Volume 3 | Number 16 | 28 April 2015 | Pages 3819–4206

Journal of Materials Chemistry C

Materials for optical, magnetic and electronic devices

www.rsc.org/MaterialsC

ISSN 2050-7526

ROYAL SOCIETY OF CHEMISTRY

HIGHLIGHT

Carmel Majidi, Michael D. Dickey *et al.*
Methods to pattern liquid metals

Journal of
Materials Chemistry C

HIGHLIGHT

View Article Online
View Journal | View Issue

Published on 31 March 2015. Downloaded by Carnegie Mellon University on 06/06/2015 20:32:19.

CrossMark click for updates

Cite this: *J. Mater. Chem. C*, 2015, **3**, 3834

Methods to pattern liquid metals†

Ishan D. Joshipura,[a] Hudson R. Ayers,[a] Carmel Majidi*[b] and Michael D. Dickey*[a]

Received 2nd February 2015,
Accepted 13th March 2015

DOI: 10.1039/c5tc00330j

www.rsc.org/MaterialsC

This highlight describes emerging methods to pattern metals that are liquid at room temperature. The ability to pattern liquid metals is important for fabricating metallic components that are soft, stretchable, conformal, and in some cases, shape-reconfigurable. Applications include electrodes, antennas, micro-mirrors, plasmonic structures, sensors, switches, and interconnects. Gallium (Ga) and its liquid metal alloys are attractive alternatives to toxic mercury. This family of alloys spontaneously forms a surface oxide that dominates the rheological and wetting properties of the metal. These properties pose challenges using conventional fabrication methods, but present new opportunities for patterning innovations. For example, Ga-based liquid metals may be injected, imprinted, or 3D printed on either soft or hard substrates. The use of a liquid metal also enables rapid and facile room temperature processing. The patterning techniques organize into four categories: (i) patterning enabled by lithography, (ii) injection, (iii) subtractive techniques, and (iv) additive techniques. Although many of these approaches take advantage of the surface oxide that forms on Ga and its alloys, some of the approaches may also be suitable for patterning other soft-conductors (*e.g.*, conductive inks, pastes, elastomeric composites).

Why pattern liquid metals?

There are at least four reasons for patterning metals or other fluidic conductors that are liquid near room temperature.

First, they enable electrical and optical components that are stretchable, soft, and deformable as shown in Fig. 1.[1] Liquid metal components encapsulated in soft materials, such as elastomers, can bend and stretch in ways that are unattainable with conventional electronic materials. Liquid metals facilitate extreme "stretchability" (*e.g.* stretchable wires that maintain electrical conductivity up to ~1000% strain[2]) and unique coupling of mechanical deformation to electronic function. In principle, soft-matter electronics can integrate into clothing, medical implants, or wearable technologies without interfering with the natural mechanics of the human body.[3]

Second, liquid metals enable simple, unconventional patterning techniques. In some cases, a liquid may not be necessary for the end-application but may be used anyhow because it is easier to pattern than solid metals. For example, it is possible to inject liquids into microfluidic channels or direct-write liquids (Fig. 1) onto a wide range of substrates. Patterning with liquid metals also allows for inexpensive and fast fabrication of devices outside of a cleanroom and without the need for vacuum processing (*e.g.*, physical vapor deposition or sputtering).

[a] *Department of Chemical and Biomolecular Engineering, NC State University, USA. E-mail: mddickey@ncsu.edu*

[b] *Department of Mechanical Engineering, Carnegie Mellon University, USA. E-mail: cmajidi@andrew.cmu.edu*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5tc00330j

Ishan D. Joshipura

Ishan Joshipura received his BS in Chemical Engineering from the University of Arizona (2012). He is currently pursuing a PhD in Chemical Engineering at North Carolina State University, under the guidance of Professor Michael Dickey. Ishan's research interests include patterning and actuation of liquid metals for soft electronic components.

Hudson R. Ayers

Hudson Ayers is currently pursuing his BS in Electrical Engineering from the University of Virginia. During Summer 2014, he was a MRSEC REU student in the lab of Professor Michael Dickey, where he conducted research in surface analysis and novel patterning methods of liquid metals.

This journal is © The Royal Society of Chemistry 2015

Published on 31 March 2015. Downloaded by Carnegie Mellon University on 06/06/2015 20:32:19.

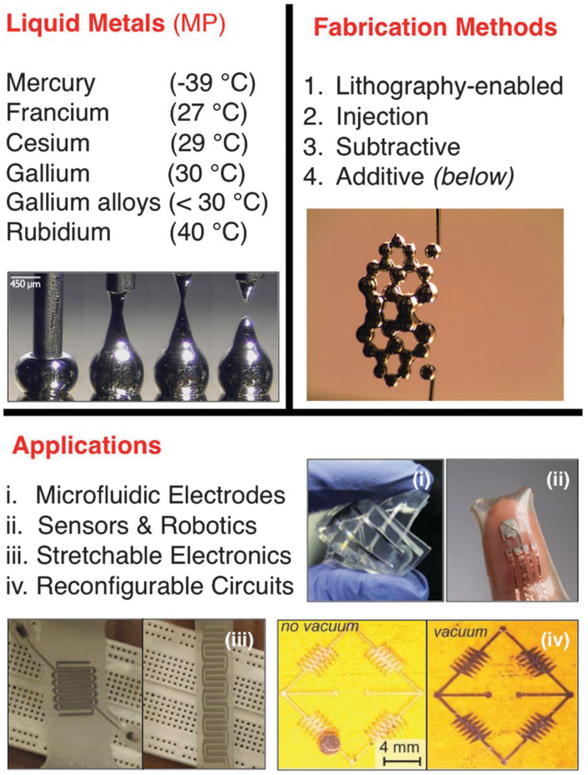

Fig. 1 Gallium and its alloys form a surface oxide, which allows them to be micro-moldable.[14] The oxide enables several patterning techniques, including direct-write (as shown above) and potential applications.[16–19] Figure from Liquid Metals adapted from ref. 14. Copyright Wiley 2011. Figure from applications (i) adapted from ref. 16. Copyright Wiley 2011. Figure from applications (iv) reprinted with permission from ref. 19. Copyright Applied Physics Letters, AIP Publishing LLC.

Third, it is possible to pattern liquid metals using room temperature processes at ambient pressures that are compatible with a variety of substrates including polymers, gels, elastomers, self-assembled monolayers, and biological materials. The deposition of solid metals often requires melting (*e.g.*, sintering, soldering) or evaporating (*e.g.*, physical vapor deposition) metals above room temperature or in vacuum in a way that is destructive or incompatible with thermally sensitive or volatile substrates. It is possible to deposit metals at room temperature using electrodeposition, but this requires electrolytes, electrical potential, and a conductive substrate.

Fourth, the ability of liquid metals to flow on demand allows for conductive elements with dynamic behavior or response; as such, these devices can be designed to be "reconfigurable".

How to pick a liquid metal?

Mercury (Hg) is the most commonly known liquid metal (M.P. −38.8 °C) and has been proposed for stretchable electrical wiring since the 1940s.[4] Hg is electrically conductive (σ = 1.04×10^6 m^{-1} Ohm^{-1}, ∼1/50th that of Cu) and has been utilized for electrochemical measurements (*e.g.* hanging drop electrodes for polarography), thermostat switches, fluorescent bulbs, thermometers, and MEMS devices.[5,6] However, Hg is toxic, which limits its application.

Gallium-based alloys, such as eutectic gallium indium ("EGaIn", 75% Ga, 25% In, by weight) and gallium indium tin ("Galinstan", 68% Ga, 22% In, 10% Sn, by weight), are promising alternatives to Hg. Both EGaIn (M.P. 15.5 °C[7]) and Galinstan (M.P. −19 °C[6]) are in the liquid state at room temperature, possess virtually no vapor pressure,[6] and are considered to have low toxicity.[8] Although both Hg and Ga-based alloys exhibit high surface tension (480 mN m^{-1}, 624 mN m^{-1}, and 534 mN m^{-1} for Hg,[7] EGaIn,[7] and Galinstan,[6] respectively), Ga-based alloys form a passivating oxide (∼1–3 nm) spontaneously in air.[7,9–13] This oxide "skin" allow these metals to be molded into non-spherical shapes,[14] as shown in Fig. 1 (left). The oxide also may lower the surface tension of the metal.[15]

The oxide skin behaves as an elastic material until the surface stress exceeds a critical point of 500–600 mN m^{-1}. Beyond this

Carmel Majidi

Carmel Majidi received his BS in Civil & Environmental Engineering from Cornell University (2001) and a PhD in Electrical Engineering & Computer Sciences from the University of California at Berkeley (2007). From 2007 to 2009 and 2009 to 2011, he was a postdoctoral fellow at Princeton and Harvard Universities, respectively. In August 2011, Carmel joined the Department of Mechanical Engineering at Carnegie Mellon University as an Assistant Professor. His research group, the Soft Machines Lab, examines the role of mechanics on the properties and behavior of soft and elastically deformable electronics and multifunctional materials.

Michael D. Dickey

Michael Dickey received a BS in Chemical Engineering from Georgia Institute of Technology (1999) and a PhD in Chemical Engineering from the University of Texas at Austin (2006) under the guidance of Professor Grant Willson. From 2006–2008, he was a post-doctoral fellow in the lab of Professor George Whitesides at Harvard University. In August 2008, he joined the Department of Chemical & Biomolecular Engineering at NC State University where he is currently an Associate Professor. Michael's research interests include patterning and actuating soft materials by studying and harnessing thin films, interfaces, and unconventional fabrication techniques.

Published on 31 March 2015. Downloaded by Carnegie Mellon University on 06/06/2015 20:32:19.

surface stress, the oxide skin breaks and the liquid flows readily (*e.g.*, within microfluidic channels).[7] Below the yield stress, the oxide holds the metal into non-spherical shapes. The mechanical properties of the oxide and its ability to adhere to many surfaces enable many of the patterning techniques described in this Highlight. Due to their low toxicity, liquid-state at room temperature, and relatively high conductivity (~1/16th that of Cu), Ga-based alloys are well-suited for a variety of applications that would not be possible using solid metals.[1] It is not the intent of this Highlight to review applications,[1,3] but rather describe the state-of-the-art patterning techniques that make them possible.

Finally, it should be noted that several other metals and their alloys exist with MPs near room temperature, such as shown in Fig. 1. However, these metals have disadvantages due to their radioactivity (Cs and Fr), short half-life (Fr), or violent reactive nature (Cs and Rb). Accordingly, these metals are not well suited for electronic applications. Therefore, this Highlight focuses on state-of-the-art patterning methods using gallium-based alloys. Hereafter, the use of "liquid metal" refers to Ga-based alloys, unless otherwise stated. However, Hg, and other fluidic conductors may be compatible with some of the fabrication techniques presented here. Similarly, molten metals (including low-melting point solders) may also be compatible for techniques and materials that can tolerate elevated temperatures.

Overview

Gallium-based alloys possess several properties that enable micron-scale patterning: (1) they are injectable into cavities and channels and onto surfaces, (2) they form a surface oxide that dramatically impacts the rheological and wetting properties of the metal, and (3) they freeze or melt at experimentally accessible temperatures.

These same properties also render these metals incompatible with many existing patterning techniques. For example, the semiconductor manufacturing industry has developed sophisticated 'conventional' micro- and nano-fabrication techniques for patterning thin films of solid-state materials (*e.g.* metals, polymers, and inorganics) on planar substrates.[20] In general, these techniques are poorly suited for patterning liquids due to their tendency to flow (both during and after processing) and inability to cast smooth, thin (<1 μm) films, as shown in the ESI† (Fig. S1). Due to their tendency to flow, liquid metals cannot easily be etched in a controlled manner. In contrast, injection-based and direct-write techniques offer a number of low cost patterning methods that are better suited for liquid metals than conventional approaches. In addition, Ga-based liquid metals may be patterned by some 'unconventional' fabrication techniques that exploit both its fluidic and moldable properties.

We organize the patterning techniques of liquid metal into four categories:‡

(i) Lithography-enabled processes: use of lithographic processes (*e.g.*, photolithography), either directly or indirectly (*e.g.*, to fabricate stencils or molds), to achieve desired patterns.

‡ Several of the techniques use principles from more than one category and thus, the categories are intended to only facilitate organization.

(ii) Injection: use of pneumatics or other forces to fill the metal into pre-defined features (*e.g.*, microchannels). Although the features are often produced with lithographic-techniques, injection represents a unique capability of liquid metals that it warrants its own category.

(iii) Subtractive: selective removal of the metal from a substrate.

(iv) Additive: formation of objects or structures by depositing the metal only in desired regions; this includes microcontact printing (μCP), direct-write 3D printing, and jetting.

Patterning techniques for liquid metals

Lithography-enabled patterning

Conventional methods. Photolithography, the most common of lithographic methods,[20] utilizes light to change the local solubility of polymer films (photoresist) coated on a substrate. Immersing the substrate into a developing solution dissolves away the soluble portions of the resist to expose the underlying substrate. Thereafter, etching processes can remove exposed metal from a metal film precoated on the substrate to create metallic patterns in a subtractive fashion. Schematics and illustrations of processes involving photolithography can be found in the literature.[20] Alternatively, physical vapor deposition or electrochemical plating can deposit metal into the openings in the photoresist. Photolithography has yet to be used to directly pattern liquid metals, but is often used to make topographical molds or stencils. Notably, liquid metal injected into microchannels can serve as a photomask to create reconfigurable patterns from a single mask with feature sizes as low as 10 μm.[21]

Imprinting. Imprinting liquid metal with elastomeric molds (*e.g.*, polydimethylsiloxane (PDMS)) is a simple patterning technique.[22] After spreading a thin film of liquid metal on a flat surface, an elastomeric mold with topographical features presses against the flat liquid metal film, which forces the liquid metal into the recesses of the mold. EGaIn, which is otherwise non-wetting on PDMS, is believed to adhere to the walls of the cavity with the aid of a Ga-oxide layer that forms at the interface between the metal and the PDMS.[7] As a result, the metal remains within the features even after removing the mold from the substrate.[22] Using this approach, it is possible to form liquid metal traces with two micron line width and submicron depth, as shown in Fig. 2.

Stencil lithography. Stencil lithography is a high throughput technique to pattern liquid metals.[23,24] In the simplest embodiment, a draw rod spreads liquid metal across a stiff stencil (*e.g.*, water-soluble poly(acrylic acid)[23] or Cu[24]) placed atop a desired substrate. The metal adheres to the substrate in exposed regions of the stencil. Depending on the stencil preparation, this method achieves features as small as 200 μm separated by 100 μm; however, the edges are often rough.[23,24] Illustrations and schematics of patterning using stencils may be found in the literature.[23,24]

Selective surface wetting. The surface composition and morphology of a substrate can influence the wetting behavior of alloys of gallium.[25–27] Spreading the metal across pre-patterned

 This journal is © The Royal Society of Chemistry 2015

Published on 31 March 2015. Downloaded by Carnegie Mellon University on 06/06/2015 20:32:19.

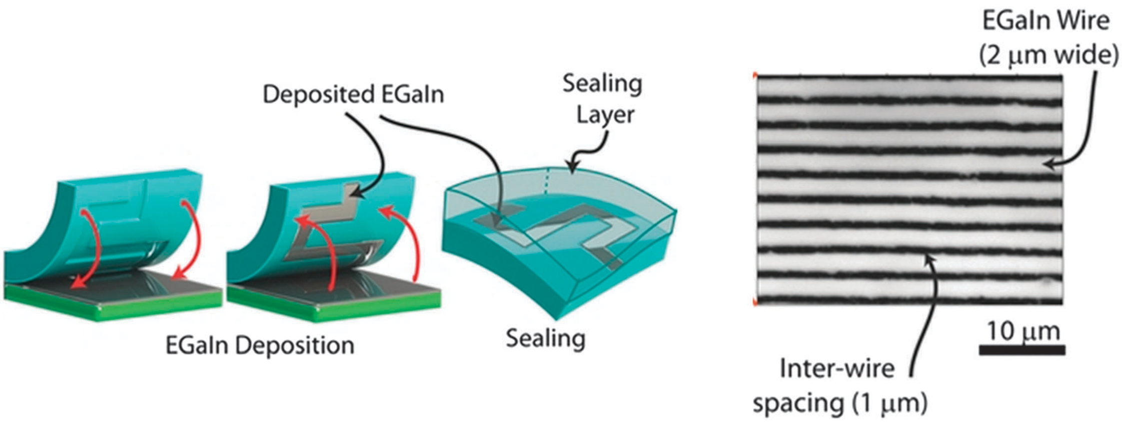

Fig. 2 Lithography-enabled techniques allow for high resolution patterning of liquid metals, such as imprint lithography.[22] Figures adapted from ref. 22. Copyright Wiley 2014.

wetting and non-wetting regions on a substrate offers another route to pattern the metal. The use of wetting substrates (*e.g.*, coatings of Sn[23] or Au[28]) and sacrificial release coatings on the stencil promotes the patterning process. A schematic illustration of selective surface wetting is shown in the ESI† (Fig. S2).

Injection

Microfluidic injection of conductors is a common approach to create soft matter electronics, due to its simplicity and ability to faithfully replicate features pre-defined by lithography or 3D printing.[3,7,18,19,28–40] These pre-defined features often have better resolution and smoother sidewalls than the other methods reported here, and result in structures in which the metal is automatically encapsulated.

A syringe injects the liquid metal into inlet holes of the microchannel. Once injected into channels, the Ga-oxide that forms adheres to the channel walls, resulting in stable microstructures.[7] Hydrochloric acid can remove the surface oxide from Ga and its alloys and thereby prevent it from adhering.[7,40–43] Alternatively, it is possible to create a slip layer between the oxide and the walls by pre-filling the channels with a carrier fluid;[44,45] such approaches allow for reversibly actuation of metal within microchannels.

As shown in Fig. 3, it is also possible to fill pores[46] or hollow fibers[2,47] with liquid metal, which can flow into the void space as long as the applied pressure exceeds the Laplace pressure.[7] To date, EGaIn has been injected into capillaries with diameters as small as 150 nm.[48] Evenly spaced posts or bars (so-called "Laplace barriers"[19]) in microchannels can be designed to block the metal and guide it to only desired areas.[29,49]

The encasing materials determine the mechanical properties of these structures, allowing for flexible and stretchable metallic components. Conversely, dissolving the encasing material (*e.g.*, PDMS) of a microfluidic channel filled with liquid metal in an appropriate solvent produces free-standing structures.[50] Injection-based patterning is well suited for other liquid conductors (*e.g.*, ionic liquids,[51] metal–salt mixtures,[52] and solders[53]). Although it is possible to inject Hg into microchannels, the metal will adopt a shape that minimizes surface energy.

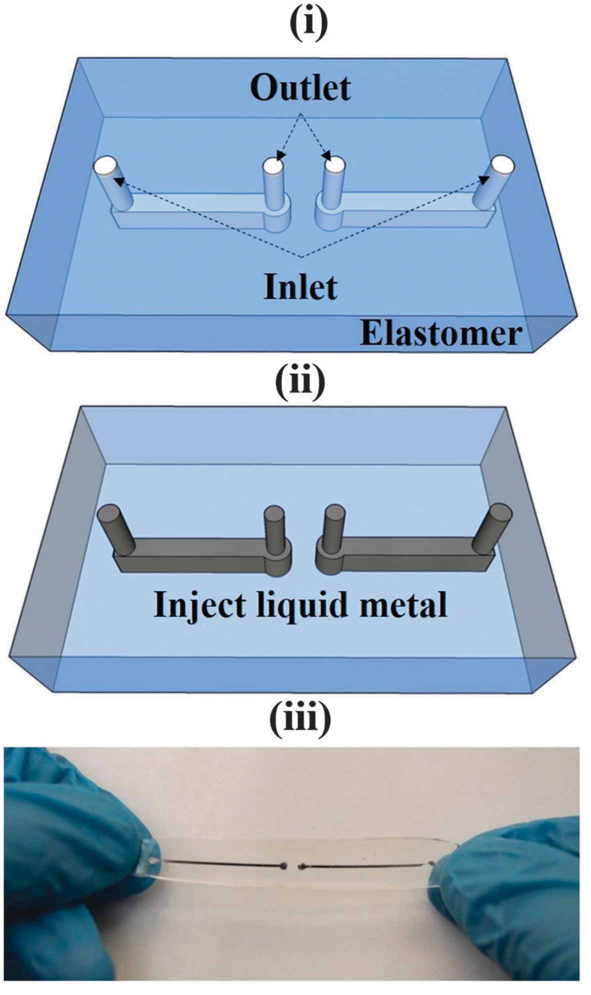

Fig. 3 Injection is a versatile technique for embedding two and three dimension metal structures in elastomers. (i) Photolithography or rapid prototyping creates an elastomeric topographical mold. An additional layer of elastomer seals the replica mold. Inlet and outlet holes are punched. (ii) A syringe (not pictured) injects liquid metal into the void space of the elastomer. (iii) A flexible and stretchable dipole antenna made by injecting EGaIn into PDMS.

Published on 31 March 2015. Downloaded by Carnegie Mellon University on 06/06/2015 20:32:19.

Vacuum filling. Vacuum filling is a process similar to the injection method, by which pre-fabricated microchannels define the shape of the metal pattern.[54] The liquid metal flows into pre-defined trenches by applying vacuum to create a pressure differential. The process does not require inlet and outlet holes, and works well for creating deep features or filling channels with step-changes in height. A schematic illustration for this technique is provided in the ESI† (Fig. S3).

Freezing the gallium alloy allows for removal and transfer of these patterns from the mold using simple tools such as tweezers, a process known as freeze casting. When performed in a temperature-controlled chamber filled with cold, dry air, the frozen gallium alloy can be assembled with rigid circuit elements and then sealed in elastomer.[54]

Subtractive

Direct laser patterning. Direct laser patterning is an inexpensive and facile approach to pattern liquid metals and other conductive materials with features as small as 100 μm.[55] The process, depicted in Fig. 4, begins with sealing or encasing a layer of liquid metal between PDMS sheets. Thereafter, a carbon dioxide (CO_2) laser (λ = 10.6 μm) traces over the surface to selectively remove the metal. The energy from the CO_2 layer evaporates the bottom layer of PDMS and displaces the metal away from undesired regions.

Recapillarity. Electrochemistry can locally reduce the oxide skin that forms on Ga and its alloys, and therefore induce these liquid metals to flow *via* capillary action.[56] This technique is termed 'recapillarity' due to the use of reductive potentials to induce capillary behavior. As shown in Fig. 4(iii) and (iv), it is possible to selectively remove liquid metal from complex microchannels by induced capillary action. Although there is no net metal lost in this process, the metal does flow out of channels to a reservoir to alter patterns in a subtractive manner.[15]

Additive

Rapid prototyping (RP), direct write (DW), and other additive manufacturing (AM) techniques are a class of techniques in which material is deposited in only desired locations. Examples include inkjet printing,[58] gravure or roll-to-roll (R2R) printing,[59,60] and direct write.[61] "3D printing" is the colloquial term for AM processes done in a layer by layer fashion to create three-dimensional objects.[62] Additive methods such as 3D printing enable high throughout patterning using automated processing and user customization by utilizing computer-aided design (CAD) models. Furthermore, these methods inherently reduce material waste and may form structures, which are often complex and may possess out-of-plane geometries.[50]

Microcontact printing (μCP). μCP is attractive for depositing inks and soft conductors in a potentially automated manner that requires limited manual labor.[63,64] μCP with gallium-based liquid metals relies on the adhesive nature of the gallium-oxide to elastomeric molds.[63] There are two primary methods to patterning liquid metals *via* elastomeric μCP: (i) manually transferring EGaIn using a topographical stamp, or (ii) depositing individual dots of EGaIn with a hemispherical PDMS tip (print head).

In the first method, a PDMS mold with protruding features of the desired geometry gently presses against a film of EGaIn. As a result, the metal oxide adheres only to the protruding features and does not invade into any cavities of the transfer mold. Thereafter, pressing the mold against the target substrate transfers the metal with mm resolution. This technique could also be considered lithography-enabled due to the use of a topographic mold.

In the latter method, a PDMS 'needle' with a hemispherical tip dips into a pool of liquid metal, which forms a bead of liquid metal on the print head.[63] The print head then contacts the substrate to transfer droplets of metal in a desired location; sequential printing of droplets coalesce to form a functional pattern. Mounting the print head and stage to a motorized 3-axis Cartesian system helps automate this process (see ESI,† Fig. S4).

Direct-write. The formation of the surface oxide enables a variety of modes of direct write printing for liquid metals. In general, direct write patterning relies on extruding liquid metal onto a substrate through the nozzle of a syringe. Extruding droplets, wires, and other structures directly from a nozzle onto a substrate using pressure produces patterns in an additive fashion. This technique produces 2D patterns[57] and 3D structures[50] that are stabilized by the oxide skin (Fig. 5).

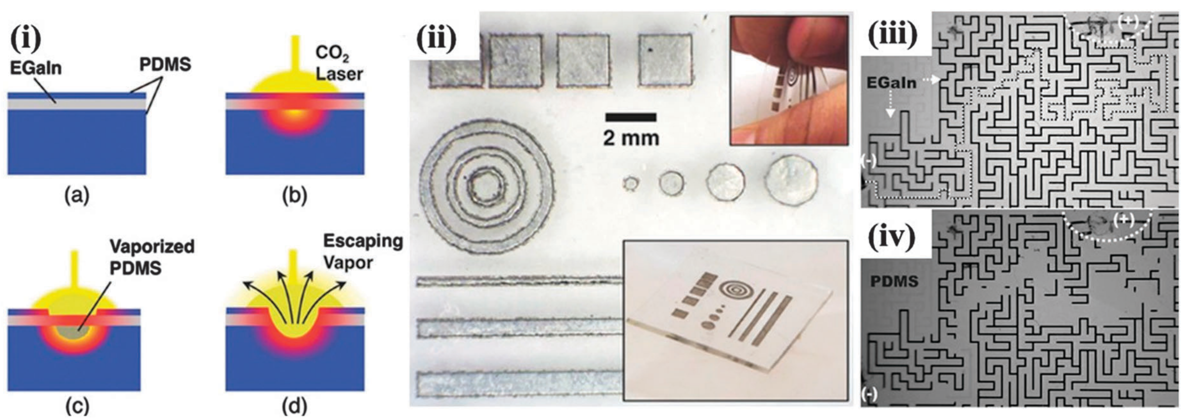

Fig. 4 Direct laser patterning (i and ii)[55] creates traces of liquid metals and other soft conductors in a rapid, subtractive, and inexpensive fashion. Meanwhile, 'recapillarity' (iii and iv)[56] selectively withdraws liquid metals from microfluidic channels by localized electrochemical reduction of the oxide layer. Figures adapted from ref. 55 and 56. Copyright Wiley 2015.

Published on 31 March 2015. Downloaded by Carnegie Mellon University on 06/06/2015 20:32:19.

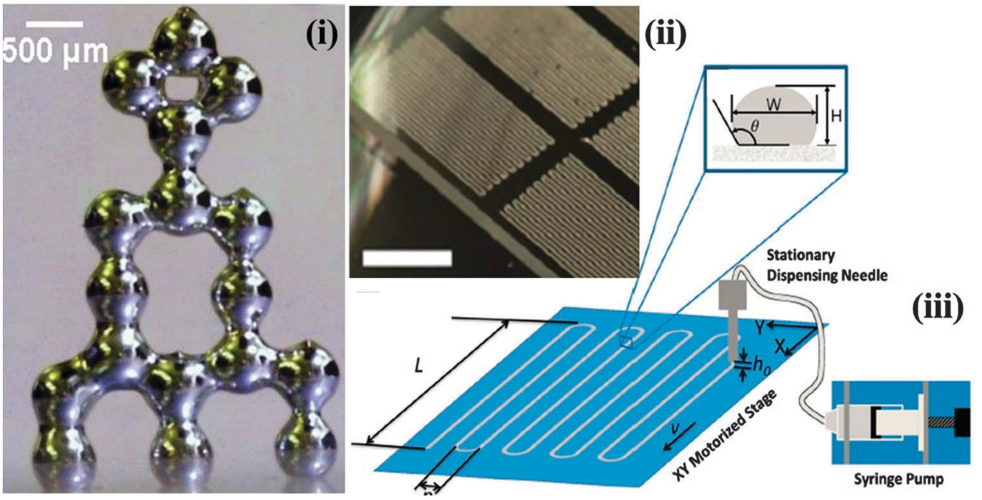

Fig. 5 Additive patterning techniques produce free standing 3D structures (i),[50] and conformal 2D (ii and iii).[57] Scale bar on (ii) is 5 mm. Figure (i) adapted from ref. 50. Copyright Wiley 2013. Figures (i) and (ii), adapted from ref. 57. Copyright Wiley 2014.

The nozzle inner diameter, distance between direct-write tip and substrate, and extrusion flow rate are important parameters effecting the geometry and diameter of wires and traces, both in 2D and 3D.[57] Stacking droplets of the metal while shifting a translational stage is one approach to form free-standing 3D structures of liquid metal. Lowering the stage or platform of the substrate while extruding liquid metal can form free-standing wires, with heights up to ~1 cm.[50] The 3D printing approach has the appeal of not requiring a mold and the ability to make out of plane structures.

Although electro-hydrodynamic jetting (e-jetting) is a common approach to directly print colloids, biological materials, and inks, this technique is not yet possible with liquid metals.[65,66] The surface oxide clogs the nozzle, even in oxygen near-free environments, and thus impedes the process.[63] However, using a nozzle comprised of a porous material (*e.g.*, paper or PDMS), which is impregnated with acid, allows for printing of liquid metal without clogging from the oxide.[67]

Current challenges and opportunities with Ga-based liquid metals

This Highlight describes state-of-the-art methods to pattern liquid metals into a wide variety of structures or patterns and focuses almost exclusively on the use of Ga and its alloys. However, there are challenges with patterning this class of liquid metals, which provide opportunities for further work.

Resolution. The methods described here have relatively poor resolution compared to conventional fabrication techniques. For example, the best resolution of the methods reported including imprint (~2 μm), injection (~10 μm), and direct-write (~100 μm) need to be improved. Challenges include the formation of the oxide layer, and overcoming the large surface tension of the metal,[15] which provides an energetic barrier for coercing the metal into smaller features. Gallium has been found inside the hollow core of carbon nanotubes,[68,69] which suggests that it may be possible to get liquid metal into finer features.

Sharp features. All of the metal patterning techniques reported to date have some finite level of curvature, presumably due to the surface tension of the metal. That is, it is difficult to pattern the metal into sharp features, including corners or sharp tips.

Precision. Precision of patterning features is important for large-scale manufacturing processes. The patterning resolution is characterized by two important metrics: (i) critical dimension (CD),[20] which is the size of the smallest feature, and (ii) line edge roughness (LER), which measures the spatial variation of the width of the CD.[70] Standard manufacturing practices require that the LER should be within two or three standard deviations from the CD.[20] Several of the methods (*e.g.*, imprinting, stencil lithography, and μCP) described exhibit poor LER. The roughness is likely due to the rheology of the oxide-coated liquid; that is, it flows along the path of least resistance and not necessarily uniformly. This issue of LER can be overcome by injecting into microchannels because the metal fills the void space. It would be useful to find ways to pattern the metal outside these confinements, yet with high resolution and low LER.

Smooth films. New methods for creating flat, thin, and uniform films of high quality are an area of opportunity. Many conventional patterning methods start with a smooth film. However, it is difficult to spread thin, uniform films of liquid-phase metal (ESI,† Fig. S5).[63] Thick films possess a smooth surface finish, but often exhibit a curvature due to the surface tension of the metal. Since spin coated films of liquid metal are not uniform, thin films must be spread manually, which are often rough or have holes. In general, handling gallium and its alloys can be messy because these metals adhere to most surfaces due to their oxide.

Adhesion. The techniques described here benefit from or are influenced by the adhesion of the oxide-coated metal to substrates it contacts.[71] The adhesion of these oxide-coated metals to a substrate depends on the roughness,[25,26] dryness,[44] and composition[72] of the substrate. Furthermore, the ability of the oxide to break and reform as it is injected, spread, or manipulated

Published on 31 March 2015. Downloaded by Carnegie Mellon University on 06/06/2015 20:32:19.

further complicates its adhesive behavior. The influence on this dynamic process on adhesion is only beginning to be understood.[26]

Contacts. Most devices require connecting the metal to other components. Gallium is known to alloy with many other metals (*e.g.*, Cu, Al, Fe, and Au).[6] This feature could be used strategically to make ohmic contacts, but can also lead to inadvertent destruction of the contact and handling challenges. In addition, the oxide is resistive, which could create an issue for sensitive external electrical contacts. Finding the best way to contact these liquid metals electrically is an open question, although initial work suggests graphene or other forms of conductive carbon may offer a solution to this challenge.[73]

Scalability. Most of the techniques developed to date rely on laboratory techniques. Although additive manufacturing approaches (*e.g.*, contact printing or direct-write) seem promising for large-scale production, liquid metal patterning may also be possible by adapting existing manufacturing techniques, such as roll-to-roll printing and slot-die coating. It remains to be proven how well these methods scale to high throughput processes. Likewise, recent work on deposition of liquid metal particles by atomization shows promise for large throughput printing but lacks the resolution offered by other methods.[74]

Improved materials. Gallium and its alloys are expensive. Given the small volumes needed in microsystems, the cost should not be prohibitive for systems that benefit from the properties of a fluid conductor. Nevertheless, new materials should be explored that lower cost, improve conductivity, or provide some additional benefit such as new rheological properties. Although this Highlight focuses on patterning with gallium-based alloys, many of these techniques can be used with other soft conductors (*i.e.*, liquid-phase metal–salt mixtures[52] and semiconductors,[52] inks[60] and elastomeric composites[31,75]) given their physical properties allow for printing or patterning.

Reconfigurability. Improving shape reconfigurability remains an active area of research. The use of liquid metals could enable shape reconfigurable metallic components. The oxide skin adheres to channel walls and forms a residue on the walls upon evacuation of the metal from the channel. This adhesion limits the ability to reconfigure the shape of the metal. Potential solutions include the use of acid,[21,42,43] non-wetting surfaces,[27,72,76] slip layers,[44,45] or electrochemistry[15,56] (to remove the oxide).

Outlook

This Highlight suggests there are a wide variety of methods to pattern Ga-based liquid metals from the micron to mm length scales. Many of these methods are simple and provide new approach for patterning that are not possible with conventional approaches. These patterning techniques are opening up new approaches for making stretchable electronics, metallic microfluidic components, and conductors for soft robotics and sensors. We hope this Highlight raises awareness of these techniques and inspires better patterning techniques that transcend current challenges and obstacles.

Acknowledgements

M.D.D. acknowledges support from the Air Force Research Lab and the NSF (CAREER CMMI-0954321, ERC EEC-1160483, CMMI-1362284, Research Triangle MRSEC on Programmable Soft Matter DMR-1121107) and the efforts of many colleagues who made this Highlight possible. The authors also thank Collin Ladd, Lazar Panich, and Dishit Parekh for assistance with the cover art.

References

1 M. D. Dickey, *ACS Appl. Mater. Interfaces*, 2014, **6**, 18369–18379.
2 S. Zhu, J.-H. So, R. Mays, S. Desai, W. R. Barnes, B. Pourdeyhimi and M. D. Dickey, *Adv. Funct. Mater.*, 2013, **23**, 2308–2314.
3 S. Cheng and Z. Wu, *Lab Chip*, 2012, **12**, 2782.
4 R. J. Whitney, *J. Physiol.*, 1953, **121**, 1–27.
5 G. Beni, S. Hackwood and J. L. Jackel, *Appl. Phys. Lett.*, 1982, **40**, 912–914.
6 T. Liu, P. Sen and C.-J. Kim, *J. Microelectromech. Syst.*, 2012, **21**, 443–450.
7 M. D. Dickey, R. C. Chiechi, R. J. Larsen, E. A. Weiss, D. A. Weitz and G. M. Whitesides, *Adv. Funct. Mater.*, 2008, **18**, 1097–1104.
8 J. E. Chandler, H. H. Messer and G. Ellender, *J. Dent. Res.*, 1994, **73**, 1554–1559.
9 L. Cademartiri, M. M. Thuo, C. A. Nijhuis, W. F. Reus, S. Tricard, J. R. Barber, R. N. S. Sodhi, P. Brodersen, C. Kim, R. C. Chiechi and G. M. Whitesides, *J. Phys. Chem. C*, 2012, **116**, 10848–10860.
10 M. J. Regan, H. Tostmann, P. S. Pershan, O. M. Magnussen, E. DiMasi, B. M. Ocko and M. Deutsch, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1997, **55**, 10786–10790.
11 F. Scharmann, G. Cherkashinin, V. Breternitz, C. Knedlik, G. Hartung, T. Weber and J. A. Schaefer, *Surf. Interface Anal.*, 2004, **36**, 981–985.
12 A. Plech, U. Klemradt, H. Metzger and J. Peisl, *J. Phys.: Condens. Matter*, 1998, **10**, 971.
13 J. M. Chabala, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **46**, 11346–11357.
14 R. C. Chiechi, E. A. Weiss, M. D. Dickey and G. M. Whitesides, *Angew. Chem., Int. Ed.*, 2008, **47**, 142–144.
15 M. R. Khan, C. B. Eaker, E. F. Bowden and M. D. Dickey, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 14047–14051.
16 H. Koo, J. So, M. D. Dickey and O. D. Velev, *Adv. Mater.*, 2011, **23**, 3559–3564.
17 P. Roberts, D. D. Damian, W. Shan, T. Lu and C. Majidi, in *2013 IEEE International Conference on Robotics and Automation (icra)*, IEEE, New York, 2013, pp. 3529–3534.
18 A. Fassler and C. Majidi, *Smart Mater. Struct.*, 2013, **22**, 055023.
19 B. L. Cumby, G. J. Hayes, M. D. Dickey, R. S. Justice, C. E. Tabor and J. C. Heikenfeld, *Appl. Phys. Lett.*, 2012, **101**, 174102.
20 M. J. Madou, *Fundamentals of microfabrication and nanotechnology*, CRC, Boca Raton, Fla., 3rd edn, 2012.
21 D. Kim, J. H. Yoo, W. Choi, K. Yoo and J.-B. Lee, in *2014 IEEE 27th International Conference on Micro Electro Mechanical Systems (MEMS)*, 2014, pp. 540–543.

This journal is © The Royal Society of Chemistry 2015

View Article Online

Published on 31 March 2015. Downloaded by Carnegie Mellon University on 06/06/2015 20:32:19.

22 B. A. Gozen, A. Tabatabai, O. B. Ozdoganlar and C. Majidi, *Adv. Mater.*, 2014, **26**, 5211–5216.
23 R. K. Kramer, C. Majidi and R. J. Wood, *Adv. Funct. Mater.*, 2013, **23**, 5292–5296.
24 S. H. Jeong, A. Hagman, K. Hjort, M. Jobs, J. Sundqvist and Z. Wu, *Lab Chip*, 2012, **12**, 4657.
25 R. K. Kramer, J. W. Boley, H. A. Stone, J. C. Weaver and R. J. Wood, *Langmuir*, 2014, **30**, 533–539.
26 K. Doudrick, S. Liu, E. M. Mutunga, K. L. Klein, V. Damle, K. K. Varanasi and K. Rykaczewski, *Langmuir*, 2014, **30**, 6867–6877.
27 D. Kim, D. Jung, J. H. Yoo, Y. Lee, W. Choi, G. S. Lee, K. Yoo and J.-B. Lee, *J. Micromech. Microeng.*, 2014, **24**, 055018.
28 H.-J. Kim, C. Son and B. Ziaie, *Appl. Phys. Lett.*, 2008, **92**, 011904.
29 J.-H. So and M. D. Dickey, *Lab Chip*, 2011, **11**, 905–911.
30 N. Pekas, Q. Zhang and D. Juncker, *J. Micromech. Microeng.*, 2012, **22**, 097001.
31 T. Sekitani, Y. Noguchi, K. Hata, T. Fukushima, T. Aida and T. Someya, *Science*, 2008, **321**, 1468–1472.
32 S. Rosset, M. Niklaus, P. Dubois and H. R. Shea, *Adv. Funct. Mater.*, 2009, **19**, 470–478.
33 J. Park, S. Wang, M. Li, C. Ahn, J. K. Hyun, D. S. Kim, D. K. Kim, J. A. Rogers, Y. Huang and S. Jeon, *Nat. Commun.*, 2012, **3**, 916.
34 C. Majidi, R. Kramer and R. J. Wood, *Smart Mater. Struct.*, 2011, **20**, 105017.
35 Y.-L. Park, C. Majidi, R. Kramer, P. Bérard and R. J. Wood, *J. Micromech. Microeng.*, 2010, **20**, 125029.
36 J. Vetrovec, A. S. Litt, D. A. Copeland, J. Junghans and R. Durkee, *Liquid metal heat sink for high-power laser diodes*, ed. M. S. Zediker, 2013, p. 86050E.
37 K.-Q. Ma and J. Liu, *Phys. Lett. A*, 2007, **361**, 252–256.
38 M. Gao and L. Gui, *Lab Chip*, 2014, **14**, 1866–1872.
39 D. Kim, Y. Lee, D. Lee, W. Choi and J. B. Lee, in *2013 Transducers Eurosensors XXVII: The 17th International Conference on Solid-State Sensors, Actuators and Microsystems (TRANSDUCERS EUROSENSORS XXVII)*, 2013, pp. 2620–2623.
40 J. Wang, S. Liu and A. Nahata, *Opt. Express*, 2012, **20**, 12119–12126.
41 J. Wang, S. Liu, S. Guruswamy and A. Nahata, *Appl. Phys. Lett.*, 2013, **103**, 221116.
42 D. Kim, P. Thissen, G. Viner, D.-W. Lee, W. Choi, Y. J. Chabal and J.-B. Lee, *ACS Appl. Mater. Interfaces*, 2013, **5**, 179–185.
43 D. Kim, R. G. Pierce, R. Henderson, S. J. Doo, K. Yoo and J.-B. Lee, *Appl. Phys. Lett.*, 2014, **105**, 234104.
44 M. R. Khan, C. Trlica, J.-H. So, M. Valeri and M. D. Dickey, *ACS Appl. Mater. Interfaces*, 2014, **6**, 22467–22473.
45 C. Koo, B. E. LeBlanc, M. Kelley, H. E. Fitzgerald, G. H. Huff and A. Han, *J. Microelectromechanical Syst.*, 2015, DOI: 10.1109/JMEMS.2014.2381555.
46 H.-J. Kim, T. Maleki, P. Wei and B. Ziaie, *J. Microelectromechanical Syst.*, 2009, **18**, 138–146.
47 K. P. Mineart, Y. Lin, S. C. Desai, A. S. Krishnan, R. J. Spontak and M. D. Dickey, *Soft Matter*, 2013, **9**, 7695.
48 W. Zhao, J. L. Bischof, J. Hutasoit, X. Liu, T. C. Fitzgibbons, J. R. Hayes, P. J. A. Sazio, C. Liu, J. Jain, J. Badding and M. H. W. Chan, *Nano Lett.*, 2015, **15**, 153–158.
49 M. R. Khan, G. J. Hayes, J.-H. So, G. Lazzi and M. D. Dickey, *Appl. Phys. Lett.*, 2011, **99**, 013501.
50 C. Ladd, J.-H. So, J. Muth and M. D. Dickey, *Adv. Mater.*, 2013, **25**, 5081–5085.
51 H. Ota, K. Chen, Y. Lin, D. Kiriya, H. Shiraki, Z. Yu, T.-J. Ha and A. Javey, *Nat. Commun.*, 2014, **5**, 5032.
52 F. Hensel, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 593–606.
53 A. C. Siegel, D. A. Bruzewicz, D. B. Weibel and G. M. Whitesides, *Adv. Mater.*, 2007, **19**, 727–733.
54 A. Fassler and C. Majidi, *Lab Chip*, 2013, **13**, 4442–4450.
55 T. Lu, L. Finkenauer, J. Wissman and C. Majidi, *Adv. Funct. Mater.*, 2014, **24**, 3351–3356.
56 M. R. Khan, C. Trlica and M. D. Dickey, *Adv. Funct. Mater.*, 2015, **25**, 671–678.
57 J. W. Boley, E. L. White, G. T.-C. Chiu and R. K. Kramer, *Adv. Funct. Mater.*, 2014, **24**, 3501–3507.
58 P. Calvert, *Chem. Mater.*, 2001, **13**, 3299–3305.
59 G. A. of America, G. E. Foundation, *Gravure: Process and Technology*, Gravure Association of America, Gravure Education Foundation, Rochester, NY, 1991.
60 E. Hrehorova, M. Rebros, A. Pekarovicova, B. Bazuin, A. Ranganathan, S. Garner, G. Merz, J. Tosch and R. Boudreau, *J. Disp. Technol.*, 2011, **7**, 318–324.
61 K. K. B. Hon, L. Li and I. M. Hutchings, *CIRP Ann. - Manuf. Technol.*, 2008, **57**, 601–620.
62 F42 Committee, Terminology for Additive Manufacturing Technologies, ASTM International, 2012.
63 A. Tabatabai, A. Fassler, C. Usiak and C. Majidi, *Langmuir*, 2013, **29**, 6194–6200.
64 C. A. Gunawan, M. Ge and C. Zhao, *Nat. Commun.*, 2014, **5**, 3744.
65 S. Lee, J. Song, H. Kim and J. Chung, *J. Aerosol Sci.*, 2012, **52**, 89–97.
66 S. N. Jayasinghe, A. N. Qureshi and P. A. M. Eagles, *Small*, 2006, **2**, 216–219.
67 D. Kim, J. H. Yoo, Y. Lee, W. Choi, K. Yoo and J.-B. Lee, in *2014 IEEE 27th International Conference on Micro Electro Mechanical Systems (MEMS)*, 2014, pp. 967–970.
68 Y. Gao and Y. Bando, *Nature*, 2002, **415**, 599.
69 Z. Liu, Y. Bando, M. Mitome and J. Zhan, *Phys. Rev. Lett.*, 2004, **93**, 095504.
70 G. M. Gallatin, *Proc. SPIE*, 2005, **5754**, 38–52.
71 S. H. Jeong, K. Hjort and Z. Wu, *Sensors*, 2014, **14**, 16311–16321.
72 D. Kim, D.-W. Lee, W. Choi and J.-B. Lee, in *2012 IEEE 25th International Conference on Micro Electro Mechanical Systems (MEMS)*, 2012, pp. 1005–1008.
73 P. Ahlberg, S. H. Jeong, M. Jiao, Z. Wu, U. Jansson, S.-L. Zhang and Z.-B. Zhang, *IEEE Trans. Electron Devices*, 2014, **61**, 2996–3000.
74 S. H. Jeong, K. Hjort and Z. Wu, *Sci. Rep.*, 2015, **5**, 8419.
75 M. Z. Seyedin, J. M. Razal, P. C. Innis and G. G. Wallace, *Adv. Funct. Mater.*, 2014, **24**, 3104.
76 G. Li, M. Parmar, D. Kim, J.-B. (JB) Lee and D.-W. Lee, *Lab. Chip*, 2014, **14**, 200.

This journal is © The Royal Society of Chemistry 2015