

## 3D structures of liquid-phase GaIn alloy embedded in PDMS with freeze casting

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Liquid phase electronic circuits are created by freeze casting gallium–indium (GaIn) alloys, such as eutectic gallium–indium (EGaIn), and encapsulating these frozen components within an elastomer. These metal alloys are liquid at room temperature, and can be cast using either injection or a vacuum to fill a PDMS mold and placing the mold in a freezer. Once solidified, a GaIn alloy segment can be manipulated, altered, or bonded to other circuit elements. A stretchable circuit can be fabricated by placing frozen components onto an elastomer substrate, which can be either patterned or flat, and sealing with an additional layer of elastomer. Circuits produced in this fashion are soft, stretchable, and can have complex 3D channel geometries. In contrast, current fabrication techniques, including needle injection, mask deposition, and microcontact printing, are limited to 2D planar designs. Additionally, freeze casting fabrication can create closed loops, multi-terminal circuits with branching features, and large area geometries.

### 1 Introduction

Elastomers embedded with microfluidic channels of liquid-phase gallium–indium (GaIn) alloys function as elastically soft circuit wiring, sensors, and antennas.<sup>1–4</sup> In contrast to rigid and flexible circuits, these soft-matter technologies are highly stretchable (up to ten times their natural length) and elastically compatible with human tissue. They have the potential to contribute to the advancement of wearable computing, medical robotics, and any other application that depends on physical human-machine interaction that is safe and preserves natural bodily function and mobility. However, while promising, GaIn-filled soft microfluidics exhibit only a limited range of electronic and electromechanical functionalities. Further progress in electrically-powered soft-matter technologies depends on new fabrication methods that allow liquid-phase GaIn features to be patterned into any arbitrary three-dimensional geometry and embedded in elastomer along with other conductive or electrostatically-responsive materials.

Liquid GaIn circuits are currently produced with needle-injection,<sup>2–4</sup> masked deposition,<sup>5–8</sup> and microcontact printing.<sup>9</sup> While reliable for creating planar/2D circuits, these techniques cannot be used to make 3D features such as the electrode arrays in Fig. 1a for a parallel-plate comb capacitor or the box antenna in Fig. 1b. Instead, we produce these structures with a proposed *freeze casting* technique. To mold GaIn

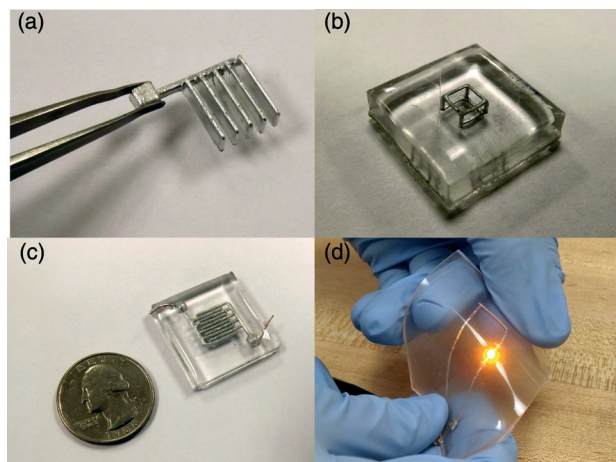
alloy into any arbitrary 3D shape, we fill a PDMS mold with the liquid alloy, freeze it, assemble the casted features along with other materials in a temperature-controlled chamber, and then seal the assembly in a soft silicone elastomer, as shown in Fig. 1c. At room-temperature, the sealed GaIn alloy melts and the liquid-embedded elastomer can be stretched and flexed without losing electronic functionality (Fig. 1d).

Freeze casting with liquid-phase GaIn alloys builds on fabrication methods in soft lithography,<sup>10</sup> soft microfluidics,<sup>11</sup> and microsolidics.<sup>12,13</sup> In microsolidics, low melting point metal alloys and solders (such as indium, indium–tin, and indium–lead) are injected into microchannels embedded in a soft elastomer. While flexible, these microsolidic structures are solid at room temperature and have limited stretchability. In contrast, the liquid GaIn alloys used in freeze casting are liquid at room temperature and the microfluidic structures remain intact as the surrounding elastomer is stretched several times its original length. Freeze casting allows GaIn alloys to be easily handled and manipulated using tools such as tweezers – something that cannot be done with a liquid. We have not observed fracture or cracking during freezing and have not found the need to pretreat microchannels to increase the wettability, as is commonly done in microsolidics.

In this manuscript, we introduce techniques for freeze casting GaIn alloy in a PDMS mold based on needle injection and vacuum perturbation. We show that these frozen components can be modified using additive and subtractive manufacturing techniques such as cutting and bonding. As with conventional electronics, complex liquid-phase electronics can be rapidly assembled from a diverse selection of

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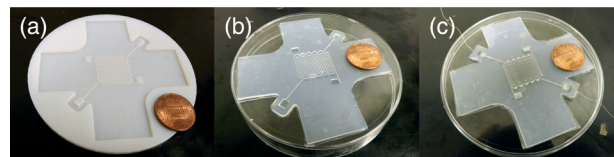
**Fig. 1** (a) EGaIn can be frozen into geometries with deep features and safely manipulated. The frozen EGaIn can be encapsulated in elastomer to create electronic circuits and devices such as this cube antenna (b) and capacitor (c). (d) The softness of the elastomer enables these circuits to be stretched and bent.

simple GaIn circuit elements. After presenting several sealing techniques, we demonstrate that these unique 3D soft microfluidic electronics remain functional under extreme elastic deformation.

## 2 Background

Stretchable electronics with liquid-phase metal originated with the Whitney strain gauge, which was composed of mercury embedded in a rubber tube.<sup>14</sup> Originally used for human muscle contraction, the Whitney strain gauge measured hyperelastic stretch from the change in electric resistance of the elongating liquid-phase mercury wire. Building on advancements in soft lithography,<sup>10,11</sup> this paradigm in elastically soft electronics has been recently revisited using non-toxic GaIn alloys like eutectic gallium–indium<sup>2,15</sup> (EGaIn) and gallium–indium–tin<sup>16</sup> (Galinstan). Microelectronics composed of microfluidic channels of liquid-phase GaIn alloy embedded in PDMS and other soft silicone elastomers exhibit a broad range of hyperelastic sensing and circuit functionalities and represent an intrinsically soft alternative to flexible and “wavy” circuits<sup>17–19</sup> for wearable and implantable electronics. Current applications include mechanically-tunable antennas for wireless communication,<sup>4,20,21</sup> soft-matter diodes<sup>22</sup> and memristors<sup>23</sup> for computer logic, and pressure,<sup>24,25</sup> curvature,<sup>26</sup> and shear sensors<sup>6</sup> that could be used as “artificial skin” for assistive wearable technologies and biologically-inspired soft robotics.

Referring to Fig. 2, liquid GaIn circuits are typically produced with replica molding and needle-injection. For fluidic channels with sub-millimeter dimensions ( $\sim 10$ – $100\ \mu\text{m}$ ), the mold is produced with SU-8 photolithography. For larger feature sizes, the elastomer may be cast in a 3D printed or CNC machined mold. For the example<sup>27</sup> shown in the figure, elastomer is cast in a 3D printed mold (Objet 24; Stratasys, Inc.) that contains negatives of the microfluidic features. After the

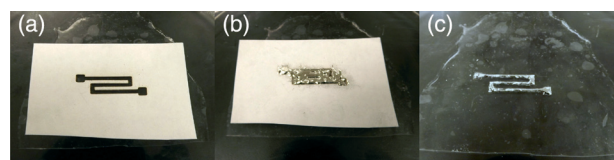


**Fig. 2** Injection fabrication: (a) A mold with micro features is fabricated using 3D printing technology. (b) An elastomer is cast within the mold. (c) The patterned elastomer is bonded to a sealing layer and a GaIn alloy is injected into the enclosed channels.<sup>27</sup>

microfluidic channels are cast and sealed, they are injected with liquid GaIn using a needle and syringe. Lastly, external wires are inserted in the circuit terminals and sealed with small drops of silicone elastomer. While reliable, this fabrication method significantly limits circuits to planar geometries that allow air to escape as the microfluidic channels are filled with GaIn. Channel branching and intersections, large planar areas, and geometries with numerous terminal features can be challenging to fabricate since air can easily be trapped within the channels. It is possible to manually align and bond multiple planar layers of silicone elastomer to create simple 3D channel geometries. Additionally, using self healing polymers as the encapsulating material, a straight wire can be cut and reconfigured into a multidimensional shape.<sup>28</sup>

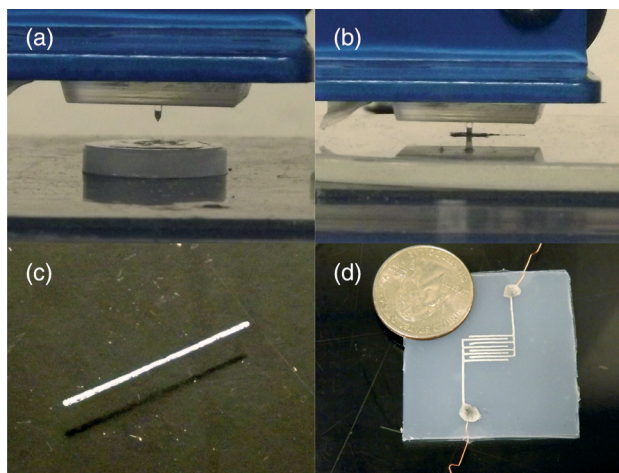
With masked deposition or stencil lithography (Fig. 3), a mask (stencil) is placed on an elastomer substrate and liquid GaIn alloy is deposited on top of the mask. When the mask is peeled off or etched, the liquid metal remains wetted to the exposed portions of the substrate. Next, external wiring is inserted, the liquid GaIn is frozen, and the circuit is sealed with additional silicone elastomer. For simple circuit geometries with non-intersecting features and  $\geq 100\ \mu\text{m}$  sized features, masked deposition may be performed with a laser-patterned or 3D printed stencil.<sup>5,6</sup> For miniaturized circuits with closed loops and intersections, deposition requires a sacrificial mask produced with photolithography.<sup>7</sup> In addition to allowing for a broader range of circuit geometries, masked deposition can be performed with laser-patterned films of adhesive elastomer such as VHB<sup>TM</sup> tape (3M<sup>TM</sup>).<sup>8</sup> This allows liquid GaIn circuits to be produced in minutes rather than the hours required to produce molds and cure silicone elastomer.

Microcontact printing ( $\mu\text{CP}$ ) represents another versatile technique for producing planar GaIn circuits.<sup>9</sup> Referring to Fig. 4, an elastomer sphere tipped cone (print head) mounted on a 3-axis Cartesian robot repeatedly dips into a pool of



**Fig. 3** Mask deposition: (a) a sacrificial mask is placed on an elastomer substrate. (b) Galn alloy is spread over the mask. (c) The mask is removed, leaving the Galn alloy in the pattern of the mask on the substrate. The Galn alloy is encapsulated using an additional layer of elastomer to seal the device.





**Fig. 4** Microcontact printing: (a) an elastomer print head is dipped into a pool of liquid GaIn alloy, a small amount of the alloy wetting to the tip of the print head. (b) The print head relocates over an elastomer substrate where it stamps onto the surface, depositing a "pixel" of the metal. (c) Repeating this process with small incremental displacements can create planar circuit geometries. (d) The circuit is then encapsulated in an additional layer of elastomer.<sup>9</sup>

GaIn alloy and deposits individual droplets of liquid alloy on an elastomer substrate. After printing, external wires are inserted at the terminals and the circuit is sealed with additional elastomer. Although slower than inkjet printing, this automated method for producing any arbitrary 2D circuit pattern can be performed in air with an inexpensive 3-axis stage. In contrast, jetting with GaIn alloy requires an oxygen-free environment ( $<1$  ppm  $O_2$ ) to prevent oxidation and accumulation of liquid at the tip of the nozzle.<sup>16</sup>

While adequate for planar/2D circuits, these existing fabrication methods cannot be used to embed soft elastomer with 3D liquid alloy features. Although replica molding and needle-injection can be used to produce some non-planar geometries, these are largely limited to circuit vias, bridges, and other features that require careful alignment between cured layers of elastomer. To produce non-planar circuit elements and antennas with liquid GaIn, we introduce a versatile fabrication technique based on freeze casting. This method, describe below in Sections 3 and 4, is compatible with a broad range of materials and allows for manual assembly of circuits from prefabricated components.

This proposed freeze casting allows for a broad range of three-dimensional geometries and surface textures. It complements another recently reported method for producing complex liquid metal structures based on 3D printing.<sup>29</sup> With 3D printing, liquid GaIn is extruded through a capillary as droplets or thin wire. This method produces three-dimensional geometries composed of extruded wires and spherical beads that could then be integrated into a circuit and elastomer sealed using the techniques presented in Sec. 4.

### 3 Freeze casting

Two methods have been developed for the casting of liquid gallium indium alloys: vacuum perturbation and injection.

These processes represent the first stage in a series of steps to produce a soft matter electronic device with freeze casting. We have chosen to use EGaIn as our conductive liquid as it is commonly used in soft microfluidic electronics and has a higher freezing temperature (melting point, MP = 15 °C) when compared to Galinstan (MP = −19 °C).<sup>1</sup> Preliminary work with Galinstan has shown that our methods will also work with this alloy and should work with other GaIn based alloys. Mercury is not considered because of its toxicity. The molds used for casting the metal alloy are created by casting PDMS (Sylgard 184; 10 : 1 base-to-catalyst ratio; Dow Corning) in a master mold printed with an Objet 24 (Stratasys, Inc) 3D printer. Using either of the techniques described in the following sub-sections, the PDMS mold is filled with liquid GaIn at room temperature. Next, the sample is frozen and the cast GaIn is removed from the mold while still in its solid state. As with conventional replica molding, the solidified alloy is easily removed from a soft silicone mold – using a rigid mold would cause brittle fracture during removal.

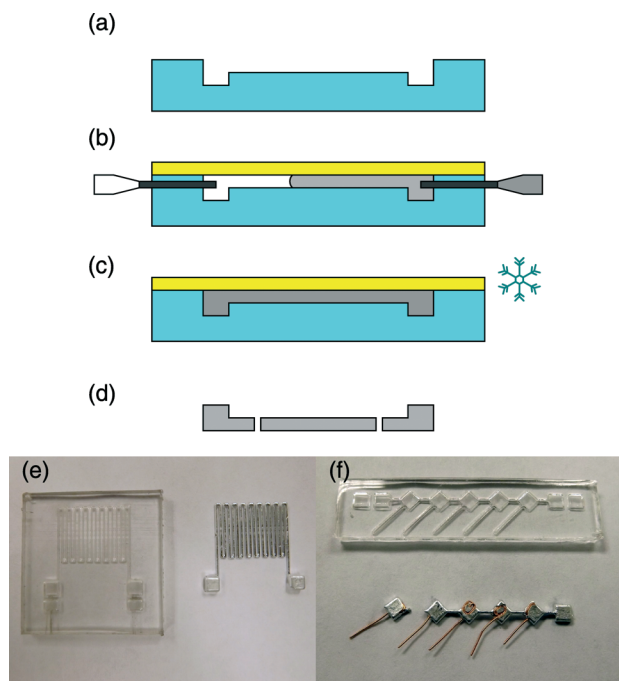
#### 3.1 Injection casting

One way to cast EGaIn is to inject it into the mold using a needle and syringe. Although individual circuit elements produced with this *injection casting* method are limited to simple geometries with two terminals (for the injection inlet and air outlet), freeze casting allows these elements to be assembled into complex 3D structures. Referring to Fig. 5a, the PDMS mold is placed against the surface of a flat glass substrate in order to seal the surface features of the mold. Next, a needle and syringe is used to inject EGaIn into a reservoir at one end of the channels, with a second needle at the other end to evacuate the air (Fig. 5b). A small amount of pressure on the PDMS mold may be required to maintain the seal during injection. Once the channels are filled, the substrate and mold are placed in a freezer (Fig. 5c). When the EGaIn solidifies, the mold can be separated from the glass substrate so that the metal alloy can be removed (Fig. 5d).

This method of casting is best for circuits that have long flat features. With conventional needle injection, in which the cast PDMS is bonded to a sealing layer of elastomer, the channels may collapse if not using an appropriate height-to-width aspect ratio.<sup>10</sup> With injection based freeze casting, the height-to-width aspect ratio should still be considered, but as there is no bonding of the mold to the glass substrate, any channel collapses that occur will not be permanent. Abrupt changes in channel height should be avoided since this can cause air to be trapped during injection.

After it is removed from the mold, a frozen EGaIn component can either be immediately assembled with other parts or modified with subtractive machining. Tools such as tweezers and pliers can be easily used to handle or alter the frozen components. For example, injection casting could be used to make a series of electrodes that are joined by breakable connectors, as seen in Fig. 5f. The connectors allow EGaIn to be injected from one end of the array and air to





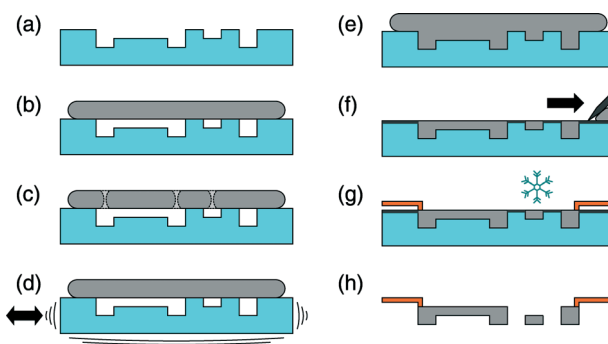
**Fig. 5** A patterned PDMS mold is fabricated (a) and placed against a flat glass substrate (b). EGaln is then injected into the channels (b) and frozen (c). The frozen EGaln can then be removed from the mold and easily manipulated or altered (d). This process can make basic components such as serpentine wire segments for resistive strain sensing (e) and terminal ends (f). (f) Creative positioning of channels enables copper wire to be frozen within terminal ends as the EGaln only flows into channels from which air can escape. Additionally, single terminals can be separated from the larger structure.

evacuate from the other. After casting, the individual elements can be broken off or cut from the structure. The terminals used for the injection inlet and outlet can then be discarded. Components such as copper wire and LEDs can be incorporated into this injection process such that they are partially encased in EGaln when frozen so that they can be easily incorporated into the final circuit. Lastly, the cast EGaln features can be manually assembled with other circuit elements in a temperature-controlled chamber that keeps the temperature below the melting point of the alloy.

### 3.2 Vacuum casting

Alternatively, an open PDMS mold can be filled by pouring liquid EGaln over the features and using vacuum and perturbation to remove trapped air. This approach eliminates the requirement in injection casting for a channel inlet and outlet. Referring to Fig. 6, this method of *vacuum casting* utilizes a pressure difference to pull EGaln into the open channels of a mold. First, a thin layer of EGaln, approximately 1–2 mm thick, is spread over the features of the mold (Fig. 6b). The mold is then placed in a vacuum, during which the air from the channels is drawn out (Fig. 6c).

Under moderate vacuum, trace amounts of  $O_2$  in the dessicator causes the surface of the EGaln to oxidize and leave holes where air has escaped. In order to remove the holes, the



**Fig. 6** A PDMS mold (a) is covered in a thin layer of EGaln (b). The system is then placed in a vacuum, and the air creates holes in the EGaln layer as it escapes (c). The system is perturbed (d) to reform the EGaln layer, and the vacuum is released to fill the channels of the PDMS mold (e). Excess EGaln is scraped off the top of the mold (f) and the mold can be then be placed in a freezer (g). Copper wires can be inserted into the channels before freezing if desired. Once the EGaln is solidified, it can be removed from the mold (h).

sample must be gently perturbed while still in the evacuated dessicator (Fig. 6d). The vacuum is then released, and the resulting pressure difference between the channels and environment forces the liquid EGaln into the channels (Fig. 6e). If any air is still trapped in the channels, the processes of vacuuming and perturbing can be repeated. The excess EGaln is then scraped off (Fig. 6e,f) and the mold is placed in a freezer (Fig. 6g). External copper wiring may be inserted into the circuit terminals prior to freezing.

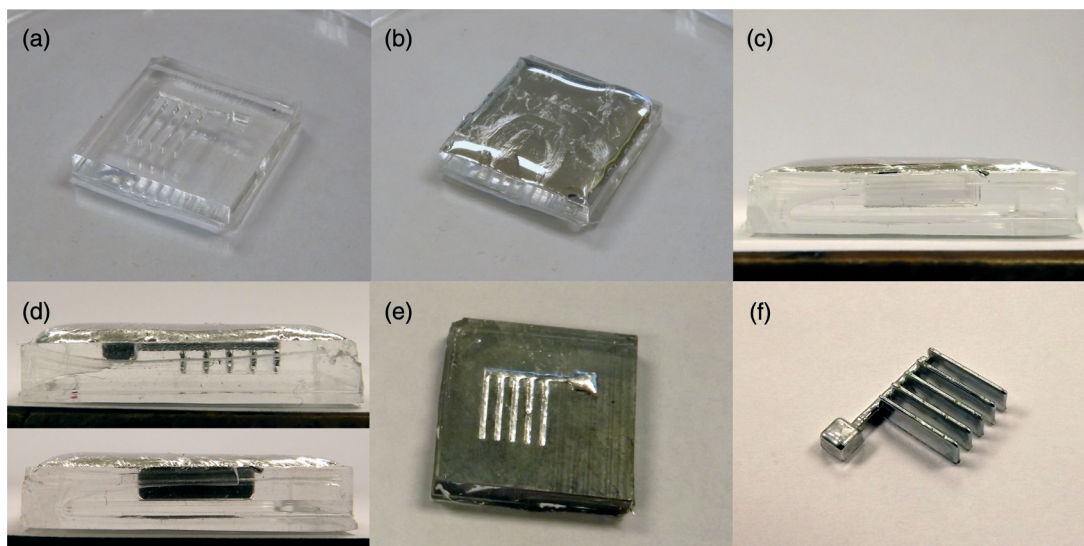
This method resembles a technique developed by Cumby *et al.*<sup>30</sup> in which Laplace and vacuum pressure is used to fill microchannels of reconfigurable electronics. In their technique, liquid metal is located in a gap between two air-tight polymer films, one of which is patterned with channels. When a vacuum is applied between the films, the pressure generated collapses the gap and forces the liquid into the channels. The vacuum casting technique that we use does not require a top film and instead uses the GaIn to separate the channel from the environment, resulting in a pressure difference.

Vacuum perturbation casting enables the creation of deep features and is especially useful for producing components with abrupt changes in height, as demonstrated in Fig. 7, which shows the mold of a comb capacitor electrode being filled using vacuum casting. Unlike injection casting, this method also enables the creation of intersecting and branching features with multiple terminals.

## 4 Circuit fabrication

Frozen EGaln parts are encapsulated within an elastomer to create a soft matter circuit or device. It is important to work in a cold and preferably dry environment while handling frozen EGaln components in order to prevent the metal from melting. We used a cold plate (CP-200TT; TE Technology, Inc.) enclosed in a custom built open chamber with a dry air input (Fig. 8). A brass sheet is used to cover the top surface





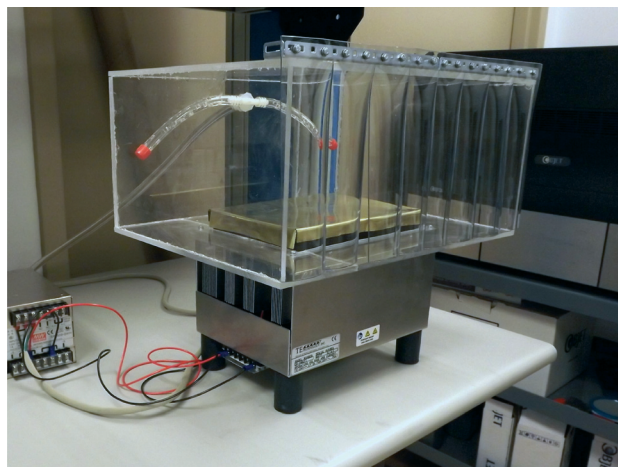
**Fig. 7** A PDMS mold (a) is covered in a thin layer of EGaln (b) (c). By using a vacuum, the EGaln is pushed into the channels of a PDMS mold (d). The excess EGaln is scraped off of the PDMS mold, leaving a grey residue on the mold, and the remaining liquid fills the channels (e). Once frozen, the EGaln can be removed from the PDMS mold (f).

of the cold plate (EGaIn is corrosive to aluminum). We cast the EGaIn in PDMS, which does not get stained by the alloy when it is frozen.

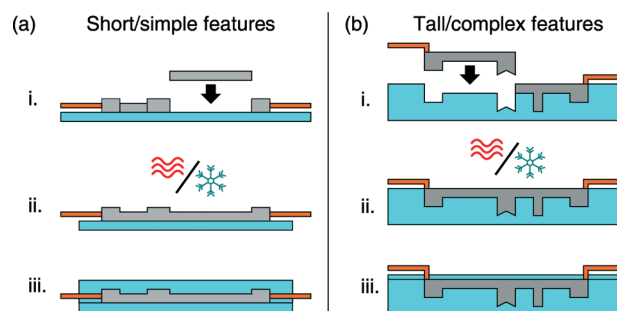
Depending on the desired depth and height-to-width ratio of the circuit, slightly different sealing techniques can be applied, as presented in Fig. 9. PDMS curing is temperature dependent, so a sample cannot be cured by placing it in the freezer. Because of this, samples are cured at room temperature (or greater), during which time the EGaIn returns to its liquid state. For simple circuit geometries composed of channel features with a height-to-width ratio ( $h/w$ ) of  $\lesssim 1$ , the GaIn's oxide skin will preserve the shape even as the alloy melts. However, for more complex circuits with taller features the metal will pool as it melts, distorting the shape of the channels.

For designs that occupy very little space in the vertical axis or require little control of channel height, frozen components can be arranged on a flat sheet of cured elastomer (Fig. 9a). Uncured elastomer can then simply be poured on top of the components, degassed, and cured. With this method, different components can be assembled together inside of the cold chamber (Fig. 8) by selectively heating joints with a soldering iron and then allowing the bonded joints to refreeze. This allows for simple circuit elements, such as straight wire segments or folded resistive sensors, to be bonded to form a complete circuit.

If large channel heights (with greater height-to-width ratios) or controlled changes in channel height are required, frozen components should be placed into a cast elastomer mold created from a master mold of the entire circuit (Fig. 9b). The cured elastomer mold maintains the vertical shape of the EGaIn while the sealing layer cures. Separate metal components can be bonded using this method as



**Fig. 8** To prevent the frozen EGaln from melting, we work on a cold plate enclosed within a custom built open chamber. Dry air is pumped into the chamber to prevent condensation.



**Fig. 9** The frozen EGaln is arranged on either a flat (a) or patterned (b) elastomer substrate depending on the desired depth of the features. The fabrication process is very similar with the exception of the substrate used: (i) First the solid metal is placed onto the substrate. (ii) It can then be selectively melted and refrozen to bond different segments of EGaln. (iii) An elastomer layer is then cured on top of the metal alloy to encapsulate the circuit.



mentioned above, but they must fit tightly within the mold. This method enables complex 3D structures like vertical sawtooth, pillar, or stair geometries.

## 5 Results

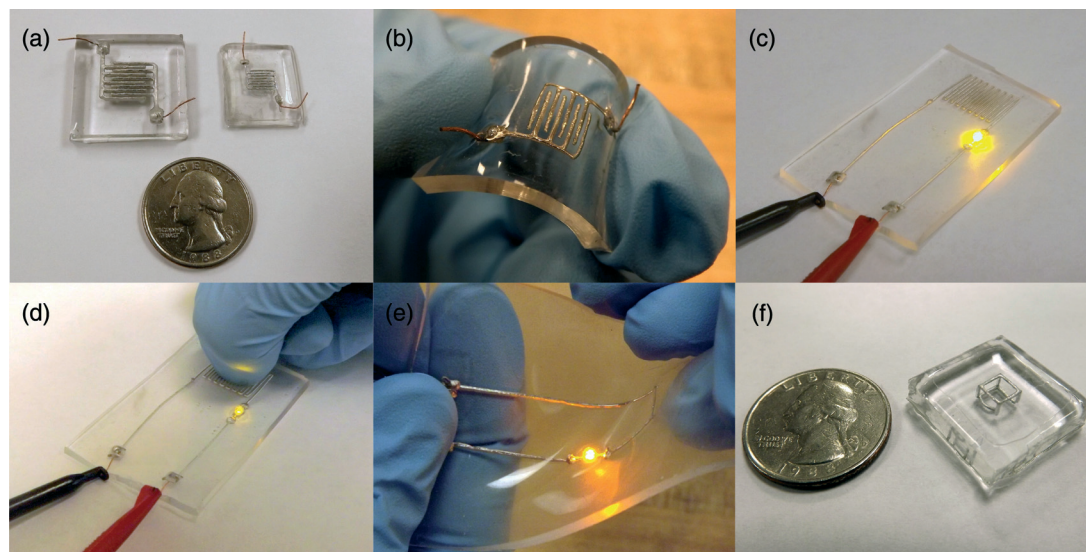
We have created a number of circuits to demonstrate the capabilities of these fabrication techniques. The capacitance of a comb type capacitor can be varied by changing the height of the fingers. Referring to Fig. 6 and 7, each electrode is produced with vacuum casting in a PDMS mold. Next, referring to Fig. 9b, the frozen electrodes are inserted into a molded PDMS template and sealed.

Two different sized comb capacitors have been fabricated from PDMS, as seen in Fig. 10a. The larger capacitor, with an element area of  $130 \text{ mm}^2$ , was found to have a capacitance of 7.3 pF (with a 1 mm finger height), 12.1 pF (1.5 mm), and 14.6 pF (2 mm) while the smaller capacitor, with an area of  $35 \text{ mm}^2$ , was found to have a capacitance of 2.3 pF (0.3 mm) and 4.4 pF (0.9 mm).

Using injection casting, we created a series of components that can be combined into an LED circuit with a resistive sensor (Fig. 10c). The pieces included are: a straight segment of length 2.5 cm and width  $500 \mu\text{m}$ , a straight segment of length 3 cm and width  $500 \mu\text{m}$ , two square terminal ends with sides of length 3 mm, an LED, and a resistive sensor with a channel width of  $400 \mu\text{m}$  and planar area of  $188.4 \text{ mm}^2$ . The LED can be dimmed by applying pressure to the sensing element as this increases its resistance and reduces the voltage across the LED (Fig. 10d). Fig. 5e and f display the resistive sensor and terminal ends incorporated in the LED device. A basic LED circuit without the sensor element has also been created, and can be seen being flexed in Fig. 10e.

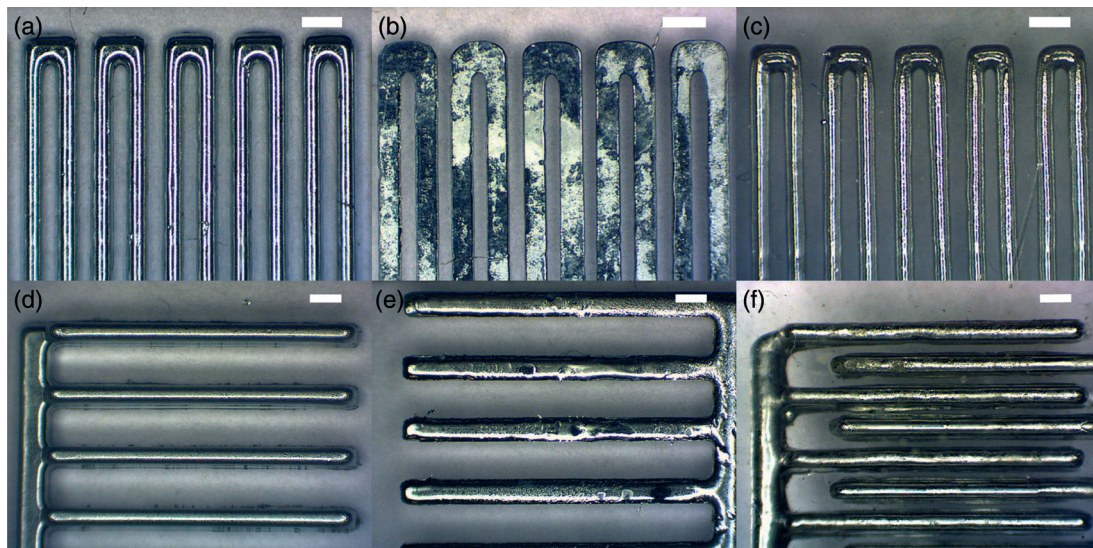
Additionally, we fabricated a cube shaped antenna inspired by Anacleto *et al.*<sup>31</sup> in order to further demonstrate the 3D capabilities of these freeze casting methods (Fig. 1b and 10f). The length of the antenna sides are 5 mm, each beam having a  $500 \mu\text{m} \times 500 \mu\text{m}$  cross section. It was fabricated using two frozen EGaIn components (created using vacuum perturbation) and a single patterned PDMS substrate with through-hole features. The first frozen metal segment, a square outline with vertical beams at each corner, is placed into the substrate so that the vertical beams protrude slightly through the bottom face of the substrate. An elastomer layer is then cured over the top face of the substrate. The second EGaIn component, composed of three sides of a square, is then bonded to the protruding portions of metal alloy on the bottom face, after which a final layer of elastomer is used to seal the channels.

An optical microscope was used to examine the fidelity of a frozen component made using each of the casting methods, as seen in Fig. 11. In both cases, the geometry was found to be accurately replicated. The resistive sensor, produced using injection casting, has rounded top features from the PDMS casting mold similar to that of the 3D printed master (Fig. 11a). The bottom side of the sensor is very flat (Fig. 11b), as this portion of EGaIn froze while in contact with a smooth glass substrate. When this component is encapsulated within PDMS (Fig. 11c) using a flat substrate, the features are safely preserved with only minor amounts of distortion located primarily at the turns of the channel. The vacuum casted component, a comb capacitor electrode of the larger size with 2 mm tall by  $500 \mu\text{m}$  wide fingers, also has rounded features where the surface was in contact with the PDMS mold (Fig. 11d). In contrast, the bottom is slightly rough, as this area was exposed to air during the freezing



**Fig. 10** (a) Two different sized soft matter comb capacitors have been created. The planar area of the capacitors are  $130 \text{ mm}^2$  and  $35 \text{ mm}^2$ . (b) PDMS is soft, allowing these devices to be repeatedly bent or stretched. (c) Frozen segments of EGaIn made using injection casting are bonded and encapsulated in PDMS to create a flexible LED circuit with a resistive sensor. (d) When pressure is applied to the sensing element, the voltage through the LED drops, diminishing the light produced. (e) LED circuits will maintain functionality while being bent and stretched. (f) A cube shaped antenna has been produced to demonstrate freeze casting's capabilities to produce 3D channel geometries.





**Fig. 11** EGaIn components examined using an optical microscope. (a) Top view of frozen resistive sensor (made using injection casting). The visible surface contacted the PDMS mold while freezing. (b) Bottom view of frozen resistive sensor. The visible surface contacted the glass substrate while freezing. (c) Top view of resistive sensor encapsulated in PDMS. (d) Top view of frozen comb electrode with 2 mm tall comb fingers (made using vacuum casting). The visible surface contacted PDMS mold while freezing. (e) Bottom view of frozen comb electrode with 2 mm tall comb fingers. The visible surface was exposed to the air while freezing. (f) Top view of a comb capacitor with 2 mm tall fingers encapsulated in PDMS. Frozen components are exposed to room temperature and humidity while viewing, so some condensation occurs and can be visible. Scale bar in each image is 1 mm.

process (Fig. 11e). Additionally, the channel widths are slightly larger at the very bottom of the electrode with an increase in line roughness, possibly from overflow within the mold while freeze casting. As with the injection casted sensor, the EGaIn maintains its structure when encapsulated within PDMS, although in this case, the frozen electrodes were inserted in a molded substrate (Fig. 11f).

## 6 Discussion

Freeze casting fabrication of EGaIn offers a number of advantages over current methods of fabrication of liquid embedded elastomer electronics. By encapsulating frozen EGaIn within an elastomer, the conductive liquid already occupies the space of the channels during sealing and can have any number of branching features since air does not need to escape from within the device. Additionally, freeze casting fabrication is able to easily create 3D geometries, especially when using vacuum perturbation casting and placing frozen EGaIn into a prefabricated elastomer molds. This includes channel geometries with large height-to-width ratios and abrupt changes in dimensions.

Freeze casting fabrication can create devices of different sizes, as demonstrated by the capacitors presented in Fig. 10a and b. Additionally, by adjusting the height of the finger channels, it is possible to tune the capacitance of a device of a given area. The smallest features created had a channel width of 200 microns, limited by the resolution of the 3D printer used to create the PDMS molds. Smaller features should be possible using freeze casting fabrication, but handling frozen components may become difficult. Handling

components may be avoided if a mask is used along with vacuum perturbation deposition, but a proper method for creating a seal between the mask and mold is required first. Aside from enabling multiple segments to be bonded, one of the reasons freezing is employed is to prevent grey residue from staining the surface of the elastomer device. A mask would shield the surface from this residue, but must have an airtight seal with the elastomer so that vacuum perturbation can be employed. Miniaturized 3D structures would enable the creation of micro capacitive strain sensors with more numerous and closely spaced electrodes and a larger capacitance.

By creating simple components and using them as building blocks for more complex devices, custom soft electronics can be made quickly and easily. For simple geometries with low-aspect-ratio features, frozen GaIn structures may be placed on a flat elastomer substrate and then sealed, as illustrated in Fig. 9a. This method is relatively fast and eliminates the need to replace the flat substrate with the molded negative shown in Fig. 9b. Nonetheless, a molded elastomer substrate is required for precise alignment or assembling geometries with tall or complex features.

Vacuum perturbation casting requires an excess of EGaIn, which can lead to wasted materials, but most of this EGaIn can be recycled. Molds, both for vacuum perturbation casting and injection casting, can be reused repeatedly.

Lastly, we can improve the fabrication method in order to reduce roughness and the slight increase in channel width observed at the bottom of vacuum casted parts. In the case of the vacuum casting method presented in Sec. 3.2, we could use a similar approach to injection casting



and place the casting mold against a rigid glass substrate. This would eliminate the need to scrape excess (Fig. 6f) GaIn from the filled mold but would also introduce the need for vents in either the mold or glass in order to allow air to escape.

## 7 Conclusion

We have developed a new technique for the production of GaIn based liquid phase electronics using freeze casting. The metal alloy, though liquid at room temperature, will solidify when brought below their freezing temperature. The geometry of the frozen components can be dictated by either injecting the conductive liquid into a mold or using pressure differences caused by a vacuum to push the liquid into a mold. Circuits can be easily constructed from multiple frozen components of GaIn because segments can easily be bonded using selective heating. For designs that require precise control of channel height, the frozen metal can be placed into a patterned elastomer mold. Otherwise, a simple flat elastomer substrate can be used.

In this study, we focus on using only EGaIn as our conductive liquid and PDMS as our elastomer. However, this fabrication technique is applicable to other soft elastomers and liquid-phase GaIn alloys (like Galinstan). In particular, ultraviolet (UV) curable elastomers should be explored as this may simplify the creation of 3D geometries. UV curable elastomers typically cure very fast, some within a few seconds, which would enable encapsulating complex 3D shapes without the need to insert frozen pieces in a molded substrate. UV light can also be exposed to the resin while the material is being chilled, allowing the stiffening process to occur at a temperature at which EGaIn is still frozen. A cast PDMS mold is currently required to maintain the shape of the EGaIn, as the metal will melt if PDMS cures at room temperature (or above). It may be possible to find an elastomer that will still cure while at low temperatures, or even find a temperature slightly below the melting point of EGaIn (MP = 15 °C) at which PDMS will still cure. This would require precise temperature control to achieve.

Further miniaturization can be achieved by using higher resolution rapid prototyping tools, ideally creating features on the scale of 10 microns. Handling of such components should be minimized, as their small features can easily be damaged and their high area to volume ratio will cause them to melt quickly. Sacrificial molds for casting the GaIn alloy may help prevent damage to the structures during removal. Using a mask with the deposition technique of vacuum casting would avoid any handling as the GaIn alloy can be deposited directly into a mold with no residue being left on the surface. Alternatively, an automated robotic system can be developed to pick up and place small frozen GaIn components. In the case of using a series of simple frozen building block segments, this would be ideal as the robotic system could construct custom soft microcircuits by selecting, orienting, and bonding pre-frozen GaIn elements.

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