ACCOUNTS of chemical research

Article

Cite This: *Acc. Chem. Res.* XXXX, XXX, XXX−XXX

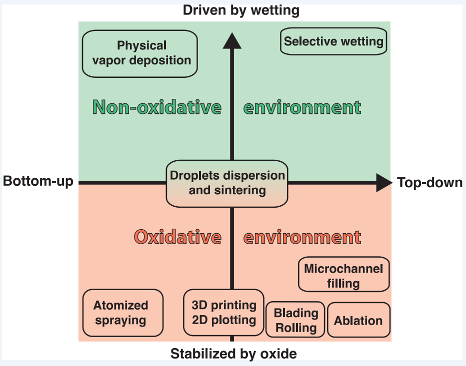
pubs.acs.org/accounts

Harnessing the Rheological Properties of Liquid Metals To Shape Soft Electronic Conductors for Wearable Applications

Published as part of the Accounts of Chemical Research special issue "Wearable Bioelectronics: Chemistry, Materials, Devices, and Systems".

Arthur Hirsch,[†] Laurent Dejace,[†] Hadrien O. Michaud,[†] and Stéphanie P. Lacour*

Bertarelli Foundation Chair in Neuroprosthetic Technology, Laboratory for Soft Bioelectronic Interfaces, Institute of Microengineering, Institute of Bioengineering, Centre for Neuroprosthetics, École Polytechnique Fédérale de Lausanne (EPFL), 1202 Geneva, Switzerland



CONSPECTUS: Emerging applications of the Internet of Things in healthcare, wellness, and gaming require continuous monitoring of the body and its environment, fueling the need for wearable devices able to maintain intimate, reliable, and unobtrusive contact with the human body. This translates in the necessity to develop soft and deformable electronics that match the body's mechanics and dynamics. In recent years, various strategies have been proposed to form stretchable circuits and more specifically elastic electrical conductors embedded in elastomeric substrate using either geometrical structuring of solid conductors or intrinsically stretchable materials.

Gallium (Ga)-based liquid metals (LMs) are an emerging class of materials offering a particularly interesting set of properties for the design of intrinsically deformable conductors. They concomitantly offer the high electrical conductivity of metals with the ability of liquids to flow and reconfigure. The specific chemical and physical properties of Ga-based LMs differ fundamentally from those of solid conductors and need to be considered to successfully process and implement them into stretchable electronic devices.

In this Account, we report on how the key physical and chemical properties of Ga-based LMs can be leveraged to enable repeatable manufacturing and precise patterning of stretchable LM conductors. A comprehensive understanding of the interplay between the LM, its receiving substrate chemistry and topography, and the environmental conditions is necessary to meet the reproducibility and reliability standards for large scale deployment in next-generation wearable systems.

In oxidative environments, a solid oxide skin forms at the surface of the LM and provides enough stiffness to counterbalance surface tension, and prevent the LM from beading up to a spherical shape. We review techniques that advantageously harness the oxide skin to form metastable structures such as spraying, 3D printing, or channel injection. Next, we explore how controlling the environmental condition prevents the formation or removes the oxide skin, thereby allowing for selective wetting of Ga lyophilic surfaces. Representative examples include selective plating and physical vapor deposition. The wettability of LMs can be further tuned by engineering the surface chemistry and topology of the receiving substrate to form superlyophobic or superlyophilic surfaces. In particular, our group developed Ga-superlyophilic substrates by engineering the surface of silicone rubber with microstructures and a gold coating layer. Thermal evaporation of Ga on such engineered substrates allows for the formation of smooth LM films with micrometric thickness control and design freedom.

The versatility of the available deposition techniques facilitates the implementation of LM conductors in a wide variety of wearable devices. We review various epidermal electronic systems using LM conductors as interconnects to carry power and information, transducers and sensors, antennas, and complex hybrid (soft-rigid) electronic circuits. In addition, we highlight the limitations and challenges inherent to the use of Ga LM conductors that include electromigration, corrosion, solidification, and biocompatibility.

INTRODUCTION

Wearable technologies are a driving force of the Internet of Things. Diverse fields such as healthcare, wellness, and gaming but also safety and connectivity benefit from continuous, real time monitoring of the body and its environment. The integration of electronics close to the body calls for new engineering efforts in materials science, manufacturing, and system integration. Electronic skin, called e-skin, provides a scientific and engineering framework to design and manufacture electronic circuits matching the large surface area and dynamic demands of the human body.[1] A wide range of materials and processes are being explored to manufacture e-skins as described in recent reviews.[2−4] Among the various

Received: September 27, 2018

DOI: 10.1021/acs.accounts.8b00489
Acc. Chem. Res. XXXX, XXX, XXX−XXX

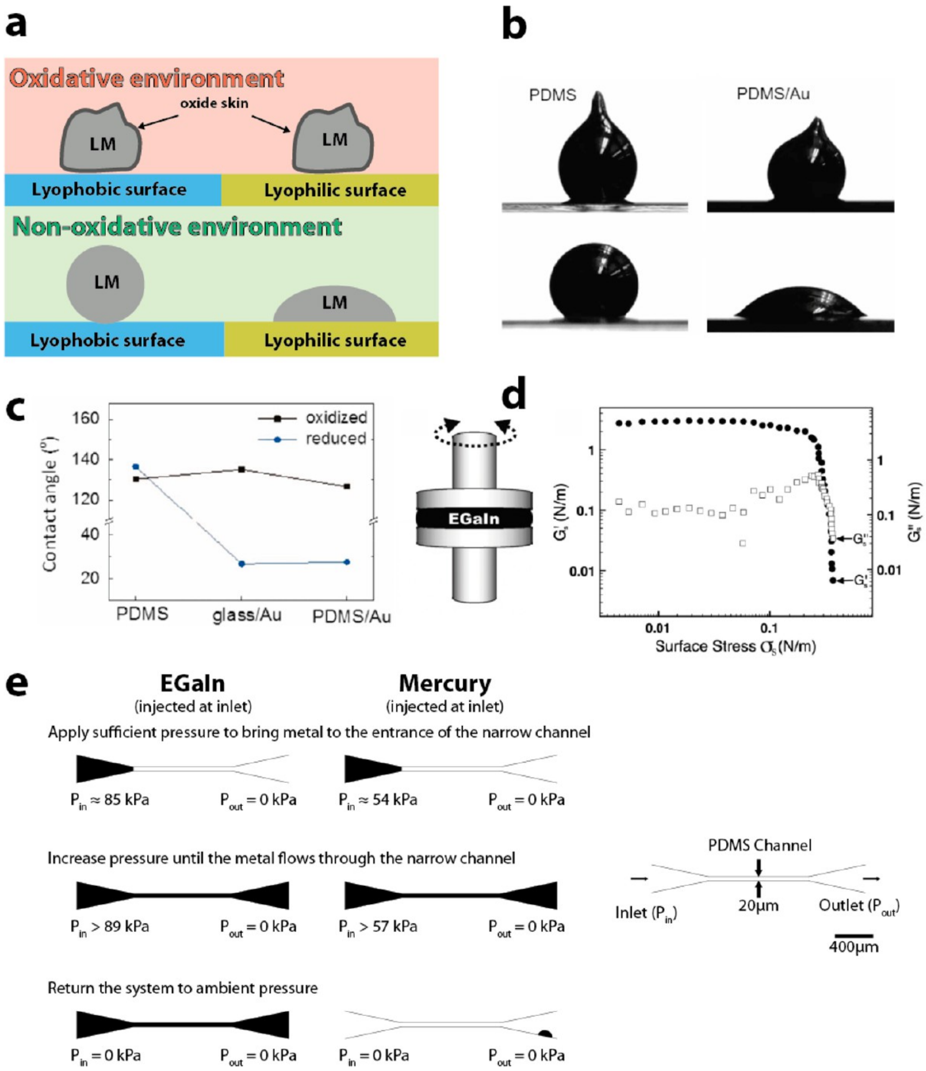


Figure 1. Properties of bulk LMs. (a) Schematic illustration of LM drops deposited on lyophobic or lyophilic substrates in oxidative or nonoxidative environments. (b,c) Contact angle of LM droplets ($Ga_{68.5}In_{21.5}Sn_{10}$ wt %) on a PDMS substrate (left) and Au coated PDMS (right) substrate before (top) and after (bottom) contact with a 10 wt % NaOH solution. Adapted with permission from ref 70. Copyright 2017 Nature Publishing Group. (d) Rheological behavior of LM (EGaIn) showing the stabilizing effect of the oxide skin below a critical yield stress. Reproduced with permission from ref 18. Copyright 2008 John Wiley and Sons (Wiley). (e) Injection of EGaIn and Hg LMs in microchannels and stabilizing effect of the oxide skin upon pressure withdrawal. Adapted with permission from ref 18. Copyright 2008 Wiley.

technological approaches, liquid metals (LMs) emerge as a particularly interesting class of "electronic materials" to prepare soft and stretchable electrical conductors, the building blocks of e-skins. They combine the ability to intrinsically rearrange, self-heal, and accommodate very large strains while maintaining high electrical conductivity. When encased in and/or patterned on a stretchable elastomeric substrate, LM conductors may carry information and power, transmit, and sense signals. Already in 1953, mercury was encased in a rubber tube and used to sense human body deformation.[5] Today, gallium (Ga)-based liquid metals have emerged as a viable and safer alternative to mercury, as the price of production has dropped with increasing demand from the semiconductor industry.[6] The physicochemical properties of LMs significantly differ from those of conventional solid metals, therefore innovative processing is needed for their robust and reliable integration in wearable devices. An exhaustive review of LM-based soft and stretchable devices and their applications was reported elsewhere.[7] Despite showing promising results, these devices still fail to be deployed at large scale out of the laboratory environment. Among the different challenges, forming and patterning high quality LM films at the industrial scale requires understanding and overcoming the limitations associated with the LM unconventional rheology and wetting properties. In this Account, we review the unique properties of Ga-based LMs, e.g., complex rheology, high surface tension, solid oxide skin, and reactivity with most metals, and report on different strategies that leverage these characteristics to create reversibly deformable electronic components and circuits.

■ KEY PROPERTIES OF GALLIUM

Ga-based liquid metal properties are particularly suitable to form stretchable conductors. Ga is liquid over a large temperature range (29.7−2204 °C) and tends to remain liquid below its freezing point due to the supercooling effect.[8−10] Combined with other metals such as indium or tin, Ga forms eutectic alloys with further reduced melting points

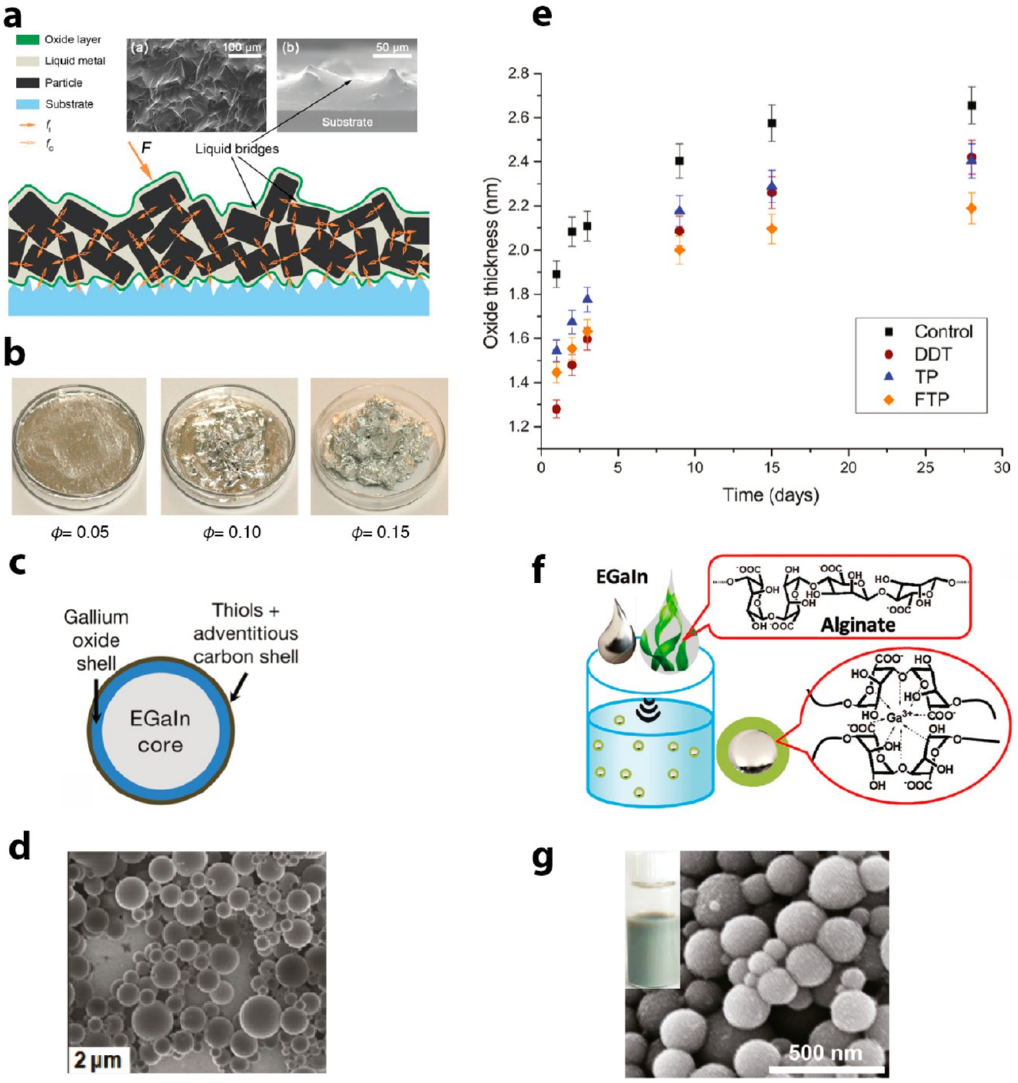


Figure 2. Liquid amalgams and stabilized dispersions. (a) Schematic of Ga amalgams and (b) pictures of Ga amalgams for different Cu particle ratios (ϕ). Reproduced with permission from ref 24. Copyright 2017 American Chemical Society. (c) Functionalization of LM (EGaIn) nanoparticles with thiols to (d) avoid coalescence and (e) control oxide skin regrowth after dispersion in solution. Reproduced with permission from refs 26 and 27. Copyright 2018 American Chemical Society and 2011 American Chemical Society, respectively. (f,g) Encapsulation of LM (EGaIn) nanodroplets with alginate to maintain colloidal and chemical stability of aqueous dispersions. Reproduced with permission from ref 29. Copyright 2018 Wiley.

(e.g., 11 °C for eutectic $Ga_{67}In_{20.5}Sn_{12.5}$ wt %, and 15.5 °C for eutectic $Ga_{75}In_{25}$ wt %).[11] At room temperature, Ga-based LMs feature a low vapor pressure,[12] low viscosity[13] and high electrical conductivity ($\approx 3.4 \times 10^6$ S·m^{-1}).[14] In the presence of oxygen, even in minute quantity (>1 ppm), a solid passivation oxide skin forms at the surface of the LM.[12,15] Despite being a few nanometers thick, this solid oxide skin impacts LM rheology at the macroscopic scale.[16]

Shaping and forming LM conductors require a good understanding and control of LM spreading over solid surfaces. Most wearable and skinlike devices use thin metallic conductors, of a length scale smaller than the capillary length of Ga (3.5 mm).[17] At this length scale, the influence of gravity on the LM is negligible. The profile of the LM is thus resulting from the interplay between adhesive and cohesive forces at the interface, and the stiffness of the formed solid oxide skin.

In the presence of oxygen, the solid oxide skin is able to counterbalance the cohesive attraction in the LM. A drop of LM can thus adopt a wide variety of metastable, nonspherical shapes depending on its strain history and the oxide skin formation (Figure 1a−c).[18] The oxide skin can withstand surface stresses up to ≈0.5 N·m^{-1}, above which it yields and allows the LM to flow (Figure 1d).[16] For example, it allows the formation of stable structures in microchannels by stabilizing injected LM in a prescribed shape upon pressure withdrawal (Figure 1e).[18]

In the absence of oxide skin, LM flows into a shape that minimizes the interfacial free energy (Figure 1a-b bottom). Nonreactive surfaces such as glass, sapphire and polymers are lyophobic toward Ga and will constrain the liquid to bead up and form drops of large contact angles (>160°).[19] On the contrary, most metallic substrates are Ga lyophilic. Ga reacts with most metals including gold, platinum or copper[20] by diffusing[21] and forming intermetallic compounds that enable reactive wetting (Figure 1c).[22,23]

Ga reactivity with metals can also be used to form Ga amalgams. For instance, dispersing Cu particles in liquid Ga leads to the formation of $CuGa_2$ intermetallic compound

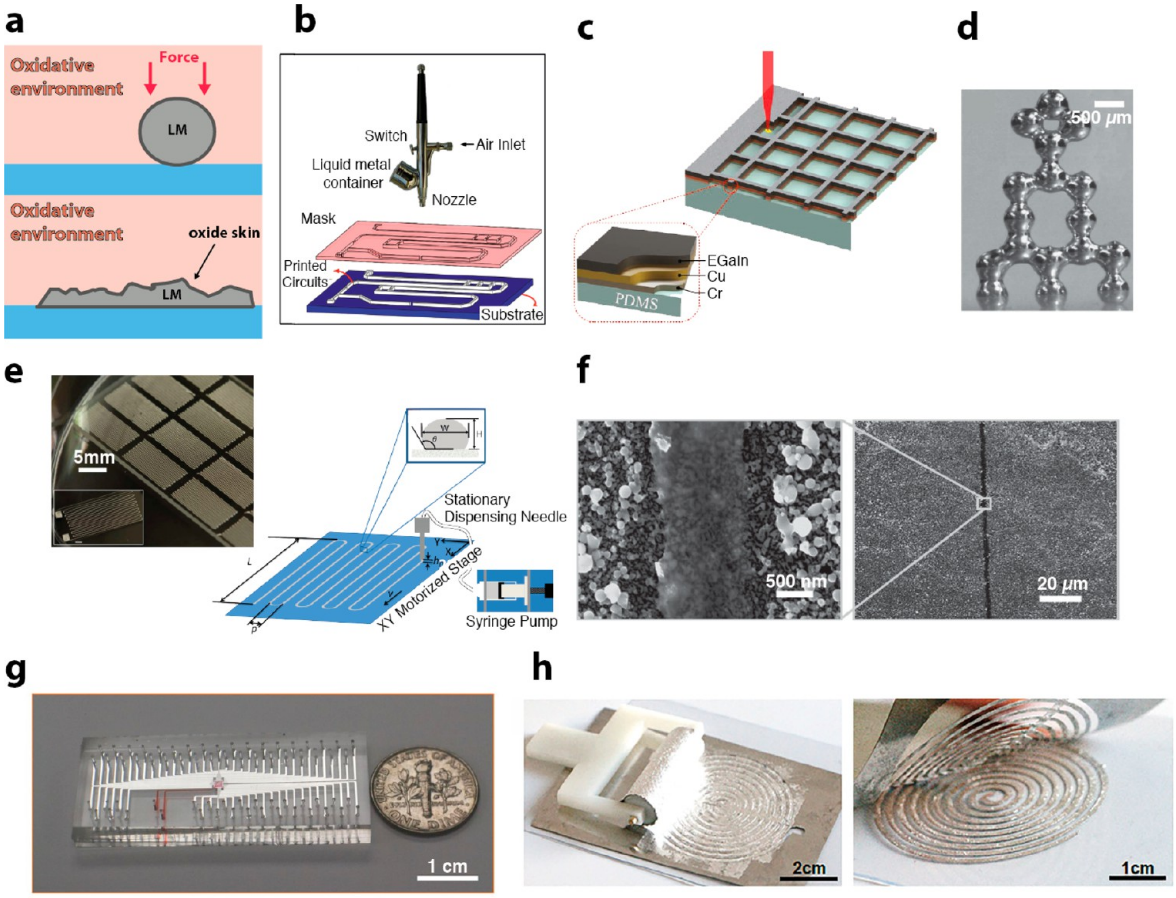


Figure 3. Patterning methods relying on stabilization by the oxide skin. (a) Schematic of the patterning principle. LM is mechanically forced into a prescribed shape in an oxidative environment and stabilized by the newly formed oxide skin. (b) Atomized spraying. Adapted with permission from ref 31. Copyright 2013 Nature Publishing Group. (c) Laser machining. Reproduced with permission from ref 71. Copyright 2018 Wiley. (d) 3D printing. Reproduced with permission from ref 33. Copyright 2013 Wiley. (e) Direct writing. Adapted with permission from ref 34. Copyright 2014 Wiley. (f) Mechanical sintering of LM (EGaIn) nanoparticles. Reproduced with permission from ref 35. Copyright 2015 Wiley. (g) Injection in microfluidic channels. Reproduced with permission from ref 36. Copyright 2013 Nature Publishing Group. (h) Rolling through stencil mask. Reproduced with permission from ref 38. Copyright 2018 Wiley.

(Figure 2a,b). Changing the Cu/Ga ratio (ϕ) enables one to tune the mechanical and electrical properties of the amalgam, transitioning from a liquid metal toward a thick, pastelike material.[24] Ga amalgams with other metals have also been proposed and studied for dentistry.[25]

Ligands can be grafted on the surface of LMs to modify their surface properties (Figure 2c−g). Thiols form self-assembled monolayers on the surface of nonoxidized Ga and have been used to stabilize and functionalize colloidal dispersions of LM nanoparticles (NPs) or delay and mitigate oxide skin formation[26−28] Yet, the long-term stability of LM NPs in aqueous solutions remains a challenge, as they tend to oxidize and precipitate over time. Alginate hydrogels have been proposed to maintain the colloidal and chemical stability of LM NPs for a period of 7 days.[29] More recently, Lin et al. stabilized LM NPs for more than 60 days using an hydrophobic polymer coating.[30]

■ ADAPTED PATTERNING TECHNIQUES

Many patterning methods have been developed or adapted to the unconventional rheology of LMs. The definition of precise layouts of LM films mostly depends on the control of the oxide skin and the negotiation of LM high surface tension.

One approach consists of forcing the liquid metal to a prescribed shape by pressurizing the liquid enough to allow the oxide skin to yield and the liquid to flow (Figure 3). The oxide skin spontaneously reforms once in contact with the oxidative environment, stabilizing the LM in shape upon release of the mechanical force. This approach is used to form LM conductors by spraying,[31] laser patterning,[32] 3D printing,[33] direct writing,[34] mechanical sintering,[35] micro-channel injection, or vacuum filling,[18,36,37] or rolling through a stencil mask.[38,39]

Alternatively, LM conductors can be formed by first removing the oxide skin in a reducing environment then allowing the LM to selectively wet lyophilic patterns (Figure 4). Methods to reduce the solid oxide skin include exposure to acidic or basic aqueous solutions,[40,41] as well as acidic silicone oil,[42] or vapor.[43] Li et al. formed patterns of LM by selectively wetting thin films of Au deposited on a PDMS substrate immersed in a HCl solution.[44] Ozutemiz et al. used a similar approach and took advantage of capillary forces to integrate and self-align surface-mount device (SMD) components.[45]

Our group reported thermal evaporation of Ga to form thin films of LM.[46] In this physical vapor deposition (PVD) process, the LM is heated up under vacuum and condenses on a receiving substrate (Figure 5a). This bottom-up approach

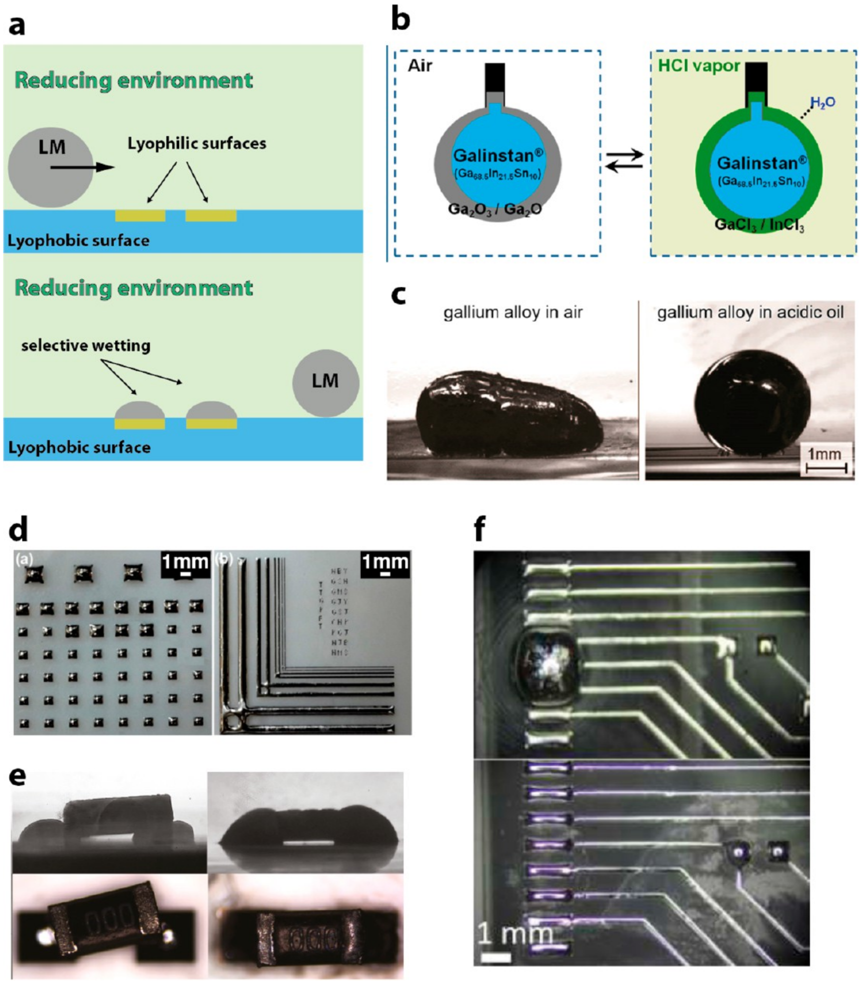


Figure 4. Patterning methods relying on selective wetting in reducing environment. (a) Schematic illustration of LM selective wetting of a lyophilic substrate in a reducing environment. (b) Schematic diagram of Ga oxides (Ga_2O_3/Ga_2O) chemical reaction with HCl vapor. The oxides (Ga_2O_3/Ga_2O), chlorides ($GaCl_3$/$InCl_3$), and water are in solid, aqueous, and liquid phases, respectively. Adapted with permission from ref 43. Copyright 2012 American Chemical Society. (c) Effect of acidified siloxane oil on Ga LM. Reproduced with permission from ref 42. Copyright 2016 American Chemical Society. (d) Complex LM patterns obtained by selective wetting of Au/Cr thin film in HCl reducing environment. Reproduced with permission from ref 44. Copyright 2015 Elsevier. (e) Side and top view images of self-alignment of surface mounted component with LM patterns before and after HCl vapor treatment and (f) images showing a circuit with and without LM bridging during the deposition step. Adapted with permission from ref 45. Copyright 2018 Wiley.

allows for a precise control of the deposited LM quantity and prevents the formation of the oxide skin until the chamber is vented. On a lyophobic substrate, condensed LM forms a nonconductive dispersion of nanodrops (Figure 5b,c).[47] On the contrary, deposition on a substrate coated with a lyophilic gold layer allows reactive wetting and formation of a continuous, conductive and stretchable biphasic LM thin film (Figure 5d,e).

In addition, engineering the surface roughness of the receiving substrate further enhances wetting effects. For example, Kim et al. microstructured the surface of silicone rubber with micropillars to create superlyophobic substrates and manipulate oxidized LM drops (Figure 6a−c).[48] Reducing the interpillar distance prevents the penetration of LM within the microstructures, similarly to the Cassie impregnation regime, and restricts its adhesion to the substrate. In our group, we engineered the topography and surface chemistry of silicone rubber with microstructured pillars and a gold precoating to produce superlyophilic substrates (Figure 6d−f).[49] Thermal evaporation of Ga on such substrates creates smooth (R_q < 100 nm) and homogeneous films by imbibition of the microstructures.[50]

The profile and roughness of the patterned LM tracks depend on the selected patterning method, substrate material and environmental deposition conditions. Patterning resolution and repeatability are also particularly relevant in applications where the LM tracks are used as electrical wiring and should interface miniature and dense electrical components. Microchannel filling techniques enable well-defined and smooth structures, matching the predefined microchannel geometry and roughness[37] but are not well suited to prepare electrical circuits. Unconfined planar deposition techniques offer less surface control but are more adapted to large scale processing and integration of surface mounted components. Park et al. showed that the height of liquid metal tracks patterned by rolling is ultimately determined by the photoresist mask thickness and reported RMS roughness of 0.61 μm (Figure 7a,b).[51] In contrast, the profile of LM traces patterned using selective wetting is dictated by the contact angle. Accordingly, the height of the features increases with their

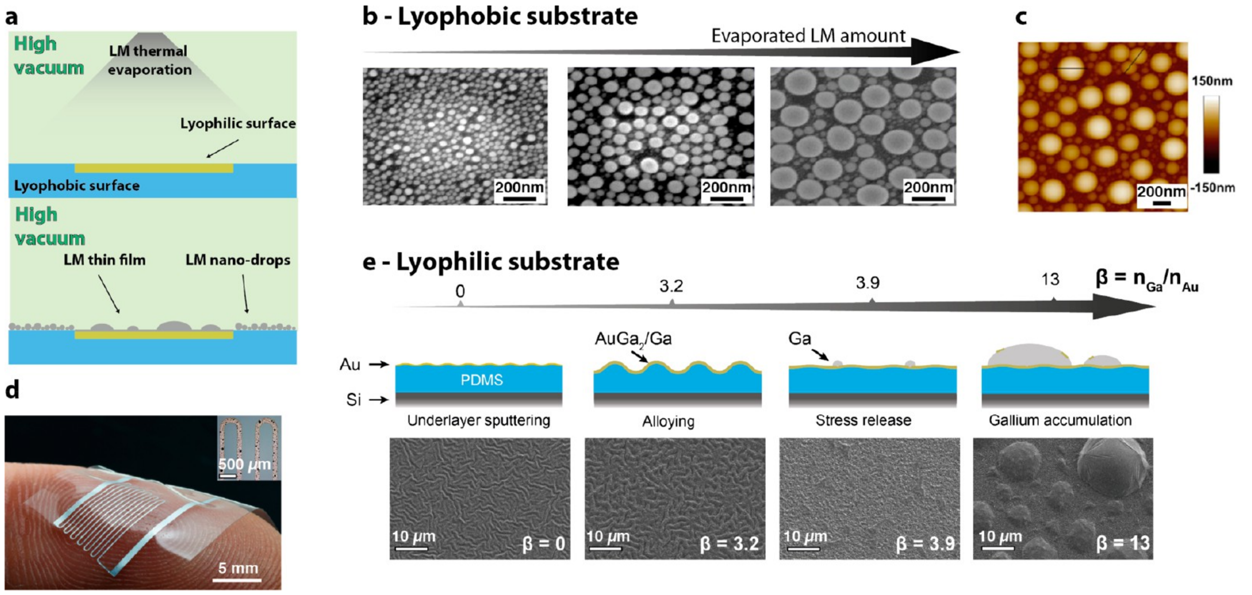


Figure 5. Physical vapor deposition of LMs. (a) Schematic representation of the process. Evaporated LM condenses in nanodrops on a lyophobic surface and a continuous film on a lyophilic substrate. (b,c) SEM and AFM images of LM (Ga−In) nanoparticles deposited on a Si wafer by thermal evaporation. Adapted with permission from ref 47. Copyright 2018 Elsevier. (d) Biphasic thin films obtained by thermally evaporating Ga on a PDMS substrate precoated with a Au thin film. (e) Growth of the biphasic thin films. Reproduced with permission from ref 46. Copyright 2016 Wiley.

width (Figure 7c,d).[44] LM thin films patterned on engineered Ga superlyophilic substrates have a very smooth surface (RMS roughness = 84 nm) independently of the LM track's width and thickness (Figure 7e,f).[49]

LIMITATIONS

The following section briefly reports on the major limitations of liquid metal conductors.

Electromigration

LMs undergoing direct current (dc) stressing are subject to electromigration as the liquid migrates toward the cathode and depletes the anode (Figure 8a,b).[52] Although this effect can be beneficial and exploited to form conformal coatings of LMs,[53] our group showed that continuous depletion of the LM at the anode results in failure of the LM conductive tracks under prolonged current stress (e.g., 1 h at 20 A·cm^{-2} or 60 h at 4 A·cm^{-2}).[54] Similarly to Black's empirical law on electromigration, we observed that the mean time to failure followed an inverse power law relationship with the current density ($t_{\text{fail}} \sim i^{-n}$ with $n = 3.2$).

Corrosion

LM-based alloys may be damaged by pitting corrosion when placed in aqueous solutions for prolonged periods of time (Figure 8c−e). Water changes the chemical composition of the oxide skin and weakens its mechanical strength.[55] After initial fissure of the passivating oxide skin, blisters, voids, and pits form and lead to the mechanical and electrical breakdown of LM metallic tracks.[56] Encapsulation with low water permeability materials or surface functionalization with ligands[57] can slow down the process of corrosion, but the long-term applicability of Ga in liquid environments remains an open question.

Solidification

Preventing solidification is fundamental to maintain the elasticity of LM conductors. Even though LMs tend to supercool and stay liquid below their melting point, solidification may be initiated by contact with a solid crystal of Ga[58] or may occur spontaneously if the metal is cooled down well below his melting temperature[59] (Figure 8f,g).

Alloying

Interfacing LMs with conventional solid state components may be challenging, in particular over time, as Ga reacts and diffuses in most metals, resulting in mechanical embrittlement or contamination.[60] Coating of electrically conductive diffusion barriers based on carbon derivatives impermeable to LMs, such as graphene, or metals with a good resistance to corrosion to Ga, such as tungsten, should be considered for long-term applications.[20,61]

Biocompatibility

Even though Ga-based LMs are considered safe to manipulate, applications involving close and prolonged contact with living tissues should be considered with caution.[62] Reports on acute and chronic toxicity of LMs are still limited, but suggest that their composition, format, and size, e.g., particle size, and mechanical agitation of the medium may play an important role in the compatibility of the LM with biological tissues. For example, Lu et al. reported the use of a dispersion of LM (EGaIn) nanospheres as an injectable drug release vehicle with no chronic toxicity in animal models for a concentration of 45 mg/kg.[28] Recently, Kim et al. investigated the cytotoxicity of EGaIn releasates on various human cells. While naturally released Ga and In ions did not impede the viability of the tested cells, sonication drastically increased the release of In ions and was associated with significant cytotoxicity (Figure 8h).[63] More studies are thus necessary to determine how to safely employ LMs in the context of biological and biomedical applications.

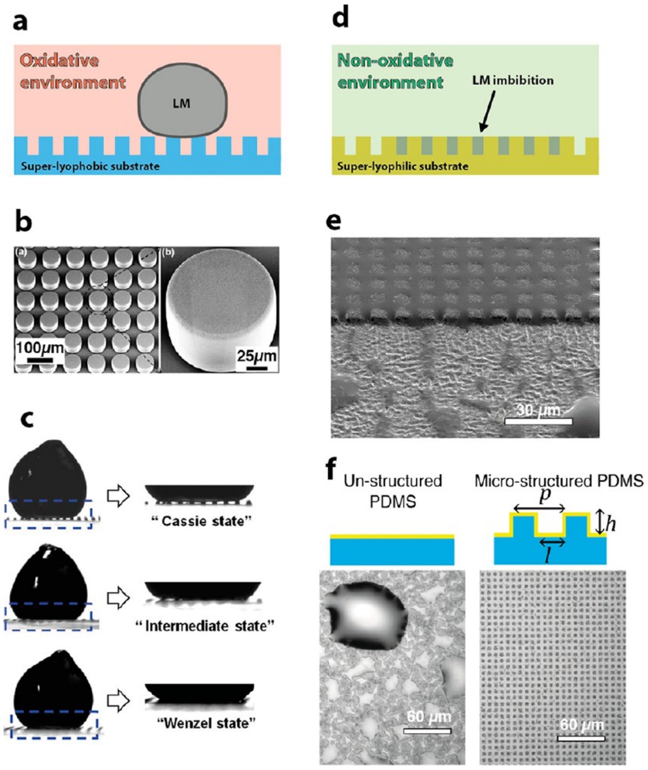


Figure 6. Effect of surface roughness on LM wetting. (a) Schematic diagram of a LM drop in “Cassie state” on a superlyophobic substrate. (b) SEM images of microstructured PDMS substrate. (c) Images of LM drops in different wetting states as a function of micropillar gap dimensions (top 150 μm, middle 200 μm, bottom 250 μm). Reproduced with permission from ref 72. Copyright 2013 IEEE. (d) Schematic diagram of a LM imbibition of a superlyophilic substrate in a nonoxidative environment. (e) SEM images of a partially microstructured lyophilic substrate after pure Ga evaporation. Reproduced with permission from ref 57. Copyright 2018 EPFL. (f) Microscope images of Ga thin films evaporated on unstructured (left) or microstructured (right) lyophilic substrate. Reproduced with permission from ref 49. Copyright 2018 Wiley.

■ APPLICATIONS TO SOFT WEARABLES

LMs have been utilized to produce a range of electrical components for soft wearable systems. We summarize a nonexhaustive list of examples below.

Interconnects

Electrical conductors are the prime implementation of Ga-based films. They are routed on a stretchable carrier substrate, similarly to interconnects on a printed circuit board (PCB). The high electrical conductivity of LMs guarantees low voltage drops across the soft interfaces, thereby enabling efficient transmission of power and/or transducing signals. For example, a complete wearable system, designed to monitor heart rate, relies on LM interconnect layout to link a voltage regular, passive components, and an integrated pulse oximeter[32] (Figure 9a). Our group used LM alloy (EGaIn) interconnects to contact extremely thin (50 nm) gold strain gauges within a soft glove system encoding motion and pressure[64−66] (Figure 9b). The LM interconnects also act as a mechanical buffer to interface delicate components or surfaces and minimize mechanical stress concentrations.

Transducers/Sensors

LM films can be integrated in soft mechanical sensors based on resistive or capacitive modes. For example, patterned biphasic thin films enable epidermal sensors (<50 μm-thick) that encode finger flexion and extension when attached to the skin[67] (Figure 9c). Other sensing modalities include proximity and pressure sensing as the LM films are used as electrodes.[46,68]

Antennas

The low electrical resistance of LM films offers a unique opportunity to integrate “soft” antennas within e-skins. LM dipoles or coil antennas prepared on stretchable substrate maintain high conductivity and transmission capabilities even under extensive deformations (Figure 9d).[39] The ability to interface standard surface-mount components also simplifies the co-integration of RFID chips and antennas in a compact, wearable system. To date, wearable LM antennas are mostly prepared with microchannel designs filled with LM or

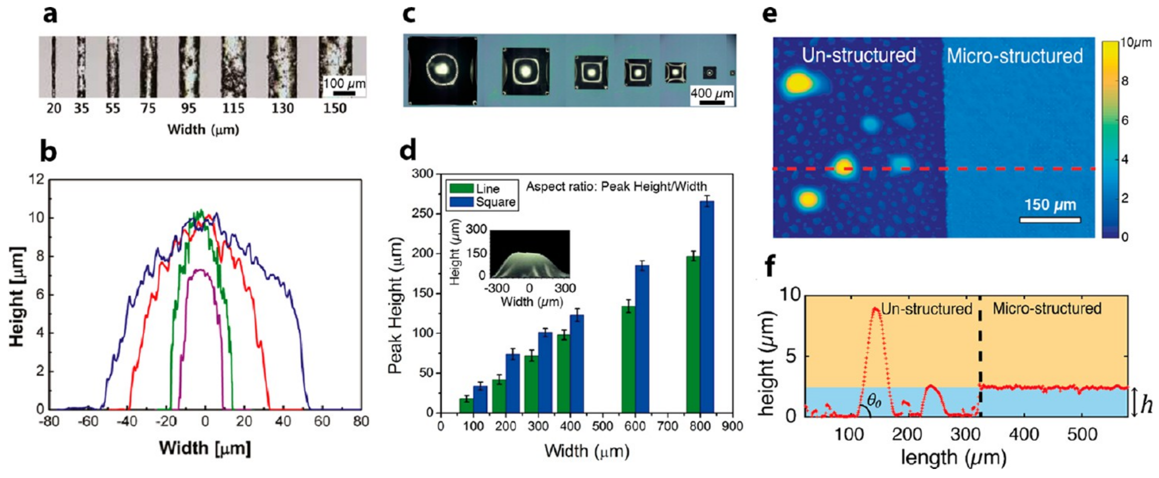


Figure 7. LM profiles prepared with different patterning methods. (a) Picture and (b) height profile of LM (EGaIn) tracks patterned on PDMS by rolling on photoresist. Reproduced with permission from ref 51. Copyright 2016 American Chemical Society. (c) Picture and (d) height profile of LM ($Ga_{68.5}In_{21.5}Sn_{10}$ wt %) patterned by selective plating. Adapted with permission from ref 44. Copyright 2015 Elsevier. (e) Topography and (f) height profile of Ga deposited on Au-coated flat and microstructured PDMS by physical vapor deposition. Reproduced with permission from ref 49. Copyright 2018 Wiley.

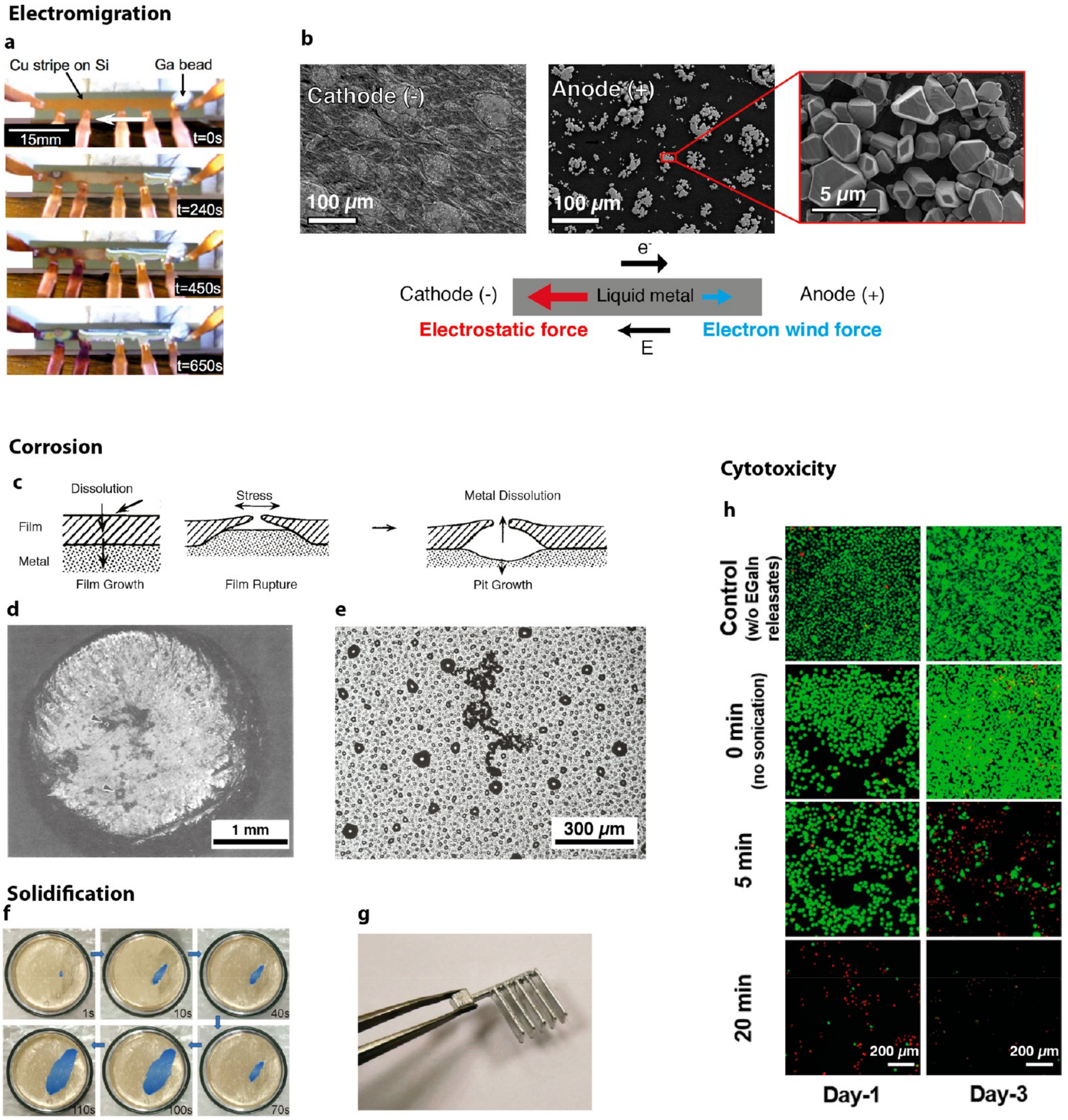


Figure 8. Limitations of LM conductors. (a) Migration of liquid Ga along the current direction on a copper stripe. Reproduced with permission from ref 53. Copyright 2009 AIP Publishing. (b) Electromigration of Ga on a biphasic Au−Ga film after prolonged current stress. Reproduced with permission from ref 54. Copyright 2017 EPFL. (c,d) Mechanism and observation of pitting corrosion of liquid Ga placed in KCl solution. Adapted with permission from ref 56. Copyright 1994 Electrochemical Society. (e) Pitting corrosion of a biphasic Au−Ga metal film after prolonged immersion in PBS solution. Reproduced with permission from ref 57. Copyright 2018 EPFL. (f) Solidification of supercooled Ga induced by contact with a solid Ga crystal and (g) freeze casting of LM (EGaIn) 3D structures. Reproduced with permission from refs 58 and 59. Copyright 2017 Wiley and 2013 Royal Society of Chemistry, respectively. (h) Human cells cultured in a growth media containing dispersed LM (EGaIn) particles. Reproduced with permission from ref 63. Copyright 2018 American Chemical Society.

electrowetting setups and offer tunability and reconfigurability.[69]

■ CONCLUSION AND OUTLOOK

In this Account, we reviewed the critical properties of Ga-based LMs to pattern stretchable conductors suitable for wearable applications. Depositing and shaping LM films across scales require a comprehensive understanding of their rheological and wetting properties, highlighted by the influence of a solid oxide skin, high surface tension, and reactivity with metals.

We accordingly classified LM patterning techniques as top-down or bottom-up approaches relying either on the solid oxide skin or on surface wetting. Guidelines were provided on how manufacturing techniques may be selected to form diverse key components of stretchable electronic circuits, such as interconnects, antennas, and sensors. Nowadays, many functional LM-based wearable devices and prototypes were

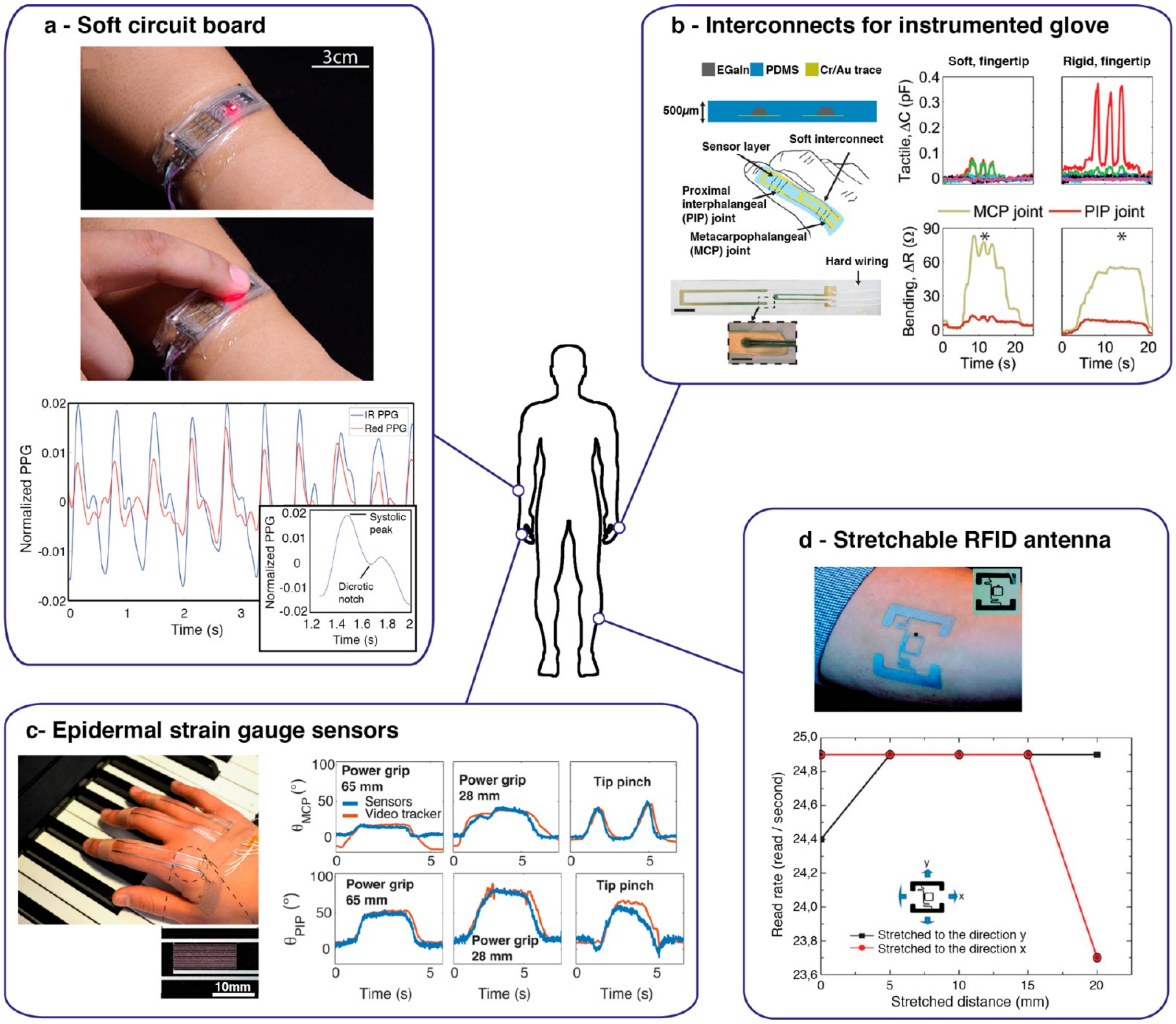


Figure 9. Examples of soft wearable sensors and systems enabled by LM conductor technologies. (a) Soft-matter printed circuit board composed of laser-micromachined EGaIn traces and containing a pulse oximeter. Adapted with permission from ref 32. Copyright 2017 American Chemical Society. (b) Instrumented glove with finger bending resistive sensors connected with EGaIn traces patterned by 2D plotting. Adapted with permission from ref 64. Copyright 2015 Wiley. (c) Epidermal sensors integrating soft resistive strain gauges made from biphasic Ga-based thin films to encode finger joints angular positions. Reproduced with permission from ref 67. Copyright 2016 IEEE. (d) Stretchable UHF RFID tag obtained by rolling of LM ($Ga_{68.5}In_{21.5}Sn_{10}$ wt %) on PDMS. Adapted with permission from ref 39. Copyright 2012 Royal Society of Chemistry.

demonstrated at the laboratory scale. Yet, the translation of these concepts toward industrialization remains relatively unexplored. We therefore discussed main limiting aspects of LMs such as electromigration and corrosion, and reported recent cytotoxicity studies of LMs relevant for body-related applications. In conclusion, we believe that future research on this exciting class of materials will enable new ways to tune and optimize the reliability and long-term robustness of LM-based devices and open up new avenues in the Internet of Things.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: stephanie.lacour@epfl.ch.

ORCID

Stéphanie P. Lacour: 0000-0001-9075-4022

Author Contributions

†A.H., L.D., and H.O.M. contributed equally.

Funding

We acknowledge financial support from the Fondation Bertarelli and nanotera.ch (20NA_143070 WiseSkin and 20NA_145923 SpineRepair), SNSF NCCR Robotics, and EPFL Innogrant.

Notes

The authors declare no competing financial interest.

Biographies

Arthur Hirsch received an engineering degree from the Institut Supérieur de l'Aéronautique et de l'Espace (Toulouse, France) and a M.S. in mechanical engineering from EPFL (Lausanne, Switzerland), both in 2013. He obtained his Ph.D. degree in Biotechnology & Bioengineering from EPFL in 2018 and is currently a postdoctoral fellow at EPFL. His current research focuses on stretchable and conformable electronics, soft bioelectronic interfaces, and wearable devices.

Laurent Dejace obtained a B.S. and M.S. in Material Science and Engineering from the Swiss Federal Institute of Technology EPFL (Lausanne, Switzerland). He is currently a Ph.D. candidate in the Laboratory for Soft Bioelectronic Interfaces under the supervision of Prof. Stéphanie P. Lacour, where he works on developing LM-based sensors for wearable applications.

Hadrien O. Michaud received an engineering degree from École Polytechnique (Palaiseau, France) and a M.S. in microengineering from EPFL (Lausanne, Switzerland), both in 2013. He obtained his Ph.D. in microengineering from EPFL in 2018 and is completing his postdoctoral research at EPFL. His research interests include stretchable metallization technologies for skin-like wearable transducers.

Stéphanie P. Lacour received her Ph.D. in Electrical Engineering from INSA de Lyon, France, and completed postdoctoral research at Princeton University and the University of Cambridge. She joined the Swiss Federal Institute of Technology in Lausanne (EPFL) in 2011. She currently holds the Bertarelli Foundation Chair in Neuroprosthetic Technology in the School of Engineering at EPFL and leads the Laboratory for Soft Bioelectronic Interfaces. Since 2018, she is the director of EPFL Center for Neuroprosthetics.

■ REFERENCES

(1) Wagner, S.; Lacour, S. P.; Jones, J.; Hsu, P. I.; Sturm, J. C.; Li, T.; Suo, Z. Electronic Skin: Architecture and Components. *Phys. E* **2004**, *25*, 326−334.

(2) Hammock, M. L.; Chortos, A.; Tee, B. C. K.; Tok, J. B. H.; Bao, Z. 25th Anniversary Article: The Evolution of Electronic Skin (E-Skin): A Brief History, Design Considerations, and Recent Progress. *Adv. Mater.* **2013**, *25*, 5997−6038.

(3) Heikenfeld, J.; Jajack, A.; Rogers, J.; Gutruf, P.; Tian, L.; Pan, T.; Li, R.; Khine, M.; Kim, J.; Wang, J.; Kim, J. Wearable Sensors: Modalities, Challenges, and Prospects. *Lab Chip* **2018**, *18*, 217−248.

(4) Chen, D.; Pei, Q. Electronic Muscles and Skins: A Review of Soft Sensors and Actuators. *Chem. Rev.* **2017**, *117*, 11239−11268.

(5) Whitney, R. J. The Measurement of Volume Changes in Human Limbs. *J. Physiol.* **1953**, *121*, 1−27.

(6) Moskalyk, R. R. Gallium: The Backbone of the Electronics Industry. *Miner. Eng.* **2003**, *16*, 921−929.

(7) Dickey, M. D. Stretchable and Soft Electronics Using Liquid Metals. *Adv. Mater.* **2017**, *29*, 1606425.

(8) Ottaviano, L.; Filipponi, A.; Di Cicco, A. Supercooling of Liquid-Metal Droplets for X-Ray-Absorption-Spectroscopy Investigations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *49*, 11749−11759.

(9) Di Cicco, A. Phase Transitions in Confined Gallium Droplets. *Phys. Rev. Lett.* **1998**, *81*, 2942−2945.

(10) Briggs, L. J. Gallium: Thermal Conductivity; Supercooling; Negative Pressure. *J. Chem. Phys.* **1957**, *26*, 784−786.

(11) Dickey, M. D. Liquid Metals for Soft and Stretchable Electronics. In *Stretchable Bioelectronics for Medical Devices and Systems*; Rogers, J. A., Ghaffari, R., Kim, D.-H., Eds.; Springer International Publishing, 2016; pp 3−30.

(12) Liu, T.; Sen, P.; Kim, C. C. J. Characterization of Nontoxic Liquid-Metal Alloy Galinstan for Applications in Microdevices. *J. Microelectromech. Syst.* **2012**, *21*, 443−450.

(13) Spells, K. E. The Determination of the Viscosity of Liquid Gallium over an Extended Range of Temperature. *Proc. Phys. Soc.* **1936**, *48*, 299−311.

(14) Cheng, S.; Wu, Z. Microfluidic Electronics. *Lab Chip* **2012**, *12*, 2782−2791.

(15) Regan, M. J.; Tostmann, H.; Pershan, P. S.; Magnussen, O. M.; DiMasi, E.; Ocko, B. M.; Deutsch, M. X-Ray Study of the Oxidation of Liquid-Gallium Surfaces. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1997**, *55*, 10786−10790.

(16) Larsen, R. J.; Dickey, M. D.; Whitesides, G. M.; Weitz, D. A. Viscoelastic Properties of Oxide-Coated Liquid Metals. *J. Rheol.* **2009**, *53*, 1305−1326.

(17) Nakakubo, K.; Nomada, H.; Yoshioka, H.; Morita, K.; Oki, Y. Gallium and Polydimethylsiloxane Molding for Self-Organized Spherical Lens Surface Fabrication. *Appl. Opt.* **2017**, *56*, 9900−9906.

(18) Dickey, M. D.; Chiechi, R. C.; Larsen, R. J.; Weiss, E. a.; Weitz, D. a.; Whitesides, G. M. Eutectic Gallium-Indium (EGaIn): A Liquid Metal Alloy for the Formation of Stable Structures in Microchannels at Room Temperature. *Adv. Funct. Mater.* **2008**, *18*, 1097−1104.

(19) Naidich, J. V.; Chuvashov, J. N. Wettability and Contact Interaction of Gallium-Containing Melts with Non-Metallic Solids. *J. Mater. Sci.* **1983**, *18*, 2071−2080.

(20) Miller, E. C. Corrosion of Materials by Liquid Metals. In *Liquid-Metals Handbook*; Lyon, R. N., Ed.; US Government Printing Office: Washington D.C., 1952; pp 144−183.

(21) Simič, V.; Marinković, Ž. Thin Film Interdiffusion of Au and Ga at Room Temperature. *Thin Solid Films* **1976**, *34*, 179−183.

(22) Kramer, R. K.; Boley, J. W.; Stone, H. A.; Weaver, J. C.; Wood, R. J. Effect of Microtextured Surface Topography on the Wetting Behavior of Eutectic Gallium-Indium Alloys. *Langmuir* **2014**, *30*, 533−539.

(23) Dezellus, O.; Eustathopoulos, N. Fundamental Issues of Reactive Wetting by Liquid Metals. *J. Mater. Sci.* **2010**, *45*, 4256−4264.

(24) Tang, J.; Zhao, X.; Li, J.; Guo, R.; Zhou, Y.; Liu, J. Gallium-Based Liquid Metal Amalgams: Transitional-State Metallic Mixtures (TransM2ixes) with Enhanced and Tunable Electrical, Thermal, and Mechanical Properties. *ACS Appl. Mater. Interfaces* **2017**, *9*, 35977−35987.

(25) Smith, D. L.; Caul, H. J. Alloys of Gallium with Powdered Metals as Possible Replacement for Dental Amalgam. *J. Am. Dent. Assoc., JADA* **1956**, *53*, 315−324.

(26) Farrell, Z. J.; Tabor, C. Control of Gallium Oxide Growth on Liquid Metal Eutectic Gallium/Indium Nanoparticles via Thiolation. *Langmuir* **2018**, *34*, 234−240.

(27) Hohman, J. N.; Kim, M.; Wadsworth, G. A.; Bednar, H. R.; Jiang, J.; Lethai, M. A.; Weiss, P. S. Directing Substrate Morphology via Self-Assembly: Ligand-Mediated Scission of Gallium-Indium Microspheres to the Nanoscale. *Nano Lett.* **2011**, *11*, 5104−5110.

(28) Lu, Y.; Hu, Q.; Lin, Y.; Pacardo, D. B.; Wang, C.; Sun, W.; Ligler, F. S.; Dickey, M. D.; Gu, Z. Transformable Liquid-Metal Nanomedicine. *Nat. Commun.* **2015**, *6*, 10066.

(29) Li, X.; Li, M.; Zong, L.; Wu, X.; You, J.; Du, P.; Li, C. Liquid Metal Droplets Wrapped with Polysaccharide Microgel as Biocompatible Aqueous Ink for Flexible Conductive Devices. *Adv. Funct. Mater.* **2018**, *28*, 1804197.

(30) Lin, Y.; Genzer, J.; Li, W.; Qiao, R.; Dickey, M. D.; Tang, S. Sonication-Enabled Rapid Production of Stable Liquid Metal Nanoparticles Grafted with Poly(1-Octadecene-Alt-Maleic Anhydride) in Aqueous Solutions. *Nanoscale* **2018**, *10*, 19871−19878.

(31) Zhang, Q.; Gao, Y.; Liu, J. Atomized Spraying of Liquid Metal Droplets on Desired Substrate Surfaces as a Generalized Way for Ubiquitous Printed Electronics. *Appl. Phys. A: Mater. Sci. Process.* **2014**, *116*, 1091−1097.

(32) Lu, T.; Markvicka, E.; Jin, Y.; Majidi, C. Soft-Matter Printed Circuit Board with UV Laser Micropatterning. *ACS Appl. Mater. Interfaces* **2017**, *9*, 22055−22062.

(33) Ladd, C.; So, J.-H.; Muth, J.; Dickey, M. D. 3D Printing of Free Standing Liquid Metal Microstructures. *Adv. Mater.* **2013**, *25*, 5081−5085.

(34) Boley, J. W.; White, E. L.; Chiu, G. T. C.; Kramer, R. K. Direct Writing of Gallium-Indium Alloy for Stretchable Electronics. *Adv. Funct. Mater.* **2014**, *24*, 3501−3507.

(35) Boley, J. W.; White, E. L.; Kramer, R. K. Mechanically Sintered Gallium-Indium Nanoparticles. *Adv. Mater.* **2015**, *27*, 2355−2360.

(36) Zhang, B.; Dong, Q.; Korman, C. E.; Li, Z.; Zaghloul, M. E. Flexible Packaging of Solid-State Integrated Circuit Chips with Elastomeric Microfluidics. *Sci. Rep.* **2013**, *3*, 1098.

DOI: 10.1021/acs.accounts.8b00489
Acc. Chem. Res. XXXX, XXX, XXX−XXX

(37) Lin, Y.; Gordon, O.; Khan, M. R.; Vasquez, N.; Genzer, J.; Dickey, M. D. Vacuum Filling of Complex Microchannels with Liquid Metal. *Lab Chip* **2017**, *17*, 3043−3050.

(38) Guo, R.; Wang, X.; Chang, H.; Yu, W.; Liang, S.; Rao, W.; Liu, J. Ni-GaIn Amalgams Enabled Rapid and Customizable Fabrication of Wearable and Wireless Healthcare Electronics. *Adv. Eng. Mater.* **2018**, *20*, 1800054.

(39) Jeong, S. H.; Hagman, A.; Hjort, K.; Jobs, M.; Sundqvist, J.; Wu, Z. Liquid Alloy Printing of Microfluidic Stretchable Electronics. *Lab Chip* **2012**, *12*, 4657−4664.

(40) Xu, Q.; Oudalov, N.; Guo, Q.; Jaeger, H. M.; Brown, E. Effect of Oxidation on the Mechanical Properties of Liquid Gallium and Eutectic Gallium-Indium. *Phys. Fluids* **2012**, *24*, No. 063101.

(41) Bilodeau, R. A.; Zemlyanov, D. Y.; Kramer, R. K. Liquid Metal Switches for Environmentally Responsive Electronics. *Adv. Mater. Interfaces* **2017**, *4*, 1600913.

(42) Holcomb, S.; Brothers, M.; Diebold, A.; Thatcher, W.; Mast, D.; Tabor, C.; Heikenfeld, J. Oxide-Free Actuation of Gallium Liquid Metal Alloys Enabled by Novel Acidified Siloxane Oils. *Langmuir* **2016**, *32*, 12656−12663.

(43) Kim, D.; Thissen, P.; Viner, G.; Lee, D. W.; Choi, W.; Chabal, Y. J.; Lee, J. B. Recovery of Nonwetting Characteristics by Surface Modification of Gallium-Based Liquid Metal Droplets Using Hydrochloric Acid Vapor. *ACS Appl. Mater. Interfaces* **2013**, *5*, 179−185.

(44) Li, G.; Wu, X.; Lee, D.-W. Selectively Plated Stretchable Liquid Metal Wires for Transparent Electronics. *Sens. Actuators, B* **2015**, *221*, 1114−1119.

(45) Ozutemiz, B.; Wissman, J.; Ozdoganlar, B.; Majidi, C. EGaIn-Metal Interfacing for Liquid Metal Circuitry and Microelectronics Integration. *Adv. Mater. Interfaces* **2018**, *5*, 1701596.

(46) Hirsch, A.; Michaud, H. O.; Gerratt, A. P.; de Mulatier, S.; Lacour, S. P. Intrinsically Stretchable Biphasic(Solid−Liquid) Thin Metal Films. *Adv. Mater.* **2016**, *28*, 4507−4512.

(47) Yu, F.; Xu, J.; Li, H.; Wang, Z.; Sun, L.; Deng, T.; Tao, P.; Liang, Q. Ga-In Liquid Metal Nanoparticles Prepared by Physical Vapor Deposition. *Prog. Nat. Sci.* **2018**, *28*, 28−33.

(48) Kim, D.; Lee, J. Micro/Nano Hierarchical Super-Lyophobic Surfaces Against Gallium-Based Liquid Metal Alloy. In *Surface Energy*; Aliofkhazraei, M., Ed.; IntechOpen, 2015; pp 265−287.

(49) Hirsch, A.; Lacour, S. P. A Method to Form Smooth Films of Liquid Metal Supported by Elastomeric Substrate. *Adv. Sci.* **2018**, *5*, 1800256.

(50) Bico, J.; Thiele, U.; Quéré, D. Wetting of Textured Surfaces. *Colloids Surf., A* **2002**, *206*, 41−46.

(51) Park, C. W.; Moon, Y. G.; Seong, H.; Jung, S.-W.; Oh, J.-Y.; Na, B. S.; Park, N.-M.; Lee, S. S.; Im, S. G.; Koo, J. B. Photolithography-Based Patterning of Liquid Metal Interconnects for Monolithically Integrated Stretchable Circuits. *ACS Appl. Mater. Interfaces* **2016**, *8*, 15459−15465.

(52) Michaud, H. O.; Lacour, S. P. Liquid Electromigration in Gallium-Based Biphasic Thin Films. *APL Mater.* **2018**, in press.

(53) Dutta, I.; Kumar, P. Electric Current Induced Liquid Metal Flow: Application to Coating of Micropatterned Structures. *Appl. Phys. Lett.* **2009**, *94*, 184104.

(54) Michaud, H. O. *Stretchable Metallization Technologies for Skin-like Transducers*, EPFL, Lausanne, 2017.

(55) Khan, M. R.; Trlica, C.; So, J. H.; Valeri, M.; Dickey, M. D. Influence of Water on the Interfacial Behavior of Gallium Liquid Metal Alloys. *ACS Appl. Mater. Interfaces* **2014**, *6*, 22467−22473.

(56) Ellerbrock, D.; Macdonald, D. Passivity Breakdown on Solid Versus Liquid Gallium. *J. Electrochem. Soc.* **1994**, *141*, 2645−2649.

(57) Hirsch, A. *Electronic Dura Mater Soft, Multimodal Neural Interfaces: Technology, Integration and Implementation to Surface Implants*, EPFL, Lausanne, 2018.

(58) Yu, Z. W.; Chen, Y. C.; Yun, F. F.; Wang, X. L. Simultaneous Fast Deformation and Solidification in Supercooled Liquid Gallium at Room Temperature. *Adv. Eng. Mater.* **2017**, *19*, 1700190.

(59) Fassler, A.; Majidi, C. 3D Structures of Liquid-Phase GaIn Alloy Embedded in PDMS with Freeze Casting. *Lab Chip* **2013**, *13*, 4442−4450.

(60) Joseph, B.; Picat, M.; Barbier, F. Liquid Metal Embrittlement: A State-of-the-Art Appraisal. *Eur. Phys. J.: Appl. Phys.* **1999**, *5*, 19−31.

(61) Ahlberg, P.; Jeong, S. H.; Jiao, M.; Wu, Z.; Jansson, U.; Zhang, S. L.; Zhang, Z. Graphene as a Diffusion Barrier in Galinstan-Solid Metal Contacts. *IEEE Trans. Electron Devices* **2014**, *61*, 2996−3000.

(62) Yan, J.; Lu, Y.; Chen, G.; Yang, M.; Gu, Z. Advances in Liquid Metals for Biomedical Applications. *Chem. Soc. Rev.* **2018**, *47*, 2518−2533.

(63) Kim, J. H.; Kim, S.; So, J. H.; Kim, K.; Koo, H. J. Cytotoxicity of Gallium-Indium Liquid Metal in an Aqueous Environment. *ACS Appl. Mater. Interfaces* **2018**, *10*, 17448−17454.

(64) Gerratt, A. P.; Michaud, H. O.; Lacour, S. P. Elastomeric Electronic Skin for Prosthetic Tactile Sensation. *Adv. Funct. Mater.* **2015**, *25*, 2287−2295.

(65) Michaud, H. O.; Teixidor, J.; Lacour, S. P. Soft Metal Constructs for Large Strain Sensor Membrane. *Smart Mater. Struct.* **2015**, *24*, No. 035020.

(66) Michaud, H. O.; Teixidor, J.; Lacour, S. P. Soft Flexion Sensors Integrating Stretchable Metal Conductors on a Silicone Substrate for Smart Glove Applications. In *2015 28th IEEE International Conference on Micro Electro Mechanical Systems (MEMS)*; 2015; pp 760−763.

(67) Michaud, H. O.; Dejace, L.; de Mulatier, S.; Lacour, S. P. Design and Functional Evaluation of an Epidermal Strain Sensing System for Hand Tracking. In *2016 IEEE/RSJ. International Conference on Intelligent Robots and Systems (IROS)*; Daejeong, Korea, 2016; pp 3186−3191.

(68) Park, Y.-L.; Chen, B.-R.; Wood, R. J. Design and Fabrication of Soft Artificial Skin Using Embedded Microchannels and Liquid Conductors. *IEEE Sens. J.* **2012**, *12*, 2711−2718.

(69) Rashed Khan, M.; Hayes, G. J.; So, J. H.; Lazzi, G.; Dickey, M. D. A Frequency Shifting Liquid Metal Antenna with Pressure Responsiveness. *Appl. Phys. Lett.* **2011**, *99*, No. 013501.

(70) Jeong, Y. R.; Kim, J.; Xie, Z.; Xue, Y.; Won, S. M.; Lee, G.; Jin, S. W.; Hong, S. Y.; Feng, X.; Huang, Y.; Rogers, J. A.; Ha, J. S. A Skin-Attachable, Stretchable Integrated System Based on Liquid GaInSn for Wireless Human Motion Monitoring with Multi-Site Sensing Capabilities. *NPG Asia Mater.* **2017**, *9*, No. e443.

(71) Pan, C.; Kumar, K.; Li, J.; Markvicka, E. J.; Herman, P. R.; Majidi, C. Visually Imperceptible Liquid-Metal Circuits for Transparent, Stretchable Electronics with Direct Laser Writing. *Adv. Mater.* **2018**, *30*, 1706937.

(72) Kim, D.; Lee, D. W.; Choi, W.; Lee, J. B. A Super-Lyophobic 3-D PDMS Channel as a Novel Microfluidic Platform to Manipulate Oxidized Galinstan. *J. Microelectromech. Syst.* **2013**, *22*, 1267−1275.