TOWARDS SUB-MICROSCALE LIQUID METAL PATTERNS: CASCADE PHASE CHANGE MEDIATED PICK-N-PLACE TRANSFER OF LIQUID METALS PRINTED AND STRETCHED OVER A FLEXIBLE SUBSTRATE

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ABSTRACT

Recently, eutectic gallium indium (EGaIn) has been actively investigated towards stretchable and wearable electronic devices with the aid of high fluidity, high electrical conductivity and low toxicity. However, high surface tension along with spontaneous oxidation makes it difficult to realize fine patterning below ~10 µm, thus physical molding into an elastomeric mold is thought to be a unique solution. Here, we present a novel manufacturing technique that enables EGaIn patterns of single-digit micrometer width without using a guide mold for the first time. First, a custom direct printing setup is constructed with a laser displacement sensor, a 3-axis motorized stage, and electronic pressure regulators to enable continuous and uniform printing of EGaIn by feedback control of the distance between the dispensing needle and the substrate. With the custom direct printing setup, a 120-µm wide linear pattern is printed on an Ecoflex, platinum catalyzed silicone elastomer. To enable a single-digit micrometer pattern, the initial printed line is stretched, frozen with deionized (DI) water, and then transferred to an unstretched Ecoflex substrate. Upon gentle heating after the pick-and-place of the EGaIn line frozen with DI water, only the stretched EGaIn line is left on the new Ecoflex substrate. Aforementioned pick-and-place transfer of the stretched EGaIn frozen with DI water is cascaded multiple times until a target width is obtained. With the proposed idea, a 2-µm wide linear pattern, 60-fold reduction with respect to the initial dimension, is acquired. For practical applications, strain and tactile sensors are demonstrated with width-reduced EGaIn patterns.

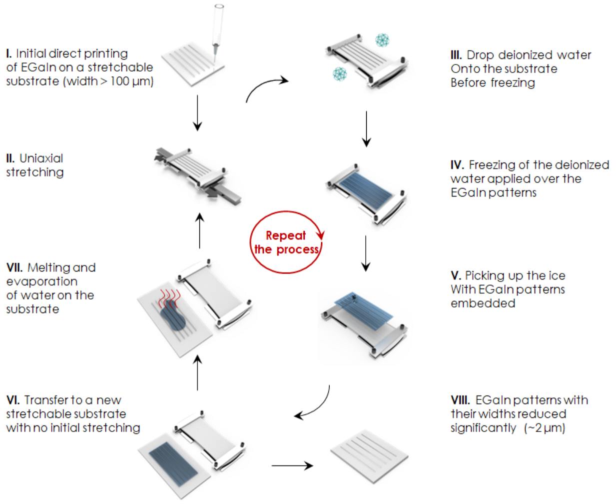

Figure 1: Fabrication process of the phase change mediated transfer of liquid metal (Eutectic gallium indium; EGaIn) patterned on a stretchable substrate.

INTRODUCTION

With the advent of wearable electronics, structurally compliant devices that are flexible, foldable, or even stretchable are actively under development in academia and industries. Liquid metals are promising candidates that can offer exceptional stretchability while maintaining electrical functionality once they are continuously printed onto or embedded in stretchable materials. In fact, liquid metals are known to be the best when both stretchability and conductivity are considered. Since the stretchability of liquid metals easily surpasses that of most flexible materials including Ecoflex and Dragon skin is practically infinite, liquid metals are best suited for applications yet explored in hyperelastic regimes. Recently, gallium based alloys such as eutectic gallium indium (EGaIn) have been of great interest due to their low toxicity and reactivity compared to mercury. Various methods including stencil lithography [1], direct writing [2], direct laser patterning [3], imprint lithography [4, 5], microfluidic injection [6], and microcontact printing [7] have been reported to pattern EGaIn onto or within substrates. In common, patterning resolutions of most techniques are approximately several tens of micrometers in width partly due to the high surface tension of the EGaIn. To date, single-digit micrometer lateral resolutions, ~2 µm, were only demonstrated by the imprint lithography [4]. The imprint lithography, however, requires lithographically fabricated polydimethylsiloxane (PDMS) molds that significantly increase the overall processing time and practically limit further improvement in pattering resolution.

In this paper, we propose a new patterning method for EGaIn, cascade phase change mediated pick-n-place transfer (hereinafter referred to as "phase change mediated transfer"), which offers a single-digit micrometer lateral resolution without using lithographically prepared PDMS molds. As shown in Figure 1, linear EGaIn patterns directly printed on a stretchable substrate are stretched to decrease the width and subsequently frozen with DI water. After the ice brick impregnating the stretched EGaIn patterns is simply picked up and placed onto a new stretchable substrate without pre-strain, the setup is heated to remove the ice and leave the stretched EGaIn patterns. These sequential processes are repeated until a target width of EGaIn pattern is acquired.

EXPERIMENT

Direct EGaIn printing with feedback control of the needle-substrate distance

In direct EGaIn printing setups used previously [2], the vertical position of the dispensing needle was fixed so that the needle-substrate distance was subject to change if the substrate was inclined or uneven. This potentially varying needle-substrate distance tends to result in non-uniform EGaIn patterns that are irregular or even broken occasionally. Two other possible sources of non-uniform EGaIn patterns are pressure fluctuation caused by the syringe pump and wetting of the oxidized EGaIn around the dispensing needle. If EGaIn patterns are used as printed, non-uniformity may be a relatively minor problem. However, if EGaIn patterns printed are transferred to another substrate, especially multiple times as the phase change mediated transfer with stretching proposed, more defects may occur as the transfer time increases. This is due to the fact that the stretching the Ecoflex substrate (process shown in Figure 1-II) with irregularly patterned EGaIn induces defects in general. To address aforementioned issues, a custom direct EGaIn printing setup with the needle-substrate distance feedback and precision pressure regulators is designed and constructed and proper coating materials and methods for the dispensing needle are investigated to promote the dewetting of the oxidized EGaIn from the dispending needle.

Figure 2(a) shows the custom printing setup. The laser displacement sensor measures the needle-substrate distance, two electronic pressure regulators precisely control the pneumatic pressure for dispensing EGaIn, and a USB microscope monitors the overall printing process. The separation distance, variable due to the local surface roughness and tilting, measured by the laser sensor is feedback-controlled to a set point, typically ranging 50 to 100 µm that guarantees continuous uniform patterning of EGaIn. Ecoflex substrates made with a white dye mixed (weight percentage of 0.1 %) enhance the laser reflection for the distance sensing. For precise pressure control, two electronic pressure regulators are employed. The first regulator maintains the output to be 2 bar which becomes a constant regulated input to the second regulator. The second regulator, then, controls the final output pressure between 0.1 and 1 bar depending on the printing speed and the discharge rate of EGaIn. To validate the direct printing with feedback control, we demonstrate the EGaIn printing onto the 10-degree tilted Ecoflex substrate. As shown in Figure 2(b), with the feedback system, the dispensing needle follows the substrate slope smoothly without collision and prints continuous EGaIn lines.

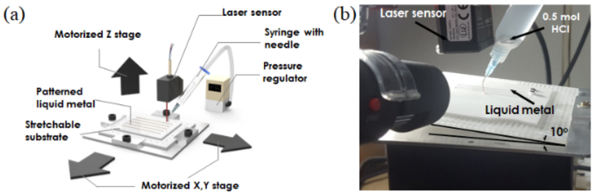

Figure 2: (a) Schematic of our improved setup for direct printing of EGaIn with the needle-substrate feedback control by using a laser displacement sensor and 3-axis motorized stage. (b) A picture showing the continuous and reliable EGaIn patterning on a 10-degree inclined substrate.

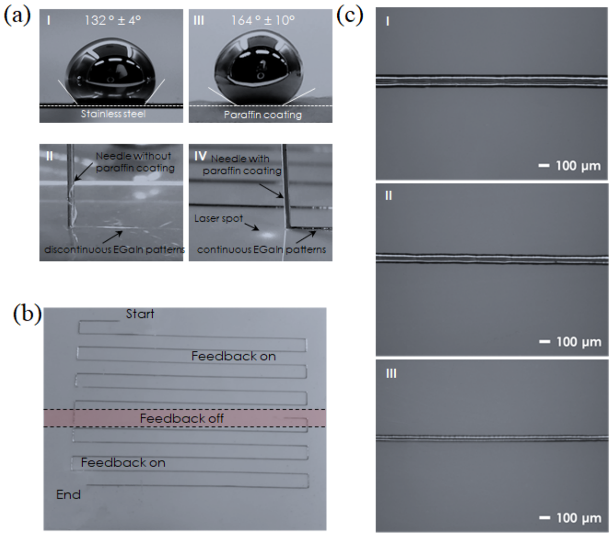

Figure 3: (a) Contact angles of EGaIn on bare (I) and paraffin-coated (II) stainless steel sheets and discontinuous (III) and continuous (IV) patterning results with bare and paraffin-coated needles, respectively. (b) Patterning result with feedback control and the paraffin-coated needle. (c) Patterning results obtained by dispensing needles with different inner diameters. Pattern widths are 120, 90, and 40 µm for (I), (II), and (III), respectively.

Besides the distance feedback and precision pressure control, the adhesion of oxidized EGaIn around a stainless steel dispensing needle should be mitigated to prevent accumulation of EGaIn that deteriorates the patterning uniformity. Therefore, it is necessary to find proper surface treatment for the stainless steel such as coating. Previous research shows that paraffin waxes, known to be waterproof and electrically insulating, enhance the dewetting of ethylene glycol as well as water. Since the enhanced by the paraffin coating may work for the EGaIn on the stainless steel, we test paraffin wax as a coating material. Figure 3(a) I and III show that contact angles of the EGaIn on the stainless steel sheet are measured to be 132 ± 4° and 164 ± 10° before and after the paraffin coating, respectively. This increased contact angle is attributed to the enhanced dewetting preventing the oxidized EGaIn from adhering to the stainless steel sheet. Figure 3(a) II and IV show discontinuous and continuous patterning results with bare and paraffin-coated dispensing needles, respectively.

After experimentally confirming the effectiveness of the paraffin coating on stainless steel sheets, the surface of stainless steel dispensing needles (25G, the inner diameter of 180 µm) is coated with the paraffin wax. When the distance feedback control, the precision pressure regulation, and the paraffin coating on the dispensing needle are combined all together, the best printing quality is expected. Figure 3(b) and 3(c) show the EGaIn patterning result and process with the paraffin-coated syringe needle configured in the custom printing setup with feedback distance control. Pattern widths are 120, 90, and 40 µm for Figure 3(b) and Figure 3(c) I, Figure 3(c) II, and Figure 3(c) III, respectively.

Phase change mediated transfer of stretched EGaIn

Figure 4 shows the sequential process of the phase change mediated transfer of the printed and stretched EGaIn on the Ecoflex substrate. The process starts with the uniform EGaIn printing on a stretchable Ecoflex substrate. After the EGaIn printing is done, the EGaIn pattern on the

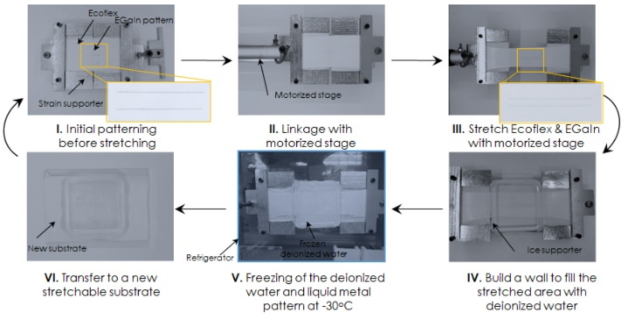

Figure 4: Sequential pictures taken during the phase change mediated transfer of EGaIn patterned on Ecoflex. After DI water poured onto the stretched EGaIn is frozen at –30℃*, the EGaIn embedded in the ice brick can be simply picked up and transferred onto a new unstretched Ecoflex substrate.*

Ecoflex substrate is moved to a strain supporter that is used to stretch the EGaIn along with the underlying Ecoflex (Figure 4-I). Then, the strain support is connected to a motorized linear stage (Figure 4-II). The motorized stage stretches the EGaIn pattern by stretching the Ecoflex uniaxially with constant speed of 1 mm/s (Figure 4-III). During the stretching process of the EGaIn pattern, the pattern length increases and the pattern width decreases because the EGaIn volume remains constant. After the EGaIn pattern is fully stretched to a target strain, the stretched Ecoflex region is enclosed by an ice supporter made with polymethyl methacrylate (PMMA) wherein DI water is filled (Figure 4-IV). Next, the whole experiment setup except the motorized stage is moved to a freezer at –30 ˚C to freeze the EGaIn pattern and DI water together (Figure 4-V). Once the EGaIn pattern and DI water is completely frozen, they can be simply picked up together and placed onto a new unstretched Ecoflex substrate (Figure 4-VI). Once the DI water melts and evaporates in an oven at 60 ˚C, the stretched EGaIn pattern is left on the new Ecoflex substrate. Figure 4-I~VI process is repeated multiple times until the target width is reached.

RESULTS

Sub 2-μm pattern with phase change mediated transfer

Figure 5(a) shows patterning results with the initial direct EGaIn printing and the phase change mediated transfer of stretched EGaIn patterns. It shows the change in the width of linear EGaIn patterns with the applied strain of 2.0 after the sequential transfer where n=1 represents an as-printed pattern and n increases by 1 after every transfer process. After 7 sequential transfers (n=8), the width of the EGaIn pattern becomes ~2 μm that is ~60-fold reduction from the 120-μm width of the as-printed EGaIn pattern. Figure 5(b) and 5(c) show the ratio of the EGaIn width before and after the transfer for different uniaxial strains. With strain values of 0.5, 1.0, 1.5 and 2.0, the averaged ratios become 80.43, 70.84, 63.68 and 56.67 % respectively. As the strain is increased, the error in the ratio is increased. Figure 5(d) displays the width of the EGaIn pattern as a function of the stretching number for strains of 0.5, 1.0, 1.5 and 2.0. The higher strain is, the less number of transfer cycles is required to achieve a desired pattern width as expected. For example, to reach the target width of ~2 μm, the strain of 0.5 requires 15 consecutive transfers while the strain of 2.0 requires 7 consecutive transfers, less than a half compared to the strain of 0.5.

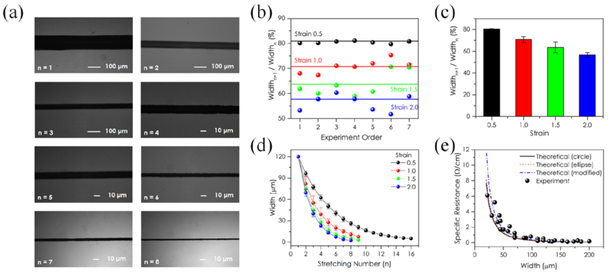

Figure 5: (a) Change in width of EGaIn lines with the applied strain of 2.0 after the sequential transfer (n=1 represents as-printed line and n increases by 1 after every transfer). (b) and (c) Ratio between the EGaIn widths after and before each transfer. (d) Width of the EGaIn line as a function of the stretching number, n. (e) Estimated and measured specific resistance (Ω/cm) as a function of the EGaIn line width.

Figure 5(e) represents a graph of experimentally measured and theoretically calculated values of specific resistance, resistance per unit length, (Ω/cm) as a function of the EGaIn width where the transfer is performed with the strain of 1.0. Measurement and calculation show similar trends in general. However, a slight difference between simply calculated (assuming that the cross-sectional area is a circle or an ellipse) and measured results exists. The reason for this difference is that the width of the EGaIn pattern is not uniformly reduced upon stretching due to the oxide film. Unlike simple assumptions, the EGaIn pattern observed by a scanning electron microscope (SEM) looks like a semicircle on the top of a rectangle. To calculate the more realistic cross-sectional area, the height of EGaIn pattern is repeatedly measured after the phase change mediated transfer with a laser sensor. The measured height of the EGaIn pattern is ~5% lower than the simply assumed height. From the cross-sectional SEM image and the measured height, we make a model with a modified cross-sectional area that estimates the resistance of the transferred EGaIn pattern better.

Application of phase change mediated transfer

For practical applications with printed and transferred EGaIn linear patterns, strain and tactile sensors are demonstrated. First, a strain sensor is fabricated and tested. Figure 6(a) shows the schematic of the fabricated strain sensor and its operation under various uniaxial strains. Our strategy to connect the EGaIn line and two electric wires relies on a flexible copper tape and soldering. To prevent the leakage of EGaIn, two connection junctions are made by using the copper tape where two electric wires are directly soldered. As the transferred frozen EGaIn pattern melts, it directly sticks to the copper tape. With this method, the two-terminal strain sensor can be bent without leakage. However, the copper tape would fail if it is stretched. Therefore, the strain sensor is divided into two regions; one is called a junction region and the other is called a stretching region (B). Those two regions are composed of different base materials. The junction region (A) made with PDMS tightly holds the copper tape and maintains electric

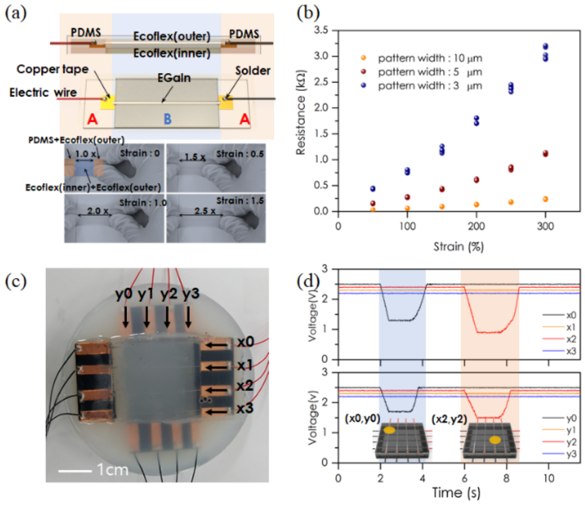

Figure 6: (a) Schematic and pictures of the strain sensor. (b) Resistance change as a function of the applied strain for 3, 5, and 10 μm wide EGaIn strain sensors. (c) Picture of the tactile sensor. (d) Voltage change induced by the applied pressure by a 400-gram weight at two intersecting points.

connection with the soldered wires while the stretching region (B) made with Ecoflex is free to deform. Once these two regions are prepared, each sensor is covered with Ecoflex for protection and reliable operation. When an external force stretches the strain sensor, only the stretching region (B) is elongated with the help of elastic modulus of Ecoflex that is orders of magnitude lower than that of PDMS. Figure 6(b) shows test results of three strain sensors fabricated by phase change mediated transferred 10, 5, and 3 μm wide EGaIn lines. Electrical resistance of each sensor is measured as a function of the applied strain. As the applied strain increases, the resistance monotonically increases for all three strain sensors. As expected, the higher resistance is observed for the narrower EGaIn line.

Next, a tactile sensor is fabricated by orthogonally transferring 4 horizontal and 4 vertical lines that define 16 intersecting points as a 4 by 4 array configuration as shown in Figure 6 (c). The tactile sensor fabricated consists of 80, 60, 40, and 20 μm wide EGaIn lines for (x0, x1), (x2, x3), (y0, y1), and (y2, y3), respectively. To test the tactile sensor, each EGaIn pattern is connected to a reference resistor in series to adjust the output signal to ~2.5 V. A 400-gram weight is placed over one of 16 intersecting points. Figure 6(d) shows the voltage change resulting from the normal pressure of ~20 kPa induced by the 400-gram weight placed on (x0, y0) at t=2 sec and on (x2, y2) at t=6 sec. When the normal pressure is applied, the EGaIn pattern's resistance inside the microchannel is increased, and the voltage from the reference resistor is dropped. Voltage drops at (x2, y2) are greater than those at (x0, y0) and voltage drops measured from horizontal patterns (x0 and x2) are greater than those from vertical patterns (y0 and y2). The observed voltage differences between (x0, y0) and (x2, y2) are attributed to different widths of EGaIn patterns. The signal increases as the EGaIn pattern becomes narrower. In addition, vertical EGaIn patterns are placed beneath horizontal EGaIn patterns, ~2.5 mm away from the tactile contact. This difference in the embedded position causes the observed signal difference. The signal increases at the embedded position becomes closer to the tactile contact.

CONCLUSION

In this paper, a custom EGaIn printing setup is constructed to enable continuous and uniform printing of EGaIn by feedback control of the pressure and distance between the dispensing needle and the substrate. EGaIn lines printed on an unstretched Ecoflex substrate are stretched, frozen with DI water, and then transferred onto another unstretched Ecoflex substrate. Upon gentle heating, only the stretched EGaIn line remains on the new Ecoflex substrate. This phase change mediated transfer of stretched EGaIn lines can be cascaded to achieve EGaIn patterns of a single-digit micrometer. For practical applications, strain and tactile sensors are demonstrated with width-reduced EGaIn patterns. Once more sophisticated stretching and pick-n-place equipment along with *in-situ* process monitoring is prepared, the minimum EGaIn width can be further improved below the submicrometer regime.

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