

Masked Deposition of Gallium-Indium Alloys for Liquid-Embedded Elastomer Conductors

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A fabrication method is introduced that utilizes masked deposition and selective wetting to produce hyperelastic electronic circuits that are composed of a thin elastomer film embedded with microchannels of liquid-phase gallium-indium (Ga-In) alloy. This method exploits the low melting-point and controllable wetting dynamics of Ga-In alloys, as well as the ability for Ga-In alloys to form irregularly-shaped, free-standing, micrometer-scale structures via gallium surface oxidation. Masked deposition eliminates the need for manual injection filling, which enables certain geometries that cannot be produced by injection and allows for the automated, high-volume production of Ga-In based “liquid-embedded elastomer electronics” (LE3). With this approach, LE3 circuits can be produced with isolated features that have planar dimensions of less than 200 μm and edge-to-edge feature separations as small as 25 μm .

stretchable radio frequency (RF) radiation sensor,^[6] wearable tactile interfaces,^[7,8] and a joint angle sensor that matches the natural elasticity of human skin.^[9] As with so-called “wavy” circuits and other stretchable electronics,^[10,11] elastomers embedded with microchannels of liquid-phase Ga-In alloy will continue to have a central role in assistive wearable technologies that match the elasticity of human tissue and preserve natural ranges of motion.

Liquid-embedded elastomer electronics (LE3) are currently produced by casting a low-modulus silicone elastomer (elastic modulus, $E \approx 0.1\text{--}1$ MPa) in a micro-machined mold, sealing the molded features with an additional layer of elastomer,

and then filling the embedded channels with Ga-In alloy using a needle and syringe. While reliable, this manual method of fabrication is labor intensive, geometry limiting, and not readily scalable to automated high-volume manufacturing. In this letter, we introduce an alternative fabrication process (seen in **Figure 1**) that eliminates needle injection and instead employs masked patterning and deposition methods that are commonly used in flex-circuit and soft lithography manufacturing. This fabrication method exploits the thin oxide skin formed by droplets of Ga-In alloy, a feature that allows the alloy to form stable, free-standing structures that can be frozen in place prior to elastomer sealing. In addition, this scalable approach to manufacturing exploits a variety of wetting behaviors between droplets of galinstan and thin metal films.^[12] This work complements several new fabrication techniques developed for Ga-In alloys, including vacuum induced patterning,^[13,14] and contact printing.^[15]

1. Introduction

Liquid-phase gallium-indium (Ga-In) alloys, such as galinstan (68.5% Ga, 21.5% In, 10% Tl, by weight) are non-toxic, low viscosity ($\eta = 2.4 \times 10^{-3}$ Pa s) fluids that are highly conductive ($\sigma = 3.40 \times 10^6$ S/m) and have a thin oxide skin that allows them to form stable free-standing structures.^[1,2] Fluidic microchannels of Ga-In alloy embedded in an elastomer film function as highly stretchable (strain > 500%) electrical wiring or sensors that change electrical conductivity in response to elastic deformation.^[3–5] Recent applications include mechanically-tunable antennae for remote strain and pressure monitoring,^[4] a

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2. Results

Figure 2 displays a test pattern used to demonstrate the possible trace widths and feature densities of the fabrication process. The test pattern included traces with widths of 1 mm, 500 μm , 200 μm , 100 μm , 50 μm , 25 μm , and 10 μm . Square features were spaced with edge-to-edge separations of the same dimensions.

The minimum trace width that the fabrication process produced is 200 μm . Upon further inspection, it is apparent that the trace designed to be 200 μm in width is considerably less than in actuality (**Figure 3a**), with the conductive liquid measuring between approximately 100 μm and 150 μm in width along various points of the trace. This discrepancy between intended trace width and actual trace width is likely due to the

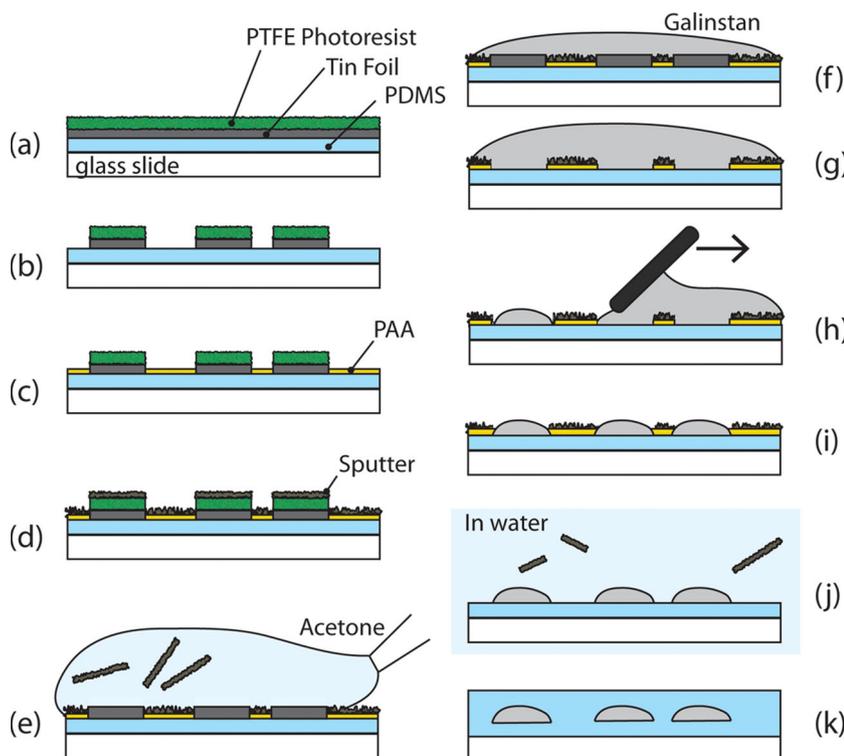


Figure 1. Process flow for liquid-embedded elastomers fabricated by selective wetting of gallium-indium alloys. a,b) Tin foil is patterned on a PDMS surface with photolithography. c) A PAA release layer is spin-coated onto the elastomer surface, and does not coat the super-hydrophobic photoresist. d,e) The surface is sputtered with indium, but the tin foil is protected by the photoresist. Lift-off is achieved by rinsing the surface with acetone. f,g) The surface is flooded with galinstan, which reactively wets the tin foil. h,i) Excess galinstan is removed by wiping the surface with a thin-film applicator. j) The remaining sputter mask is removed from the surface in water, using the PAA as a release layer. k) The liquid features are cooled in a freezer and subsequently encapsulated by coating with an elastomer.

aggressive ferric chloride etch, which over-etched the edges of the seed pattern, as seen by the dark outline surrounding the features in Figure 2. For larger features ($>500\ \mu\text{m}$), this edge-effect did not notably change the size of the resulting features. However, for the smaller traces ($<500\ \mu\text{m}$) this edge-effect dramatically decreased the overall dimensions and completely removed the traces designed to be less than $200\ \mu\text{m}$ in width. It is important to note that the seed layer for the gallium-indium alloy was altered prior to the liquid deposition on the surface, and therefore reduced feature sizes may be achievable using the selective wetting process on a more finely patterned seed layer.

Experiments with diluted ferric chloride (10–90% deionized water) were conducted to slow the etching process, as it was briefly thought that a more mild etchant may prevent over-etching and enable smaller traces. However, it was found that diluting the etchant only slowed the etching process and did not change the results. We therefore induce that achievable trace width in this process is a function of the material and etchant combination, in addition to the material thickness. That is, scalability of the feature sizes is partially limited by the aspect ratio of the seed layer, where a thinner seed film would enable finer features.

Figure 2 also demonstrates the ability to pattern densely-packed features with the liquid-embedded-elastomer fabrication process. Isolated features (squares with a feature length of $1\ \text{mm}$ in this case) are shown to be reliably patterned with an edge-to-edge separation as small as $25\ \mu\text{m}$. In addition, Figure 3b shows example profiles for both a $1\ \text{mm}$ wide conductive liquid trace and a $1\ \text{mm}^2$ square conductive liquid feature embedded in an elastomer sheet. The cross-section of these features was found using a 3D laser confocal microscope (Olympus, LEXT OLS4000), and is seen to be rounded in shape. The peak heights of the $1\ \text{mm}$ channel and $1\ \text{mm}^2$ square are approximately 80 and $90\ \mu\text{m}$, respectively. Discrepancies in feature height may be caused by fluid flow prior to encapsulation.

3. Discussion

In a previous study we examined a variety of wetting behaviors between droplets of galinstan and thin metal films.^[12] Wetting response was found to be tunable as a function of both composition and texture. Mainly, galinstan was found to wet reactively to tin foil (Sigma Aldrich, product nu. 14511, pure), but was repelled by sputtered (textured) films of tin and indium (sputter targets from American Elements, 99.999% pure), among other sputtered metals. The fabrication process given here exploits this phenomenon by patterning areas of tin foil and sputter coated metal films in order to achieve selective wet-

ting of galinstan on an elastomer surface.

It should be noted that wetting behavior of liquid-phase Ga-In alloys on a silicone elastomer (PDMS) was also studied. We found that Ga-In alloys do not wet PDMS, but rather non-uniformly stain the surface with a contact angle of $\approx 130^\circ$. This is consistent with other reports of non-wetting between Ga-In alloys and PDMS.^[1] For completeness, we also tested contact angle between the alloys and a PDMS substrate with recent exposure to oxygen plasma. Unlike for water-based liquids, this surface treatment did not notably change the wettability of the substrate for Ga-In alloys (contact angle $\approx 125^\circ$).

Another important result of that study is the equilibrium state of galinstan and tin foil. Over a time period of several days, the materials react together to develop a stable alloy of new composition. The new alloy was analyzed using energy dispersive spectroscopy (EDS) in a scanning electron microscope over five samples, with the average composition (percentage by weight) being $57.63\% \pm 0.24\%$ gallium, $22.69\% \pm 0.09\%$ indium, and $19.68\% \pm 0.20\%$ tin. The increased percentage of tin demonstrates that the underlying tin foil is absorbed into the galinstan to create this new composition. This reactive process removes the solid metal seed layer,

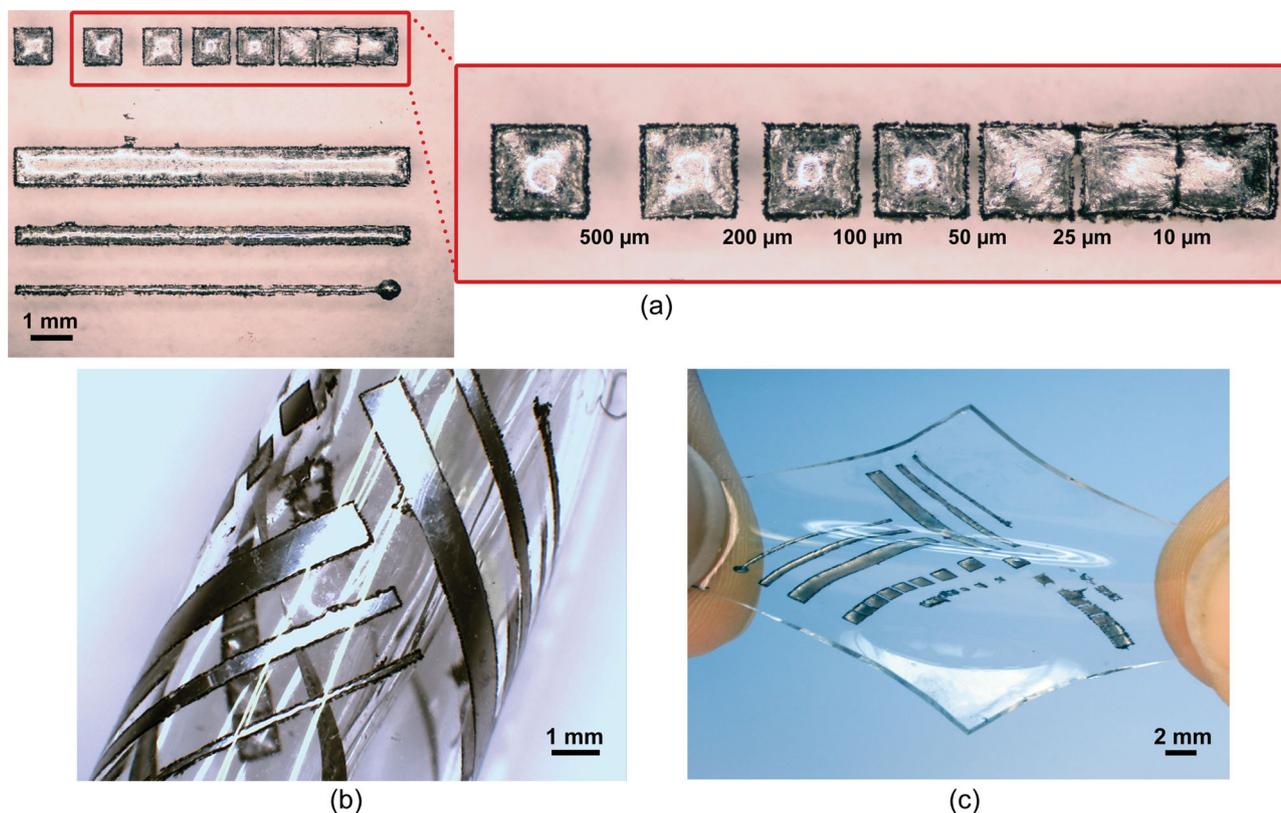


Figure 2. A liquid-embedded-elastomer patterned by selective wetting of Ga-In alloy. a) A test pattern displaying possible feature sizes and densities enabled by the fabrication process. b,c) The liquid-embedded elastomer is flexible and stretchable.

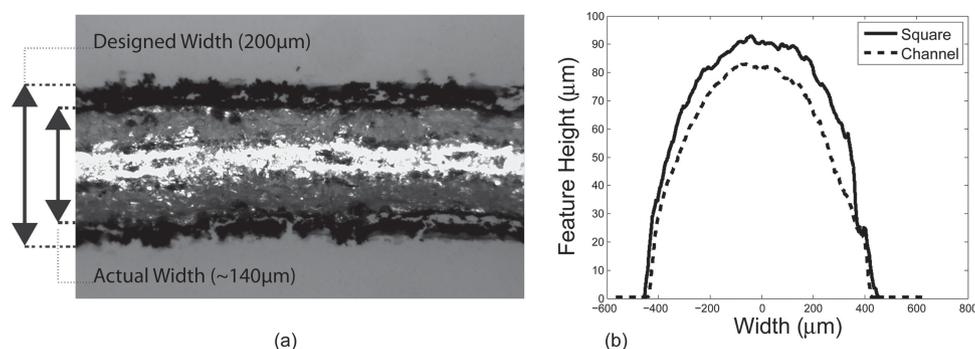


Figure 3. a) Zoomed-in image of a 200- μm wide channel. The actual channel width is reduced from the designed channel width during patterning of the seed layer. Over-etching is evidenced by the black outline surrounding the features. b) Example profiles for both a 1 mm channel and a 1 mm² square.

resulting in a composite structure of only elastomer and liquid metal, which is ideal for application to liquid-embedded-elastomer devices.

4. Conclusion

In closing, we introduce a process for producing Ga-In based LE3 circuits using masked deposition. This fabrication technique yields the ability to pattern highly conductive liquid metals within elastomer films without the need for molding,

bonding, or manual steps such as syringe-filling. This process incorporates techniques from flex-circuit manufacturing and photolithography, and exploits the wetting properties and phase change of a conductive liquid metal. Ultimately, liquid-embedded elastomer devices with features smaller than 200 μm and edge-to-edge separations as small as 25 μm are produced. This process also yields the ability to create isolated features, as no inlet/outlet locations are required for filling.

Future investigations will include further experimental fabrication techniques to continue to reduce the minimum trace width and increase feature densities. For example, gaining

more control over the trace and feature heights may inherently allow for smaller edge-to-edge separation. A different approach to deposition and patterning of the seed layer may result in smaller trace widths. Increased control over the cross-sectional area of liquid features may allow for thinner devices (the elastomer sheet shown in Figure 2 is approximately 300- μm thick with the features between 80–90 μm in height). We expect that further optimization of the process will yield the ability to create much smaller and densely packed features, and will be used to create novel devices, such as soft resistors, inductors, capacitors, and active (gated) electronic components, with applications in soft sensing skins, robotics, medical devices, soft orthotics, and stretchable electronics.

5. Experimental Section

Fabrication of liquid-embedded-elastomer devices begins with vapor deposition of a hydrophobic monolayer on a flat substrate. In this work, we use clean glass slides (50 mm \times 70 mm, Electron Microscopy Sciences). The glass slides are placed in an evacuated chamber (≈ 20 mTorr) with an open vessel containing a few drops of trichloro(1H, 1H, 2H, 2H-perfluorooctyl)silane (Sigma Aldrich) for at least 3 h. Subsequently, a layer of silicone-based elastomer is spin-coated in liquid form onto the glass slide, yielding a thin film with prescribed thickness. Here, we use polydimethylsiloxane (PDMS; Sylgard 184, Dow Corning; 10:1 mass ratio of elastomer base to curing agent), however, subsequent steps in the process are not dependent on the specific properties of PDMS and any thus any silicone-based elastomer may be used.

After curing the elastomer layer, a 20- μm -thick film of tin foil (Sigma Aldrich, product nu. 14511, pure) is rolled over the elastomer. The inherent tackiness of PDMS allows for good adhesion between the elastomer and foil. In cases where a less tacky elastomer is used, adhesion between the layers may be achieved using an amino-epoxy chemical bonding method.^[19]

The foil is fully cleaned with acetone, IPA, and deionized water, and subsequently baked on a hotplate at 85 $^{\circ}\text{C}$ for 5 min to evaporate liquids. A superhydrophobic photosensitive nanocomposite film is then spin-coated onto the surface. The superhydrophobic photoresist incorporates PTFE nanoparticles (Microdispers-200, Polysciences) into a positive photoresist matrix (1:15 ratio by weight, well-mixed with a centrifugal mixer).^[16] Experiments were completed using Photoposit SP24 (Shipley), which is a positive working resist generally used within the printed circuit board industry. Photoposit SP24 is also known to be a flexible photoresist, thus it is particularly well-suited for compliant substrates. In addition, we chose this resist due to its associated fine line resolution (1:1 resist thickness to resist geometries can be achieved, and etched dimensions of 25 μm can be produced). As no specific sensitivity chart was available from the resist manufacturer, we adapted the i-line compatible exposure process initiated by Corbett et al.^[17] Photoresist is spun onto the tin foil at 800 rpm for 20 s. After spin coating, the sample is soft-baked on a hotplate at 85 $^{\circ}\text{C}$ for 10 min. The photoresist is then exposed under a mask with a collimated UV source with an exposure energy of 2140 mJ/cm². The sample is then developed in an aqueous solution of (0.2 M) sodium hydroxide at room temperature. Post-development, exposed tin is chemically etched in a heated ferric chloride bath, where the photoresist masks the desired tin pattern from removal. Residual ferric chloride is removed by rinsing the sample in deionized water, and the remaining tin foil pattern acts as a seed layer for liquid metal deposition in later steps. The sample surface is then exposed to oxygen plasma (65 W for 30 s). Silicon-based elastomers, such as PDMS, that have recently been exposed to oxygen plasma are rendered hydrophilic by the formation of hydroxyl groups on the surface. Yet, the plasma exposure has no notable effect on the

PTFE/photoresist surface, which is hydrophobic. Hence, a solution of poly(acrylic acid) (PAA) (Polysciences, Cat nu. 00627) diluted in deionized water (10% PAA by volume) is applied to the entire surface, wherein the solution selectively wets the elastomer. The PAA solution is spin-coated at 800 RPM for 30 s to yield a thin liquid film on the elastomer surface. It should be noted that the PAA solution must be spin coated to a thickness that is less than the seed tin layer thickness to ensure good contact between the liquid metal and the seed layer in subsequent steps, due to the liquid metal's high surface tension. The sample is then baked on a hotplate at 85 $^{\circ}\text{C}$ for several minutes, to evaporate solvents in the PAA solution. Finally, the sample is sputter-coated with indium. We previously found that liquid-phase Ga-In alloys are repelled by sputtered surfaces of various compositions, including tin and indium. The non-wetting property of the films was found to be a function of the surface texture, rather than the material composition.^[12] In this particular example, we used sputtered films of indium, where a sputtering time of 10 min corresponds to a mean film thickness of approximately 1.4 μm .

Next, the sample is rinsed with acetone to lift off the photoresist layer and corresponding sputtered indium, thus exposing the underlying tin foil. The tin-patterned surface is then coated with liquid galinstan and kept in a nitrogen environment chamber for at least 24 h, while the galinstan reactively wets to the tin foil substrate. The nitrogen environment prevents the galinstan from heavily oxidizing, while the patterned sputter-coated indium behaves as a mask, preventing non-uniform wetting of the elastomer surface.

When the sample is removed from the nitrogen environment, galinstan that is not wetted to the surface is removed using a thin-film applicator (Elcometer 4340 Automatic Film Applicator). The thin-film applicator allows for definition of the liquid height, thus enabling some control over the cross-section of the liquid-embedded pattern. Any residual liquid metal is striped by placing the entire sample in a deionized water bath, where the poly(acrylic acid) on the surface of the elastomer dissolves and results in lift-off of the corresponding sputtered layer and undesired liquid metal from the surface.

Finally, the sample is placed on a hotplate for several minutes to evaporate remaining solvents, and then placed into a freezer with an operating temperature below the melting temperature of galinstan (-19 $^{\circ}\text{C}$), which causes the galinstan to harden and hold its form. This phase-change enables the cross-section of the liquid pattern to remain intact during the subsequent encapsulation step. The liquid patterns are embedded into an elastomeric matrix by spin coating a final layer of elastomer over the entire surface of the device, followed by a cure step. It should be noted that the time between removal from the freezer and spin-coating is critical, as the patterned features should not warm above the melting temperature prior to encapsulation.

Finally, the liquid-embedded-elastomer device may then be released from the glass slide substrate. Wiring may be incorporated by either inserting external copper wires at appropriate locations (as in ref. [18]) or interfacing the device with a polyimide-based flex-circuit (as in ref. [9]).

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