High-Performance Liquid Alloy Patterning of Epidermal Strain Sensors for Local Fine Skin Movement Monitoring

Bei Wang,1,2,* Kang Wu,1,* Klas Hjort,2 Chuanfei Guo,3 and Zhigang Wu1,2

Abstract

Nowadays, stretchable/epidermal electronics based on liquid alloys has attracted more and more attention, and various processing techniques have subsequently been developed to demonstrate diverse applications never seen before. However, to fully exploit its potential advantages, epidermal electronics is still searching for a technique meeting all demands on resolution, pattern complexity, and operational flexibility. In this study, we propose a technique that allows for complex and high-density patterns on thin stretchable substrates by combining ultraviolet laser patterning of a modified water-soluble mask, atomized spray deposition of liquid alloys on a flexible temporary substrate, lift-off by water dissolving, and finally, component integration and encapsulation. With this new technique, it was possible to make epidermal precision strain sensors with liquid alloy patterns of high density, which were capable of monitoring fine local skin movements such as the detailed process of wrinkle formation as well as the overall motion of the body part. In addition, this process is highly efficient and well controllable, with high potential for possible industrial automation and massive production.

Keywords: laser patterning soluble mask, liquid alloy patterning, epidermal strain sensor, two-dimensional strain sensor, local strain sensor, skin movement

Introduction

Demonstrating excellent compliancy to complex surfaces and dynamic deformations, stretchable/epidermal electronics1 exhibits high potential in various exciting new applications, such as wearable intelligence,7 health care/fitness monitoring,3,4 medical diagnostics,5 and soft machines/robotics.6,7 As one of typical applications, highly stretchable and super compliant strain sensing based on various conductive materials, for example, metal nanocomposites,8 carbon nanotubes,9-11 and graphene12,13 combined with polymers, has been intensively studied to monitor the overall movement of the knee,8 finger,14-17 hand, or arm.18,19

In particular, inheriting unlimited stretchability and unsurpassed morphological compliance from liquids, liquid alloy-based elastomeric electronics has obtained increasing attention from the community with its simple processing and low demand on infrastructure facilities. In the past few years, various devices and applications have been demonstrated that show high reliability and great potential in various scenarios, for example, antennas,20-23 tunnel junctions,24 memristors,25 self-healing circuits,26 energy harvesting27 and storage devices,28 radiation sensors,29 gait monitoring sensors,30 multidimensional strain sensors,31 and epidermal sensors.32 However, when considering high-resolution application scenarios, such as local muscle deformation monitoring or precise feedback in athletes training relying on local muscle reflex, for example, in pistol shooting, there is still no such kind of sensors demonstrated in soft technology.

By introducing a highly conductive liquid into electronics, liquid alloy-based electronics shows unique features in fabrication processing compared to thin film-based soft electronics. In recent years, many processing techniques have been developed,33 such as direct injection,20-23,34 vacuum-assisted injection,35 frozen casting,36 transfer printing,37,38 masked deposition,37,39 including atomization spraying,40

1State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, Wuhan, P.R. China.
2Department of Engineering Sciences, Uppsala University, Uppsala, Sweden.
3Department of Material Science and Engineering, Southern University of Science and Technology, Shenzhen, P.R. China.
*Both these authors contributed equally to this work.
direct writing, including roller based writing, inkjet printing, and further selective connecting alloy droplets, microcontact printing, imprinting, laser ablation, and so on. Among them, masked deposition is one of the popular techniques since it has demonstrated a relatively high resolution and excellent capability to pattern complex circuits. More importantly, it is a parallel processing technology and can be adapted to high-volume automatic production for possible commercialization in the future.

Adopting a metal masking technique, our group was the first to demonstrate masked deposition. Utilizing the strong wettability of Ga-In alloys on the specific masked surface, the deposition was shown with a resolution of about 200 μm. Combining conventional photolithography masking on a temporary rigid substrate followed by liquid alloy circuit transfer, the resolution was significantly enhanced. However, this method is time-consuming and difficult to consistently guarantee the resolution due to the large deformation when transferring liquid alloy circuits from a hard carrier to a soft substrate. Most importantly, none of these previous techniques has ever demonstrated epidermal electronics that is able to monitor the wrinkle deformation.

Recently, we have demonstrated a versatile processing technique to fabricate liquid alloy-based electronics on various substrates by spraying an atomized liquid alloy onto a tape transferred adhesive mask. However, the resolution and complexity of the pattern were severely constrained by a manual/mechanical mask peeling-off process, which makes high-density and complex patterns difficult to accomplish. Water-soluble masks, such as, polyvinyl alcohol (PVA) films, have been widely applied in industry and research. In this work, introducing laser patterning of a modified water-soluble mask followed by lift-off by water dissolving, we demonstrate a high-resolution and high-density liquid alloy circuit patterning technique for epidermal electronics. Figure 1a–e illustrates the concept of the proposed process. A laser marker is used to engrave the mask in micron scale because it is highly efficient, easily operable, and environmentally friendly compared to the conventional photolithography using a chemical etching process for epidermal electronics. Subsequently, the mask is transferred onto semicured polydimethylsiloxane (PDMS) on a temporary polyethylene terephthalate (PET) support. After atomized spraying, the whole structure is immersed and rinsed in water to remove the unwanted alloy, and finally encapsulated with uncur PDMS (when necessary, interconnecting copper strips are introduced before encapsulation). The final device, for example, a two-dimensional strain sensor shown in Figure 1f, is obtained by peeling off the PET support. Furthermore, combining Eco-flex and S3-PDMS (a modified PDMS, which is stretchable, soft, and sticky), a local epidermal strain sensor (Figure 1g) was demonstrated. By encapsulating integration of rigid components, an advanced device can be made as well (Fig. 1h and Supplementary Fig. S1 in Supplementary Data).

Results and Discussion

Figure 2 displays various patterns encapsulated in PDMS. The smallest width of the liquid alloy line was 30 μm (Fig. 2a), which was similar to the size of the focused laser spot (about 20 μm), so a more precise laser should increase the resolution. The narrowest space between lines was about 40 μm, which was determined by the mechanical properties of the PVA mask. When a narrow PVA line was transferred, it was easily deformed during the transfer process. An increased toughness may enable narrower lines for further improvement. Melted PVA residues generated during the cutting process (Supplementary Fig. S2 and Supplementary Data) may reduce the pattern quality when the PVA mask was transferred onto the surface of semicured PDMS. Figure 2c and d demonstrate the possibility of fabricating patterns of isolated masking structures, which is necessary for complex circuits. The cross-section of different width lines is presented in Supplementary Figure S3 and Supplementary Data.

The lift-off process schematically shown in Figure 3a–d is the most critical part of this patterning technique, while Figure 3e shows an inverse mesa-shaped trapezoidal cross-section of a laser-cut PVA mask that was transferred onto the semicured PDMS. In Figure 3f, we show a micrograph of
an atomized sprayed liquid alloy on the PVA-masked semicured PDMS, where the separation line between the masked and unmasked regions can be easily found. The trapezoidal cross-section, shown as dashed lines in Figure 3b, is beneficial in separating the liquid alloy on the PVA mask from that on the PDMS substrate. Assuming that the cross-section is a rectangle or reversed trapezoid, the liquid alloy would attach onto the sidewall. This would cause the liquid alloy on the substrate and that on the PVA mask to be connected and consequently damage the pattern. An uneven spraying may cause the alloy, in certain areas thick enough, to bridge/connect with the alloy on the mask, and further produce residues attached to the alloy line after dissolution. Furthermore, within the given spray angle, it was necessary to control the thickness of the sprayed alloy, for example, to less than half of the mask thickness. Apart from the geometrical effects of the mask, the roughness of the alloy line was affected by some practical operational parameters. In our situation, the width of the deposited alloy pattern shifts with the variations in spraying angle, pressure, scanning speed, and scanning time.

As discussed above, it is important to obtain an inverse mesa-shaped trapezoidal cross-section of the PVA mask. However, a mesa-shaped trapezoidal cross-section is usually obtained with laser ablation, resulting from a Gaussian distribution of the laser spot. To obtain an inverse mesa-shaped trapezoidal cross-section, we have introduced a tape transferring technology. This was enabled by making a tape made of thin semicured PDMS as adhesive on a PET film, which not only works as a substrate but also acts as an adhesive to peel off the pattern from the silicon wafer. The semicured PDMS is sticky enough to peel off the patterned PVA film, while the PET is stiff enough to support the PDMS. This strategy greatly simplifies the transfer processing and assures high-quality masking. Assuming a common acrylic tape transfer process, a three-time transferring is needed to obtain the inverse mesa shape, which easily deformed the mask and resulted in low-quality masking.

Differing from the most transparent polymers, such as polycarbonate (PC), poly(methyl methacrylate) (PMMA), and PET, which are highly transparent to visible light, but opaque to ultraviolet (UV) light, a native PVA film is transparent to UV as well. Hence, we introduced dying of the PVA to enable the

FIG. 2. Resolution and patterning capability. (a) Thirty micrometers alloy line width with different space from 40, 50, 70, 90, to 110 μm, and a zoomed micrograph. (b) the line width varies from 40, 60, 80, 100, 120, to 140 μm with the same space of 60 μm, (c) 65 μm alloy line width with 1.5 x 1.5 mm square space, and (d) 65 μm alloy circle width with different diameters from 1 to 8 mm. Color images are available online.

FIG. 3. Schematic illustration of the lift-off technique. (a) The cross-section is produced by a UV laser marker, (b) the trapezoid is formed after transfer, (c) the trapezoid effectively separates the liquid alloy on PDMS and PVA, (d) after dissolving, only the liquid alloy was attached on the surface of PDMS, (e) the micrograph of the cross-section after transfer onto the surface of PDMS, and (f) the micrograph of a trench after being sprayed. UV, ultraviolet. Color images are available online.
laser ablation and assure the quality of the cutting, especially at the edge of the line. Acetylene carbon black and blue ink were tested as dyes and both could greatly improve the cutting effect. The blue ink was eventually selected since the semicured PDMS could be contaminated by carbon black particles in the dissolving process (Supplementary Fig. S4 in Supplementary Data). The cutting substrate also affects the patterning. Glass, acrylics, and silicon (wafer) were tested as cutting substrates, and the silicon (wafer) was selected due to its best performance. In addition, PVA films do not swell PDMS as organic solvents do, which often deform PDMS substrate and relevant masks and further affect the pattern resolution. More importantly, it will bring a potential health risk to the skin for the epidermal sensors if the solvent is not completely evaporated.

Every step described in Figure 1, including preparing the PVA film, mask cutting, transferring, liquid alloy atomized spraying, residual removing, and encapsulating, can be done by modifying currently available automatic equipment and enables high fabrication efficiency. Of course, further automation and optimization of this processing technique would offer higher quality and repeatability in fabricating high-performance epidermal electronics. When having a modified PVA film, the whole process is fast and can be finished in <90 min from design to the final packaged component. In addition, this processing technology is environmentally friendly, with low-cost consumption materials and recycling of water.

To demonstrate the advantages of our new fabrication technology, two epidermal strain sensors are shown in Figure 1f and g; the meandering alloy lines of the sensors have a width of ~65 μm and a spacing of ~185 μm. Before testing, a cycling test for a single-line strain sensor was performed with a dynamic tensile system with strain from 0% to 50%. It could survive over 10,000 cycles without any electrical performance degradation (Supplementary Fig. S5 in Supplementary Data). The characterization of the maximum strain that a strain sensor could handle is demonstrated in Supplementary Figure S6 in Supplementary Data. According to our observation, the failure of the sensor often happens to the connection between the liquid alloy and rigid copper connectors instead of liquid alloy circuit itself. Due to high migration ability in metal lattice, gallium-based alloy tends to amalgamate other metals like copper and finally destroy the metal in the long term.54 The former concern can be solved by optimizing the metal connect design and integration process,55 while the later one can be solved by introducing some protective intermediate layer56 if necessary. However, these works are neither in the center of the processing of liquid alloy itself nor bring a new possibility for stretchable electronics; we will not discuss them in details in this work.

A two-dimensional sensor consisting of two local strain sensors orthogonally aligned on the substrate is shown in Figure 4a and b along with the measured signals on an elbow.

![FIG. 4. Local strain sensors and corresponding measured resistance changes. (a) A two-dimensional strain sensor adhered to an elbow (inset), (b) and its resistance change with the bending of elbow. (c) An epidermal strain sensor with two parallel-aligned local strain sensors adhered to an index finger of a female volunteer, (d) and its resistance change with the bending of fingertip. Color images are available online.](image-url)
by interfacing contacts57–59 (more details in Supplementary Figs. S5–S7 and Supplementary Data). We can observe that the strain along the X-axis was larger than along the Y-axis with elbow movement because the two-dimensional strain sensor adhered at the bottom of the elbow and its X-axis had a more acute angle with the moving direction of the elbow. Furthermore, by combining S3-PDMS and Ecoflex, a self-stuck epidermal strain sensor (~80 µm in thick) with two parallel-aligned local strain sensors was designed to monitor fine strain variations as well as overall strain in local areas <5 × 5 mm². The sensor conformably adhered to an index finger when the finger skin was in a natural relaxed state. One strain sensor (Sensor 1) was placed exactly above the joint and the other (Sensor 2) on the side toward the fingertip (Fig. 4c). Also, a fluctuation of resistance change was found for the two sensors (Fig. 4d). A strong adhesion of S3-PDMS and the low Young’s modulus of S3-PDMS and Ecoflex make it possible to accurately follow local fine skin movements synchronously. To assure the validity of our measurement, a movement from the same finger movement without sensors was recorded under the same situation. Comparing the one with our new epidermal sensor, no obvious movement distortion was observed during the whole movement (more details can be found in Supplementary Video S1 in Supplementary Data).

By observing the bending process and corresponding resistance changes of the sensors, a cycle of finger movement was extracted as that in Figure 5, to find the relationship between resistance change and finger skin movement. As mentioned previously, the sensor conformably adhered to the finger when the finger skin was in the natural relaxed state (State 0, Fig. 5a), where shallow wrinkles were formed on Sensor 1 area and the liquid alloy circuit was in a slightly wavy distribution, resistance change is in a low level. When the finger moved toward a horizontally straight state (State 1), where deep wrinkle trenches were gradually formed due to the compress of the skin and finally led to a highly narrow distribution of the liquid alloy inside the sensor, a strong peak of resistance change appears when changing from State 0 to 1 (Fig. 5c). When the finger was bent back to the nature relaxed state (State 2), where the wrinkles were flattened and the liquid alloy was recovered, the resistance of the sensor significantly decreased changing from State 1 to 2. Continuous bending of the joint to its maximal state (State 3), the skin was further stretched and the wrinkles disappeared, where liquid alloy was elongated to a narrower line. A clear resistance increase was observed when changing from State 2 to 3 and another peak resistance appeared at maximum bending. Sensor 2 also experienced a synchronous fluctuation of resistance change along the bending process (not described here in detail). In summary, according to our observations, the resistance would increase when skin was either wrinkled or elongated, while the later can be easily understood.

To discover the relationship between the resistance change and wrinkle formation, theoretical and experimental analysis of a single liquid alloy line device were conducted. The micrographs in insets (Fig. 5d), obtained from a sample with a single alloy line (Supplementary Fig. S8 and Supplementary Data), display that the microchannel filled with liquid alloy would become narrow when the sample was bent, which causes the reshape of liquid alloy in microchannel. Assuming a straight conductor at length L with a uniform rectangular cross-section with width W and height H, its electrical resistance R is proportional to \( R \propto \frac{\rho L W}{H} \), where \( \rho \) is the specific resistance of liquid alloy (Fig. 5b). According to our modeling (Supplementary Fig. S9 and Supplementary Data), any deformation from a uniform cross-section will increase its electrical resistance R. Specifically, when a wavy distribution forms, a higher curvature lead to a bigger resistance change as shown in Figure 5a–c and Supplementary Figure S10 in Supplementary Data, which is well matched with our experimental observation in Figure 5d. In addition, from a

**FIG. 5.** Interpretation of movement and resistance change. (a) Schematic illustration of length and shape change (borderline, put straight for ease of plotting) of the two strain sensors (Sensor 1 and 2) from state 0 to state 3. (b) Illustration of the resistance changing from the lateral view of microchannel for the minimum (R1), middle (R2), and the maximum (R3) of the bending state. (c) The resistance change in one cycle finger movement. (d) The resistance change of strain sensor with bending induced by a single bending, and the zoomed lateral view of micrographs of the liquid alloy deformation in the microchannel. Color images are available online.
physical perspective, the place state 0 and 2 should be same, the difference of resistance maybe caused by hysteresis of this sensor. A more detailed test in one cycle was conducted (Supplementary Fig. S11 and Supplementary Data), which exhibits very minor hysteresis when the sensor was stretched and released. Finally, three sensors working at the same time on different fingers were recorded and synchronized for each sensor during the finger movement (Supplementary Video S2 and Supplementary Data).

To summarize, our new sensor can obtain not only the information on the overall finger movement but also the detailed information on skin wrinkle formation. Furthermore, this feature owns to native liquidity of liquid alloy where the stretching and folding of finger skin can be monitoring accurately by the resistance change, while other strain sensors based on solid conductive material can never reach.

**Experimental Section**

**PVA film preparation**

PVA 0588 (Shanghai Yingjia) pellets were dissolved in deionized water at 1:6.5 weight ratio, and then mixed with blue ink (Boss, was concentrated 1.5 times before using) at 3:1 weight ratio or with acetylene carbon black (Tianjin An Nuho Chemical) at 3% weight ratio. Afterward, the solution was spun on an acrylic substrate using a spin coater (WS-650-23NPP; Laurell) at 150 rpm to achieve ∼50 μm film thickness after resting at room temperature (25–30°C) for 6 h.

**Mask patterning**

The PVA film was peeled off and transferred onto a silicon wafer with drops of isopropyl alcohol as adhesive. The designed mask pattern was ablated on the PVA film using a UV laser marker (LSU5EI; HGtech) with a scanning speed of 70 mm/s at a repeating frequency of 80 kHz.

**Transfer tape preparation**

In parallel, 100 μm thickness of PDMS (Sylgard 184; Dow Corning) with a mixing ratio of 10:1 was prepared on a 100 μm thickness PET film using an applicator (100 μm; Leaoyqi), and semicured at 75°C for 10 min in an oven (UF55; Memmert), obtaining a flexible tape with semicured PDMS acting as adhesive. PVA mask transferring: by gently and evenly pressing the transfer tape onto the PVA mask, the mask was successfully transferred onto the semicured PDMS.

**Atomization deposition**

Gallium-based liquid alloy (68.5% Ga, 21.5% In, 10% Sn; Geratherm Medical AG) was atomized and sprayed on a mask by a manual airbrush (Meec tools; Jula) coupled to a pressure regulator (ML-5000XII; Musashi).

**Mask dissolving**

The whole structure was reversely immersed into warm water (30–40°C). Every minute, the surface of the mask was rinsed by water to accelerate the residue dissolution. This process was repeated until the alloy pattern was completely developed.

**Packaging**

After drying in room environment, another layer of uncured PDMS was casted on top of the patterned semicured PDMS, and flattened by an applicator. The whole structure can be peeled off directly after curing at 75°C in an oven for 15 min.

**Contact interfacing**

After the transferring procedure in Figure 1b, part of the mask was lifted up, and the semicured PDMS below was contacted to a copper foil, which would connect to the external device later. The mask was gently pressed to adhere to the semicured PDMS (Supplementary Fig. S4 in Supplementary Data) again. This interface part should be far away from the sensing part to not affect the precision of the sensor or reduce the stretchability. This interfacing technology can also be used to hybrid integrate rigid component in the liquid alloy circuits, as shown in Supplementary Figure S7 in Supplementary Data.

**Fabricating sensor by combining S3-PDMS and Ecoflex**

The fabrication process was slightly modified from the procedure in Figure 1. Here, only changes are introduced. First, a 100 μm thick layer of Ecoflex (00-30; Smooth-On, Inc.) was prepared on a toner transfer paper (Pulsar Professional FX) using an applicator and then semicured at room temperature. Second, after alloy spraying, the Ecoflex device was covered by a water-resistant tape before the dissolving process. Finally, after packaging with a thin layer of S3-PDMS, the sensor was detached from the transfer paper with a few drops of water.

**Electrical characterization**

The sensor adhered to the skin directly after peeling off the sensor from the toner transfer paper using water. The resistance change of the sensors was measured by a Data Acquisition/Switch Unit (34972A; Keysight Technologies). In addition, a dynamic tensile system (E1000; Instron) was used to test the reliability of a single straight line strain sensor with strain from 0% to 50% for over 10,000 cycles (Supplementary Fig. S3 in Supplementary Data), and more detailed stretching and releasing tests were also carried out (Supplementary Fig. S5 in Supplementary Data).

**Micrograph**

An optical microscope (BA310MET-T; Motic) with a CCD camera was used to observe the liquid alloy patterns and the cross-section of a patterned mask. An electron microscope (Helios Nano Lab G3 CX) was used to study the sprayed line with the mask.

**Conclusions**

By introducing a new water-soluble transfer mask together with UV laser ablation, this work exhibited a possibility of fabricating high-resolution and high-density complex isolated liquid alloy patterns for epidermal electronics in a highly efficient way. Together with a fabricating technique demonstration, two types of epidermal strain sensors were successfully fabricated to verify the capability of the processing technique, and to demonstrate possibilities of monitoring fine
skin movement as well as the overall motion of the body. The combination of a superelastic material and our new processing technique could bring new possibilities of monitoring local fine skin movements in, for instance, athletes training or muscle rehabilitation. Further automation and optimization of this processing technique could offer higher quality and repeatability in fabricating high-performance epidermal electronics. Most importantly, this process is highly efficient and well controllable, and has high potential for possible industrial automation of soft electronics, such as skin sensors, soft robotics, and medical devices, massively.

Acknowledgments

The authors acknowledge the National Key Research and Development Program of China (2017YFB1303103), the National Natural Science Foundation of China (No. U1613204), and the Guangdong Innovative and Entrepreneurial Research Team Program (2016ZT06G587). Z. W. and C. G. thank the support from Chinese central government through its Thousand Youth Talents program.

Author Disclosure Statement

No competing financial interests exist.

Supplementary Material

Supplementary Data
Supplementary Figure S1
Supplementary Figure S2
Supplementary Figure S3
Supplementary Figure S4
Supplementary Figure S5
Supplementary Figure S6
Supplementary Figure S7
Supplementary Figure S8
Supplementary Figure S9
Supplementary Figure S10
Supplementary Figure S11
Supplementary Video S1
Supplementary Video S2

References


Address correspondence to:
Zhigang Wu
State Key Laboratory of Digital Manufacturing Equipment and Technology
School of Mechanical Science and Engineering
Huazhong University of Science and Technology
Wuhan 430074
P.R. China

E-mail: zhigang.wu@angstrom.uu.se; zgwu@hust.edu.cn