silicon wafers at 150°C as a function of cycle counts, etched and measured by stylus profilometry. The error bars represent the standard deviation of ten measurements.

Optional: Prepare control substrates for confirmation of growth of the conductive material. Small pieces of silicon wafers may be used to later measure deposited thickness, either with ellipsometry or etched and measured with stylus profilometry. Additionally, small pieces of silicon dioxide coated silicon wafers may be used to measure sheet resistance of deposited material with a four-point probe.

⚠ CRITICAL: Before beginning, check the pulse strength of the material precursors that you are using. If the chamber pressure increases by more than 500 mTorr during a pulse, samples will need to be contained, see troubleshooting section.

⚠ CRITICAL: Precursors with low vapor pressures will need to be heated to increase the vapor pressure and ensure flow into the chamber when pulsing. In this protocol, the ZnO precursor (DEZ) has a vapor pressure of 12.1 kPa at 20°C as reported by STREM, the distributor used for purchasing the precursors. However, the SnO_2 precursor (TDMA-Sn) only has a vapor pressure of 1.5 kPa at 20°C (as reported by STREM), so it is heated to a temperature of 80°C using a heating jacket placed around the precursor bottle to increase the vapor pressure and ensure flow. The vapor pressure of the oxidant precursor is comparable, with water having a vapor pressure of 2.3 kPa at 20°C, but does not require any additional heating to ensure flow. The ozone precursor used here is a gas precursor produced by an ozone generator, therefore the gas flow is more easily controlled than that of the vapor precursors (see key resources table for additional details).

16. Vent ALD vacuum chamber, load materials into the chamber, and pump the system (Figures 3B and 3C).

17. Ensure chamber reaches base pressure with an appropriate nitrogen flow rate. Our system achieves a base pressure of approximately 156 mTorr with a nitrogen flow rate of 40 sccm using an Edwards 18 vacuum pump. 40 sccm of nitrogen allows for appropriate purging of the chamber during the ALD process.
18. Run the ALD process for AlO_x seed layer using the conditions in the table below.

Optional: Deposition of a thicker seed layer is possible if desired or necessary (see troubleshooting section), but a base of at least 100 cycles (~10 nm) is required to ensure later growth of conductive materials.

19. Run ALD process for conductive material using one of the processes described in the tables below.

ALD process parameters

Parameter	Values for AlO_x seed layer	Values for ZnO_x layer	Values for SnO_x layer	Values for AZO layer
Deposition Temperature	100°C	150°C	160°C	150°C
Precursor 1	Trimethyl aluminum (TMA)	Diethylzinc (DEZ)	Tetrakis(dimethylamino)tin (TMDA-Sn)	Diethylzinc (DEZ)
Precursor 2	Water (H_2O)	Water (H_2O)	Ozone (O_3)	Water (H_2O)
Number of pulses of Precursor 1	3	3	3	3
Number of pulses of Precursor 2	2	2	2	2
Purge time after Precursor 1	11 s	11 s	11 s	11 s
Purge time after Precursor 2	13 s	13 s	13 s	13 s
Precursor 3	n/a	n/a	n/a	Trimethyl aluminum (TMA)
Number of Pulses of Precursor 3	n/a	n/a	n/a	3
Purge time after precursor 3	n/a	n/a	n/a	11 s
Number of cycles with Precursors 1 and 2	n/a	n/a	n/a	19
Number of cycles with Precursors 3 and 2	n/a	n/a	n/a	1
Number of cycles	100	200	200	200 (10 rounds of 20 cycles)
Expected deposition rate	1.21 Å/cycle	1.75 Å/cycle	1.35 Å/cycle	1.67 Å/cycle

Note: The deposition rate can vary slightly for different ALD machines or as a precursor is used and the vapor pressure decreases. The total number of cycles (Figure 3D), the deposition temperature, and the precursors can be modified to achieve the desired conductivity of the material, see Huddy et al. (2022). Air flow in the chamber can also cause non-uniformities in deposited thickness.

20. Vent chamber and remove samples.
21. Check the conductivity of the samples using a multimeter to verify growth. Resistance should be in the range of 100's – 1000's Ω before electrode deposition. If the resistance reading shows an overload, then the material did not deposit, see troubleshooting section.

Metal electrode deposition

Timing: 20 min

Deposition of metal electrodes (gold) onto the sample allows for reliable electrical measurement across the device and consistent device measurements for comparing different 3D structures. Physical masking allows control over the aerial coverage of the sputtered metal.

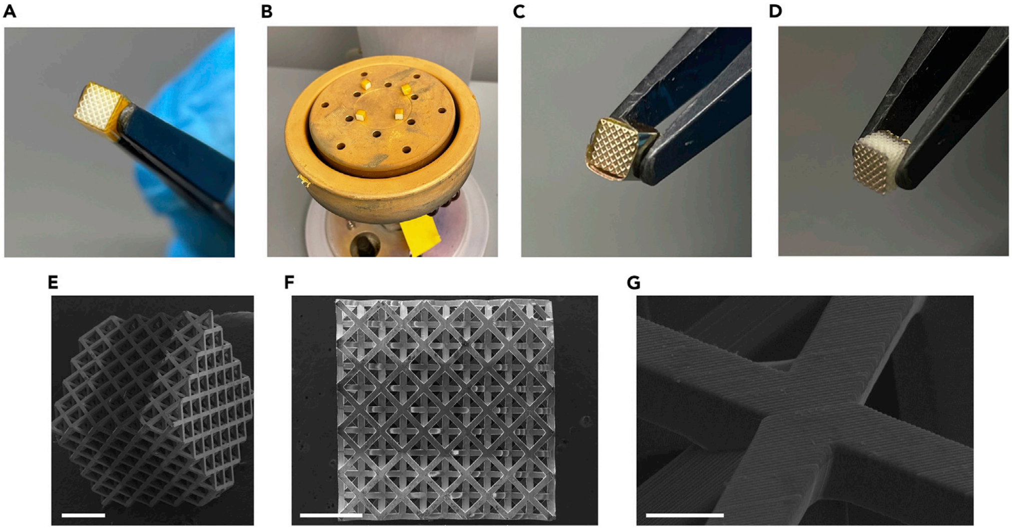

Figure 4. Metal electrode deposition and imaging of 3D-printed mesostructures

(A–D) 3D-printed mesostructured (A) masked for electrode deposition, (B) in the gold sputterer, (C) masked after electrode deposition, and (D) unmasked after electrode deposition.

(E–G) SEM images of 3D-printed mesostructures with scale bars of 1 mm (E and F) and 100 μm (G), reproduced with permission from Huddy et al. (2022). SEM images show samples masked with thinner channels to emphasize contrast between sputtered and non-sputtered regions.

22. Mask the sample with a high vacuum compatible tape, such as Kapton tape, leaving multiple areas exposed to coat with gold and form electrodes for electrical measurement (Figure 4A). This can be done by using a pair of tweezers to pinch or flatten the tape smoothly against the structure, careful not to apply too much pressure and break the structure.

⚠ CRITICAL: The ALD coating is strong and will not be scratched off by handling with tweezers or pulled off by the tape. However, it is possible to break the 3D-printed polymer structure by applying too much pressure with the tweezers, so it is important to use minimal force when handling the structures.

Optional: Only two electrodes are required for resistance measurement, however multiple areas can be left unmasked to create additional electrodes for other electrical measurements.

23. Load samples into sputterer (Figure 4B).
24. Sputter 20 nm of metal.

Optional: Flip samples after sputtering half of the desired thickness for a more uniform metal coating.

25. Remove samples from sputterer (Figure 4C).
26. Remove tape from samples by slowly peeling off the tape as it was put on the structure (Figure 4D).

Note: The ALD coating will not come off with the adhesive, but, if using a razor or tweezers to remove the tape, it is important to use minimal force to avoid breaking the structure. Gentle scraping or pulling of the tape is encouraged. Cutting the tape with a razor can damage the ALD coating and/or break the part.

27. Check the conductivity of single sputtered electrode using a multimeter. Place both electrical contacts on the same face coated in metal. The resistance across a single electrode should read 5 Ω or lower. If the resistance exceeds 20 Ω see the troubleshooting section.

Optional: Imaging can be helpful to ensure that printed structures achieve the desired architecture and have smooth faces that can allow uniform growth of thin coatings by ALD. Scanning electron microscope (SEM) images of sample mesostructures can be seen in Figures 4E–4G. These images also display the contrast produced between oxide coated regions and metal coated regions, which can be used to evaluate the patterning of the sputtered electrodes (Huddy et al., 2022).

Optional: In order to further engineer the electrical behavior of the conductive oxides, it is possible to conduct thermal post-annealing of the samples. Post annealing can also be done in other atmospheres to change electrical properties and can reach 160°C without damaging the samples.

Optional: Material characterization of the coatings can be helpful to confirm that the film deposited on the sample has the appropriate composition and stoichiometry. Energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) are two methods that can be used to confirm deposition of the material as shown in Figures 5A and 5B.

EXPECTED OUTCOMES

This protocol allows for the fabrication of conductive μSLA printed structures amenable to various electronic applications, for example, sensors and actuators embedded in 3D-printed assemblies. In this regard, we printed intentionally designed 3D mesostructures using μSLA and a UHR resin that allows for high-resolution printing as well as ALD deposition temperatures up to 160°C, reaching even higher temperatures of 175°C with a different photopolymer resin (BMF's HTL resin). After curing the samples and fully converting from a resin to a hard plastic, samples were coated by ALD. First an AlO_x seed layer was deposited to passivate the surface and allow for deposition of conductive materials. Without a seed layer, growth of the conductive materials is inhibited on the AM structure and in the immediate vicinity around the sample (for details see Huddy et al., 2022). Following that, ZnO, AZO, or SnO_x was deposited on the samples to make them conductive. Next the samples were masked, and gold was sputtered to form electrodes for device measurements.

Repeated measurement of a single sample or multiple samples processed with the same resin should yield the same resistance. Resistance of an individual part is tunable by changing the structure of the device, conductive material, and material thickness. The octet lattice structures described here have been shown to have resistances in the range of 1–100 kΩ for ZnO, 100–2000 Ω for AZO, and 100–2000 Ω for SnO_x coatings in the range of (10–200 nm). For more details on the resistance measurements and the impact of temperature and thickness on conductivity see Huddy et al. (2022).

The lattice structures in this protocol have been shown to work as chemical, thermal, and mechanical sensors (see Huddy et al., 2022 for details). However, the ALD coatings and mechanical structure could be further modified to determine the optimal mechanical and electrical structures for each sensor type. Additionally, modifications to the coatings and structure of these 3D-printed materials could introduce other electronic device applications within microelectronics or energy storage.

QUANTIFICATION AND STATISTICAL ANALYSIS

The effective resistance of a 3D structure can be measured using the following steps:

1. Place the sample on a semiconductor probe station using micromanipulators to contact the electrodes (Figure 5C).

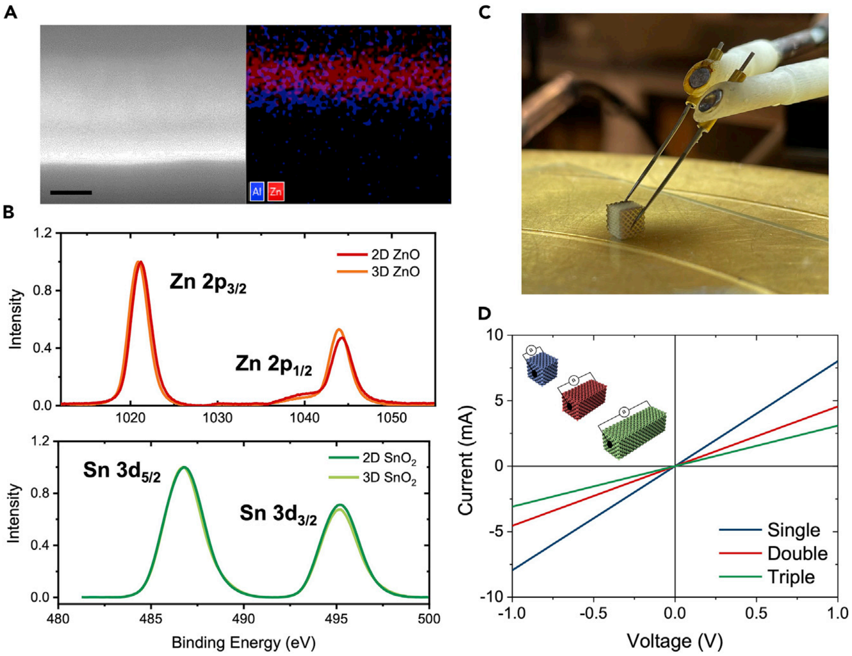

Figure 5. Electrical and material characterization of ALD coated 3D mesostructures

(A) Cross-sectional SEM image of an individual beam of a 3D-printed part (scale bar 100 nm) with EDS showing distinct deposited ZnO and Al_2O_3 layers.

(B) XPS analysis of ALD coated mesostructures, showing similar chemical composition of conductive oxide coatings deposited on 2D (silicon wafer) or 3D (mesostructure) substrates.

(C) Image of a 3D-printed part on a semiconductor probe station, contacted with tungsten needles controlled by two micromanipulators.

(D) IV curves for 3D-printed lattice structures with varying numbers of unit cells, with inset showing measurement across single, double, and triple length lattices. A-B. reproduced with permission from Huddy et al. (2022).

2. Apply a bipolar voltage sweep and measure the current through the device with a source measurement unit (SMU). The 3D structures fabricated by our process generally have resistances in the range of 100 Ω–1 kΩ. For a nominal voltage range of -1 V to +1 V, the current will be in the range of 1 mA–10's mA (Figure 5D).
3. If the IV curve is linear, then a simple extraction of the resistance by Ohm's law is appropriate (R_{3D} = V/I).
   a. If the response is non-linear, there could be an issue with the contact to the structure. Check the probe connections.
4. Multiple measurements on one sample should yield results with a COV of 2% or less. Samples outside of this range may have issues with their gold electrodes (see troubleshooting section).

Note: Measurements on replicate samples should yield results with a COV of 12% or less. COV can be calculated by dividing the standard deviation of resistance measurements by the average resistance. COV for single samples were calculated using five repeated measurements on the same sample while COV for replicate samples were calculated using four identical samples.

LIMITATIONS

Printing resolution is limited by the pixel size used in the μSLA process and the maximum size of conductive 3D parts is limited by the volume of the ALD chamber. The thickness of the deposited material also faces practical limitations due to the cyclic nature of the ALD process. We have observed that films must be thicker than 5 nm in order to ensure uniform coverage on the 3D polymer mesostructure. Films thicker than 100 nm are possible but require deposition times of several hours or longer. ALD is impractical for μm-scale films because deposition time scales with cycle count, taking 30–35 s per cycle. Growths of coatings 100 nm or thinner can be completed within several hours but, if thicker (1 μm) films are desired, another method for deposition would be more suitable. We also note that our thermal ALD processes have not proved effective for depositing the conductive films at temperatures significantly above the glass transition temperature (T_g) of the polymers used in the μSLA process. The process used here has been proven successful between 80°C – 175°C. Higher deposition temperatures with this resin will exceed the glass transition temperature, which inhibits growth of continuous and conductive films. However, higher temperature deposition is possible with resins that have higher T_g. Lower deposition temperatures may be possible with this resin as well and would be desirable for soft polymers that have much lower T_g. However, lower temperature depositions often result in more amorphous films with lower conductivity, so it is important to consider how the coating process will change with the temperature.

TROUBLESHOOTING

Problem 1

The number of slices in the .zip file does not match the number of slices the printer is going to perform (step 7).

Potential solution

If this is the case, the number next to "Total Layers" in the print software and the last number in the "To Layer" column on the print page of the software do not match. First, verify that you have uploaded the correct .zip and .csv files by checking the file names on the top left of the print software labeled "Model File" and "Parameter File." If these are incorrect, load the correct files. If these are correct, then there is a problem with the .csv file. Open the .csv file, adjust the number in the last "tolay" column to match the "Total Layers" number from the print software. Save and reupload the fixed .csv file. Then, again, check the number next to "Total Layers" in the print software and the last number in the "To Layer" column on the print page of the software, they should now match. Note that the numbers can also be adjusted in the software, but the file needs to be saved and re-uploaded within the print software to ensure that the changes are translated to the print.

Problem 2

The μSLA printed part did not yield, print was unsuccessful (step 11).

Potential solution

First ensure that the print bed is flat. This can be done by first removing the resin bath and placing a piece of printer paper over the projection area. Next, lower the print head to the zero position and try to move the paper between the print bed and the print plate. If the paper can be slid out from between the print plate and the print bed, the machine is not calibrated in the z-direction, see the manual for the machine for calibration. If the paper slides underneath one or two corners when agitated, the z-calibration is good, but the print plate is not level. If this is the case, unscrew the ball and stick joint of the print plate and adjust the positioning. Retighten the ball and stick joint and check the leveling again. If the paper is loose in one or more corners repeat until the paper rests firmly under all four corners when agitated. This step is important because when the print plate is not level the cured layer may not adhere to the print plate, causing the print to fail.

If the print plate is level after the print fails, the supports of the sample are likely the cause of print failure. The supports on the sample part are important to the success of the print because the uncured part is vulnerable to capillary forces during the printing process. If the part did not yield, first try changing the supports on the sample. Increasing the number of supports for the part and/or increasing the contact area between the supports and the part can both increase the probability of success when printing, however, it may take some optimization to find the best supports for a specific sample. If the part still will not yield after changing the supports, the part itself is likely too fragile to sustain the forces exerted by the resin during the print. In this case, rotating the part before adding supports can improve the yield by orienting finer features at oblique angles relative to the build plate and resin bath. Tall, thin features in a part used to connect large, flat features will often result in print failure because the tall, thin features do not have the ability to support the large, flat features.

Problem 3

The μSLA printed part broke or was damaged when removing supports (step 14).

Potential solution

If there are many supports on a part or the connection between the support and the part is too large it may be difficult to remove the supports without damaging the part. If it is possible to shrink the supports without jeopardizing the integrity of the print, decrease the number of supports and/or the contact area between the supports and the part and print again. If it is not possible to shrink the supports, reprint the parts and remove the supports earlier in the protocol (after steps 12 or 13) when the sample is not yet fully cured. This will allow for easier removal of the supports.

Problem 4

Sample is missing from ALD chamber after running a deposition (step 20).

Potential solution

When a sample is missing from the ALD chamber after deposition, the sample was blown into the exhaust when the precursors were pulsing into the chamber. When this is the case, retrieve the part from the exhaust line and restart deposition. To ensure that this doesn't happen again, check the pulse strength of the precursors by reading the critical notes before step 16. If the pulse strength is very high, decrease the intensity by decreasing the flow rate of your precursor if using a gas precursor. If this is not possible, tie a thin piece of wire around the sample and place the sample in the chamber. Then place a piece of silicon or another ALD compatible substrate on the wire (but not the sample) to prevent the sample from blowing away. Some adhesives have been shown to inhibit growth in the ALD chamber, so avoid using adhesives if possible.

Problem 5

Samples are not conductive when checked with a multimeter (step 21).

Potential solution

If the samples are not conductive when probed by a two-point measurement with a multimeter, it is because the conductive layer did not deposit or is too thin to be a continuous and conformal conductive coating. First confirm that the precursors have not run out, this can be done by pulsing the precursors into the chamber and verifying a pressure increase (see the critical notes before step 16). If there is not a pressure increase when pulsing, this means that a precursor has run out, refill the precursor and repeat the deposition, including the seed layer. If the precursors have not run out, verify that there is growth in the chamber using control substrates (see optional note before step 16). A silicon control sample can be used for ellipsometry, if the thickness measured matches the expected thickness, then the material has deposited. An SiO_2 coated silicon die can be used as a control for four-point probe measurements to determine the coating sheet resistance. If the sample conducts under four-point probe measurement, then the material has deposited. If the material has not deposited on the other substrates, there is a problem with the machine. If there is not a problem with the machine, repeat the deposition with a thicker seed layer (200–300 cycles of AlO_x instead of 100). If the sample is still not conducting, use a different oxidizing precursor (i.e., ozone, oxygen, or water). Some oxidizing precursors produce more insulating films, while others produce more conductive films. For example, SnO_2 deposited using water as the oxidizing precursor is insulating, whereas SnO_2 deposited with ozone as the oxidizing precursor is conductive. Changing the oxidizing precursor can ensure conductive films.

Problem 6

The electrode resistance is higher than expected (step 27).

Potential solution

When the electrode resistance is high, the gold electrodes are not thick enough to effectively conduct across the 3D surface. Increase the thickness of the sputtered electrodes until the resistance of the metal single electrode itself reaches approximately 20 Ω or less.

Problem 7

The resistance measurement across the sample with the semiconductor probe station is not working or is much higher than expected (quantification and statistical analysis step 2).

Potential solution

Inconsistent measurements or very high resistance could result from weak contact with the sample, poor electrode conductance, or the lack of a conductive coating. First, try moving the probes to another position on the sample or increasing the contact pressure of the probe on the sample then remeasure. If the sample still isn't conducting, check the electrode resistance (step 27). If the electrode resistance is above 20 Ω refer to problem 6 for troubleshooting. If the electrode resistance is below 5 Ω, check the conductivity of the sample with a multimeter as in step 21. If the sample is not conducting, refer to problem 5 for troubleshooting.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, William Scheideler (William.j.scheideler@dartmouth.edu).

Materials availability

This study did not generate new unique reagents.

Data and code availability

The published protocol contains all of the data/code generated during this study.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.xpro.2022.101523.

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AUTHOR CONTRIBUTIONS

J.E.H. and W.J.S. conceived the idea and planned experiments. J.E.H. completed device fabrication and analysis. All authors contributed to manuscript preparation and revisions.

DECLARATION OF INTERESTS

Authors declare their work on the patent titled "FUNCTIONALIZATION OF MICROSCALE 3D-PRINTED POLYMER STRUCTURES WITH NANOSCALE VAPOR DEPOSITED ELECTRONIC LAYERS." US Patent App. No. 63/235,799. The authors declare no competing interests.

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