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Hydroprinted Electronics: Ultrathin Stretchable Ag−In−Ga E-Skin for Bioelectronics and Human−Machine Interaction

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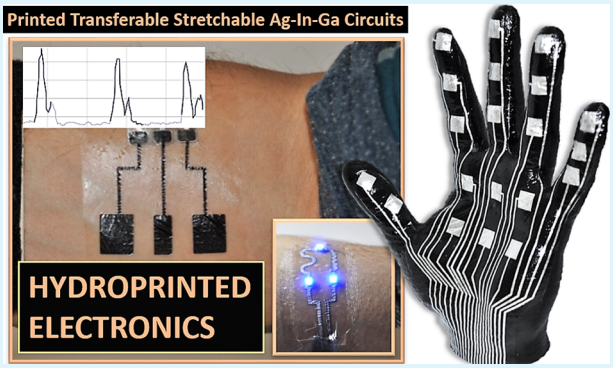
Supporting Information

ABSTRACT: We introduce a soft ultrathin and stretchable electronic skin with surface-mounted components that can be transferred and wrapped around any three-dimensional (3D) surface or self-adhere to the human skin. The ∼5 μm thick circuit is fabricated by printing the pattern over a temporary tattoo paper using a desktop laser printer, which is then coated with a silver ink and eutectic gallium−indium (EGaIn) liquid metal alloy. The resulting "Ag−In−Ga" traces are highly conductive and maintain low electrical resistivity as the circuit is stretched to conform to nondevelopable 3D surfaces. We also address integration of surface-mounted microelectronic chips by introducing a novel *z*-axis conductive interface composed of magnetically aligned EGaIn-coated Ag−Ni microparticles embedded in polyvinyl alcohol (PVA). This "*z*PVA conductive glue" allows for robust electrical contacts with microchips that have pins with dimensions as small as 300 μm. If printed on the temporary tattoo transfer paper, the populated circuit can be attached to a 3D surface using hydrographic transfer. Both printing and interfacing processes can be performed at the room temperature. We demonstrate examples of applications, including an electronic tattoo over the human epidermis for electromyography signal acquisition, an interactive circuit with touch buttons, and light-emitting diodes transferred over the 3D printed shell of a robotic prosthetic hand, and a proximity measurement skin transferred over a 3D surface.



KEYWORDS: *liquid metal, EGaIn, silver lnks, hydroprinted electronics, anisotropic conductor, stretchable electronics, electronic tattoo, printed electronics*

INTRODUCTION

Electronics circuits that interface with the human body or surface of objects can enable functionalities such as acquisition of biosignals, detection of human touch, proximity, temperature, and energy harvesting.[1,2] These circuits can also integrate antennas and display[3] over the surface of the object, and turn them into an interactive reciprocal surface, which has applications in human−machine interfaces (HMIs) and large area displays. Moreover, when integrated over the human epidermis, these circuits enable applications in wearable computing and health monitoring. Recent efforts have focused on additive manufacturing techniques to create integrated, three-dimensional (3D) material systems that achieve these functionalities.[4,5] These 3D printing techniques have been extended to cover a wide material palette: carbon nanotubes for super capacitors,[6] ferromagnetic photopolymers for magnetic sensors,[7] shape memory polymers for "4D printing",[8] and conductive materials for strain or pressure sensors.[9,10] There have also been recent demonstrations of printing electronics and other functional materials over an existing 3D surface[11] or on the human body.[12]

Although promising, direct printing over three dimensional surfaces is a complex process, requiring the print head to precisely follow the surface morphology to deposit a conductive ink or paste. This is generally a slow and not a scalable process. One possible alternative is 2D printing of circuits which can be transferred to a 3D surface. This can be accomplished through hydroprinting, in which patterned thin films floating on the surface of a water bath are transferred to the surface of 3D objects as the objects are removed from the batch. Hydroprinting can be an alternative to 3D printing of electronics over the surface of the object or the human skin. However, extension of this technique to printed electronics can be challenging because successful transfer of a 2D circuit over a

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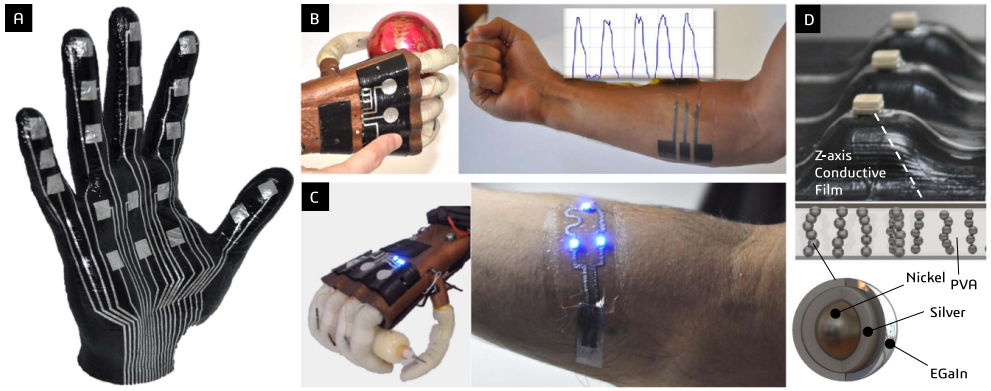

Figure 1. Hydroprinted electronics. (A) Example of the capacitive proximity sensor mesh printed over the transfer paper and hydroprinted over a 3D printed hand model. (B) Example of a functional printed circuit, hydroprinted over 3D printed shell of a prosthetic hand and electronic tattoos over the human skin for acquiring biopotentials. (C) The ultrathin carrier film of the TTP can be populated with SMD chips prior to transfer, thanks to the anisotropic *z*PVA matrix developed in this work. (D) The *z*PVA interface is composed of Ag-coated Ni particles with an additional EGaIn coating layer in a PVA gel. These particles form conductive columns that conduct electricity only on the *z*-axis, which facilitates interfacing of small SMD components.

complex, nondevelopable 3D surface requires the circuit not only to bend but also to stretch. To accomplish this, engineers have developed "epidermal electronics" composed of sensors and digital integrated circuit chips incorporated into an ultrathin carrier film that can readily transfer to the human skin.[13] These can function like an "electronic tattoo" and have been used for biomonitoring,[13] implantable energy harvesting,[14] pulse oximetry,[3] and neural interfaces.[15] Seminal efforts on fabrication of soft-matter electronics have focused on deterministic circuit architectures in which stretchable functionality is achieved with circuit traces that have a wavy or serpentine geometry.[13] However, although promising, these approaches typically rely on cleanroom lithography or specialized processing steps that are difficult to perform with low-cost printing or rapid prototyping methods. Extending epidermal electronics to applications in robotics, HMIs require continued exploration of new material architectures and processing techniques that are accessible to a wider user community. In particular, these approaches should have limited dependency on clean-room fabrication methods (e.g., photolithography) or high-temperature processing steps. Moreover, such circuits should be able to directly interface with microelectronic chips or printed circuit boards (PCBs) for data processing and transmission without the need for external electrical wiring.

Here, we demonstrate a novel method for rapid fabrication of tattoo-like, thin-film circuits with integrated microelectronics that utilizes desktop printing and hydrographic transfer techniques. The current work greatly simplifies these manufacturing techniques by eliminating the need for microfabrication, post sintering, thin-film metal deposition, and lithographic patterning. Unlike other methods for producing ultrathin and epidermal electronics, fabrication can be performed using a commercially-available desktop printer and eliminates the need for expensive processing steps or custom-built equipment. Circuits can be printed on a transfer tattoo paper (TTP) or hydrographic paper and transferred to the body or a 3D surface (Figure 1A). The TTP used in this work is composed of an ultrathin (<5 μm) carrier film, a water soluble polyvinyl alcohol (PVA) layer, and backing paper (Figure S1). When in contact with water, the carrier film separates from the paper, and floats over the surface of the water, which can be then transferred in a water tank over various materials, for example, skin, cloth, plastic, metal, and glass (Figure 1A–D). Circuits are created by first printing a circuit template on TTP using a desktop printer. Recently, we have shown that circuits can be produced by printing silver nanoparticle (AgNP) ink using an inkjet printer and then coating the printed traces with a liquid-phase eutectic gallium–indium (EGaIn 75.5 wt % Ga, 24.5 wt % In, melting point: 15.7 °C) alloy.[16] EGaIn coating increases the conductivity of the printed AgNPs by 6 orders of magnitude and makes the circuits considerably tolerant to mechanical strain.

Here, we show a novel method to produce "Ag–In–Ga" circuits, which starts by using a desktop laserjet to print a nonconductive template with print toner and then coat the template with silver paste. The silver paste will selectively adhere only to the printed toner ink and function as a wetting layer on which to deposit the EGaIn. In both cases, the resulting circuits are highly conductive, and after the transfer, they conform to nondevelopable 3D surfaces without losing their conductivity. When compared to AgNP inks, this method is simpler and faster because it eliminates the need for modification of an inkjet printer, cleaning, and filling the cartridges with the ink, as well as periodical ink filtering, ink sonication, and replacement or cleaning of the cartridge due to clogging. Also, conductive pastes are made with microparticles or microflakes; they are considerably easier to produce and customize in terms of conductivity and adhesion, by changing parameters such as the filler content, the filler size, and the carrier material. Therefore, they exist in a wider variety and are more affordable when compared to AgNP inks. However, previously their deposition had required stencils and a postbaking step, which is a disadvantage compared to inkjet printing. Both of these requirements have been eliminated with the current technique.

Although the presented method significantly facilitates printing of the circuit interconnects, actual application of these circuits still depends on development of methods for robust electrical interfacing with external circuits and direct interfacing of the printed pattern with microchips. In this article, we address both by introducing a novel *z*-axis conductive interface (Figure 1D). The interface is composed of vertically aligned magnetic particles embedded in a PVA

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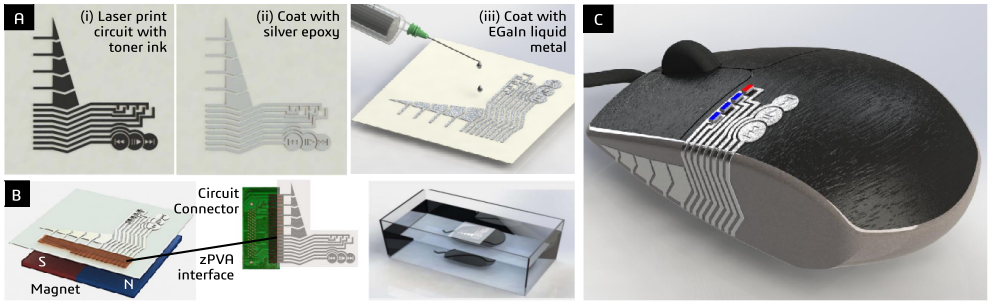

Figure 2. Fabrication steps overview. Fabrication can include printing, interfacing with microelectronic chips or external circuits, and hydroprinting. After printing the pattern with a desktop laser printer [A(i)], the circuit template is coated with subsequent layers of Ag paste [A(ii)] and EGaIn alloy [A(iii)]. The excess metallic coatings are rinsed away after each deposition step. Surface-mounted electronics or external circuits are connected using an anisotropic "*z*PVA glue" (B). Finally, the circuit can be transferred over a surface using hydrographic transfer (C).

film. This gel-like "*z*PVA glue" can be used for interfacing the thin-film skin with microelectronics and flex circuits. The gel to solid transformation of *z*PVA is achieved by evaporation of water in the solution, which can be performed at room temperature. Compared to previous PDMS-based anisotropic conductors,[17,18] *z*PVA adheres to a wider range of materials, including the PVA-based transfer paper.

BACKGROUND

Our approach to thin-film stretchable electronics builds on previous efforts in "biphasic" material architectures that combine EGaIn with metallic templates to create mechanically robust circuits. In these previous techniques, EGaIn is coated on a sputter-deposited thin film of the metal (Au, Ag, or Cu) that is patterned using either photolithography[19−21] or UV laser micromachining.[22,23] Other research efforts focused on synthesis of EGaIn nanoparticles[24] that can be printed on a stretchable substrate and "mechanically sintered" to create conductive traces.[25,26]

We improve upon this past work by introducing "facile" fabrication techniques that enable patterning on a TTP thin film using any standard commercial desktop printer. The analysis of the EGaIn-assisted room temperature "sintering" of the AgNP ink is not the focus of this article and was covered in a recent companion study.[16] Instead, we focus on techniques that allow for rapid fabrication of thin-film circuits without dependency on a clean-room or specialized processing equipment. As a case study, we demonstrate applications to human−machine interaction and demonstrate how one can be rapidly printed and transfer these thin-film circuits to 3D surfaces, and use it as a sensing skin. In particular, we show that the circuits can be transferred over complex non-developable 3D surfaces (i.e. spherical features), and over sharp edges using hydroprinting methods. We also demonstrate that such circuits can self-adhere to the human epidermis for acquisition of biopotentials from muscle activity, for example, electromyography (EMG).

Although free-standing nanofilms composed of the poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS) polymer[27] and printed Ag ink[28] have been previously shown as thin-film conductors that can be released in water, the current work improves over its predecessors by taking advantage of "Ag−In−Ga" interconnects which are stretchable and allows the transfer to be performed over more complex surfaces, including 180° folding. In addition, sealing the circuit with a *z*PVA anisotropic conductor allows the surface to be populated with SMD components and enables robust interfacing with external electronics. Finally, the facile fabrication technique presented here allows stencil-free disposition of viscous silver pastes that permits rapid prototyping of customized circuits, such as multielectrode patterns for conformal and imperceptible tattoo-like circuits for biomonitoring applications.

RESULTS

The fabrication process is composed of four stages: circuit printing, materials postprocessing, microchip integration, and hydrographic transfer. In the first stage, a circuit is produced through selective deposition of silver paste or epoxy on a TTP film after printing the pattern by a desktop laser printer (Figure 2A). In order to improve electrical conductivity and stretchability, the circuits are then coated with EGaIn using the steps presented in Figure 2A, Movie S1, and described in the Materials and Methods section. The liquid metal (LM) alloy selectively wets to Ag traces when exposed to a weak (2 wt %) acetic acid solution or hydrochloric acid vapor (Figure 2A, and Movie S1). That is, after the initial deposition, EGaIn oxide wets the TTP surface, including the printed and nonprinted areas. However, treating EGaIn with CH_3COOH or HCl removes its surface oxide (Ga_2O_3), which results in dewetting from the uncoated TTP (because of the high surface tension of nonoxidized EGaIn) and stronger adhesion (and possible alloying) to the silver particles. Oxide reduction can also be performed with aqueous solutions of NaOH,[29] in which case the silver particles act as "anchoring points" that prevent the LM from dewetting and rinsing away.

The resulting "Ag−In−Ga" circuit is sealed with a coating of *z*PVA composite (Figure 2B), which is composed of vertically aligned conductive particles embedded in a PVA gel (Figure 1D). The seal is conductive only through its thickness and enables the formation of electrical vias between the terminals of the circuit and pins of surface-mounted microelectronics and circuit board connectors. The composite is prepared by mixing Ag-coated Ni particles with PVA. A thin film of the mixture is applied over the circuit using a thin-film applicator (ZUA12-ZEHNER), and the components are placed over the film. Alternatively, screen printing or spin-coating can be used to deposit a thin film of the *z*PVA mixture. The circuit is then placed over a magnet, while the water is being evaporated from the film. In this way, the Ag−Ni particles align to form vertical columns that conduct electricity only through the film thickness. This can be used to interface flex circuits and microelectronics components and other PCBs (Figure 2B). Movie S5 shows the transferring process for a circuit populated

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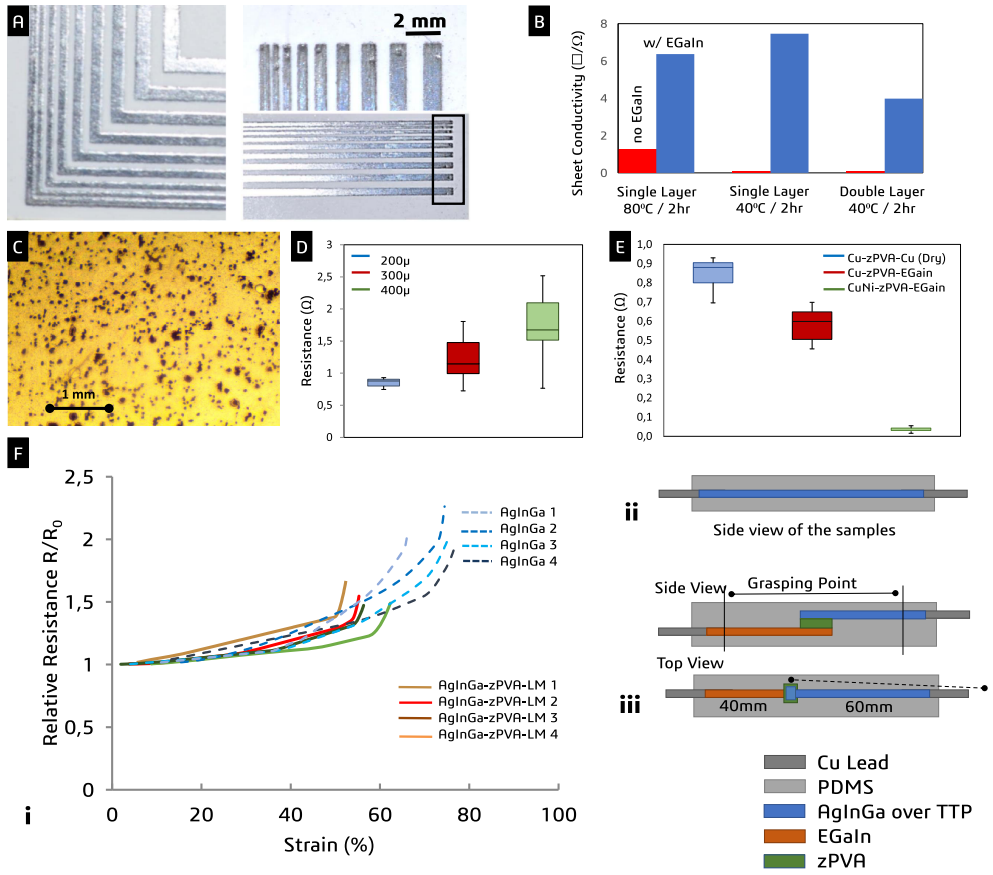

Figure 3. Characterization of printing resolution, sintering and interfacing materials and techniques, and resistance change vs strain. (A) Benchmark circuit printed with the laser printer and produced with the "Ag−In−Ga" method. (B) Sheet resistance of printed traces before and after EGaIn deposition for three different curing temperatures of Ag-epoxy and also for double Ag epoxy deposition. (C) Microscopic image from the 200 μm zPVA film. (D) zPVA resistance for three different film thickness, using copper pads on both sides of an already dried zPVA, measured with the four-terminal sensing method. (E) z axis resistance for a zPVA film sandwiched between various pairs of conductor materials. (F) Change of resistance vs strain for samples of "Ag−In−Ga" sandwiched within the PDMS layer with [F(iii)] and without the zPVA interface [F(ii)].

by light-emitting diode (LED) chips and interfaced with the flexible PCB (FPCB) through zPVA. Contact resistance and electromechanical integrity can be further improved by coating the contact pads or Ag−Ni particles with a thin layer of EGaIn.

Circuits produced with the aforementioned method can be transferred to other surfaces using hydrographic transfer, also referred to as water transfer printing or immersion printing (Figure 2C and 4A). First, a host object is fully immersed in a water bath or tank. Next, the "Ag−In−Ga" circuit is suspended on the surface of a water bath. After some seconds, the water-soluble middle layer of the TTP substrate dissolves and separates the 5 μm carrier film from the backing paper. The carrier film then clings to the object and conforms to its surface as the object is subsequently lifted out of the water bath. Because it is thin and stretchable, the film is able to follow closely the shape of the surface and can even support 180° self-folding or bending around a thin part (Figure 4A). After removal from the bath, the substrate and circuit are allowed to dry. After transfer, the circuit may be spray coated with a protective plastic seal. The procedure for the film transfer differs slightly based on the type of the transfer paper used. As an example, the hydrographic paper requires different steps than the TTP—for the hydrographic paper, the carrier film is made out of PVA and polyvinyl acetate (PVAc), and there is no separate water soluble layer. In this case, the backing paper is removed manually prior to floating over water. In addition, the host surface should approach the film from above and enter the water when bonding with the circuit. The fabrication and transfer process is also shown in Movie S1.

In order to establish the patterning resolution, a test circuit was printed using a laser printer, followed by the Ag and EGaIn deposition, as previously described. Referring to Figure 3A, lines with equal width and spacing from 50 to 1000 μm were printed and observed after deposition of Ag epoxy and EGaIn coating. As can be seen in the figure, this technique is able to successfully print lines with a pitch of 200 μm. Smaller spacing resulted in unintended connections between adjacent lines. Referring to Figure 3B, the GaIn-coated Ag traces exhibit at least a 6 order of magnitude improvement in electrical conductivity. To determine this, we tested the conductivity of 10 samples after laser printing and Ag paste deposition. After deposition of EGaIn, nonconductive traces of Ag paste showed a sheet resistance of 0.13 Ω/□ (average of 10 measurements), on these samples, and Ag circuits were cured at 40 °C for 2 h, prior to EGaIn deposition. In this way, Ag adheres to the underlying printed toner, and thus excessive Ag can be easily removed by a lint-free cloth. Alternatively, Ag paste can be dried at room temperature for 24 h. If heated to higher temperatures (e.g. 80 °C), circuits demonstrate a sheet resistance of 0.80 Ω/□ prior to EGaIn deposition and 0.16 Ω/□, after EGaIn deposition. When dried at lower temperature, there is a significant difference between the bonding forces of

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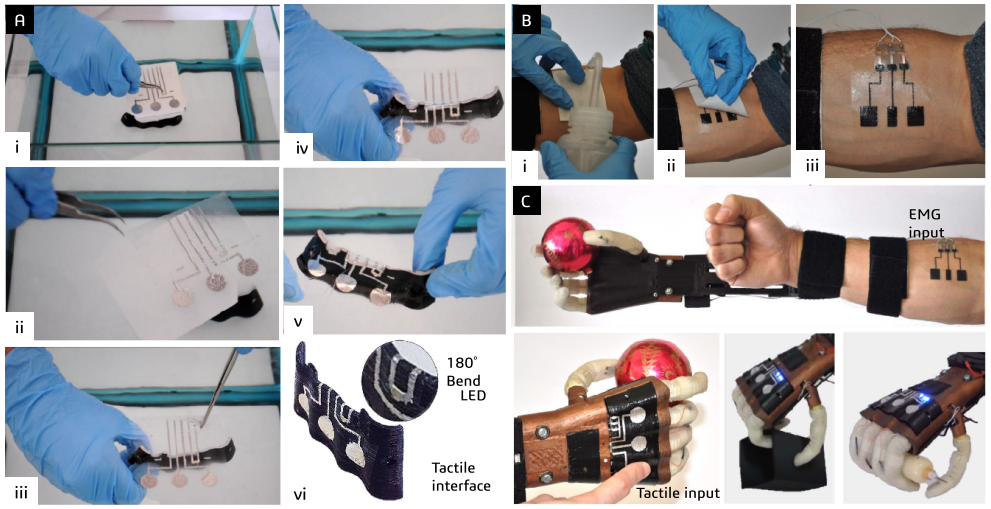

Figure 4. Hydrographics transfer method and applications for a prosthetic hand. (A) Process for hydroprinting of the thin-film electronics composed of capacitive tactile input sensors and surface-mount LEDs over the 3D printed shell of the prosthetic hand, including (B). Process for application of an electronic tattoo over the forearm for EMG signal acquisition (C). The hand can be controlled by EMG input or by the hydroprinted circuit over the hands shell. This contains tactile inputs and surface-mount LEDs for reciprocal human−machine interaction.

Ag over the printed circuit and rest of the substrate. This makes it easy to remove the excessive Ag with a piece of cloth and mild mechanical force and without damaging the circuit. Curing at higher temperature improves the bonding of the deposited Ag with the whole substrate, which makes it necessary to apply an additional force, which can damage the circuit. In addition, at higher temperature, the carrier film deforms through thermal expansion, which affects the subsequent transfer of the film.

In order to characterize the *z*-axis resistance of *z*PVA, we deposited films of 200, 300, and 400 μm thickness over glass and then released the film by peeling it from the glass after it dried. Two pieces of the flex circuit with round contact pads of 3 mm diameter were placed on both sides of the *z*PVA film, and the resistance between them was measured with four-terminal sensing. Figure 3D shows average results for 10 measurements. As expected, the resistivity increases with the film thickness. In another test, we deposited a 200 μm film of *z*PVA directly over a copper substrate and allowed it to dry. Afterward, we spray-coated 3 mm diameter circles of EGaIn over the *z*PVA film, using a laser-patterned stencil (Figure S4). Spray deposition was performed with atomized droplets of the LM similar, using a spray gun similar to the method presented in ref 30. Within this setup, the average value of *z*-axis resistance was reduced from 0.86 Ω for the Cu−*z*PVA−Cu interface to 0.57 Ω for the Cu−*z*PVA−LM interface (Figure 3E). This improvement can be explained by the number of Ag-coated Ni particles that are able to connect and form a continuous electrically conductive pathway between the opposite sides of the *z*PVA film. Such conductivity is aided by the ability of the LM alloy to fill the interface and form a more conformal contact. When replacing the Cu substrate with a conductive fabric (Cu/Ni-coated nonwoven fabric—3M CN-3490), the resistance of the *z*-axis interface was further reduced by over a factor of ten (average = 0.03 Ω; see Figure 3E). This dramatic enhancement can be explained by the ferromagnetic properties of the nickel coating of the conductive fabric. When *z*PVA is drying over the magnet, the Ag-coated Ni beads can make strong adhesion with the underlying Ni coating, which contributes to better conductivity.

In order to characterize the electrical behavior of these circuits under mechanical strain, we performed a set of electromechanical tests (Figure 3F). The test includes measuring the relative resistance of the circuits when subject to uniaxial strain. One set of tests includes samples of printed "Ag−In−Ga" over the TTP, which was prepared by the method referred above, and then sandwiched between two PDMS layers (Figure 3F(ii)). More information on sample preparation can be found in the Materials and Methods section. Results show that "Ag−In−Ga" samples can withstand a maximum strain of 73.1% (std = 4.7%). When integrating *z*PVA (Figure 3F(iii)), this value reduces to 56.7% (std = 4.2%). As expected, the sample with *z*PVA breaks at a lower strain rate because of the difference in the Young's modulus of *z*PVA and TTP. All these samples broke at the *z*PVA interface. Also, the changes on the resistance of samples against strain is the modest (R/R_o = 1.5, std = 0.22), at 60% strain. This is an important beneficial factor for application in stretchable digital circuits. Last, "Ag−In−Ga" circuits are very robust when in contact with water. Figure S3 shows a functional circuit floated on water and Movie S4 shows a circuit that is immersed in a water tank and remains functional after being removed from water.

APPLICATIONS

Figure 4 presents two examples of how the circuits can be used for applications in robotics and human−machine interaction. Both circuits are designed to improve the user control over a prosthetic hand. As we previously reported, despite rapid advances in the mechatronics of prosthetic hands, the HMI still has limited functionality, that is, the amputee does not have enough control inputs to operate all available grasping postures of an advanced prosthetic hand.[31] Here, we show how hydroprinted electronics can improve HMI functionality in a low cost manner. In one implementation, we can create an electronic tattoo that is placed over the human forearm and collects EMG signals (Figure 4B). The user can use the "EMG tattoo" to control a robot hand prosthetic. In second implementation, the surface of the prosthetic is coated with LEDs for visual feedback and a tactile interface for additional

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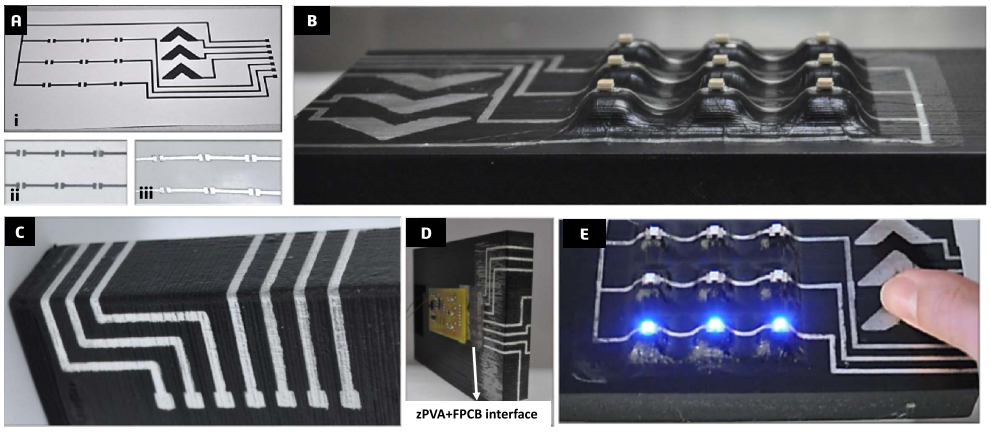

Figure 5. Printed "Ag−In−Ga" circuit with capacitive proximity sensors and LEDs transferred over a complex 3D surface. (A) Initial print with a laser printer (i), after silver epoxy deposition (ii), and after EGaIn deposition (iii). (B). Circuit transferred over the 3D printed part (C). During the transfer, interconnects bend over and effectively adhere to the host surface (D). The end points are then interfaced with a PCB through a flex circuit and *z*PVA (E). Final circuit: hand proximity turns the LEDs on.

control inputs: (i) closing further the hand, (ii) emergency opening, and (iii) changing the closing pattern. Figure 4A shows how the circuit with tactile inputs is transferred over the 3D printed shell of the prosthetic hand, including a 180° bend. Figure 4B demonstrates how the "electronic tattoo" with acquisition electrodes is applied over the human hand. Figure 4C and Movie S2 demonstrate application of both EMG and tactile input. Note that there is no need to change the original design of the 3D printed shell to accommodate the circuit. Both tactile inputs and surface mount LEDs adhere to the surface and function as they are programmed. Because circuits are produced by desktop laserjet printing, they are highly customizable in terms of design, dimensions, and graphics. They are also low cost and can be rapidly fabricated and applied in ∼30 min. Control of the hand both with the EMG sensor and the tactile input are also demonstrated in Movie S2.

Movie S5 shows an example of a circuit transferred to the human forearm (Figure 1C). The circuit is populated with SMD LEDs as well as a FPCB interface to which cables are soldered. Another example is presented in Figure 5 and Movie S3, which shows three proximity sensors and nine LEDs mounted to the film. Each row of three LEDs turns on when the respective proximity sensor is activated. Also, the light intensity can be controlled by changing the distance of the hand from the surface. These thin-film circuits were first printed with a laser printer, followed by Ag paste, and LM deposition (Figure 5A). Figure 5B shows the circuit after the transfer. By adding the tactile inputs and LEDs, the 3D-printed front side of the surface is turned into a reciprocal user interface, and the processing circuits can be hidden on the backside when necessary. Figure 5D shows *z*PVA for interfacing the applied E-skin, an intermediate flex circuit, and the backside PCB.

When in contact with water, the PVA film of the hydrographic paper transforms to a gel state, which carries the "Ag−In−Ga" traces. The PVA gel conforms to the host surface and texture, and achieves a permanent bond when dried. In this case, the circuit becomes an integrated part of the host that cannot be peeled off. For increasing the resistance to wear and humidity, other polymers can be coated over the circuit, for example, by spray coating, as can be seen in Movie S1. PVA achieves a strong bond with most of the daily use materials such as wood, paper, fabric, and most plastics and metals.

DISCUSSION

Hydroprinted electronics have a potentially transformative impact on the way we fabricate and mount thin-film electronics onto robots, machines, and other 3D objects. The ultrathin carrier film that we use here conforms to nondevelopable 3D surfaces and "Ag−In−Ga" circuits are able to follow the surface morphology without losing their conductivity. As has previously been shown, thin-film soft electronics also represent a step toward a new generation of electronic tattoos that can be used for biomonitoring purposes. Here, we presented a new material architecture and fabrication method that simplifies the ability of making these 3D-transferrable electronic skins (E-skin). This novel approach is enabled by "Ag−In−Ga" circuits that can be produced rapidly in ambient conditions with relatively simple and low-cost patterning techniques. By eliminating the need for high-temperature curing, this technique may be used for printing on a wide range of soft and elastic substrates.

We have selected EGaIn as the LM because it is nontoxic and fuses with silver particles to form a semisolid substance that exhibits high electrical conductivity and low electro-mechanical coupling. This room-temperature method for metallic fusion of silver particles eliminates the need for heat treatment or thermal sintering.[15] Although elevated temperatures are typically required for inducing electrical conductivity in silver pastes or epoxies, they can permanently damage the TTP substrate. This postprocessing results in a mechanically robust circuit that can be populated with surface-mounted electronics and transferred to a 3D surface.

In addition to a new approach to E-skin circuit printing, we have introduced a novel *z*PVA anisotropic conductor composite that enables interfacing between these circuits with surface-mounted electronics or flex cables. Commercial anisotropic conductors, (e.g. 3M *z*-axis films) claim a *z*-axis resistance of ∼0.2 Ω for a 50 μm anisotropic film for Cu−Cu interfacing. However, these values greatly depend on materials being interfaced, the assembly method, the pressure applied, and the film thickness. Some of these parameters has been discussed in,[17] where a *z*-axis resistance of ∼1 Ω was obtained for a 9 mm^2 pads with a 173 μm thick *z*PDMS. The new

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composition of zPVA was intended for being compatible to the TTP, and the host surface, because PVA bonds to a wide variety of materials.

When exposed to water, the zPVA glue becomes soft and moldable and can easily conform to 3D objects. In general, it is capable of bonding to a wide range of materials and is safe for the human skin. For applications of interest, the composite functions as an array of z-axis vias that connect the terminals of the embedded "Ag−In−Ga" circuit with the pins of surface-mounted electronics. In addition, zPVA provides two particularly interesting features that contribute to successful thin-film transfer. First, in some transfer films, the carrier film is made out of a mixture of PVA and PVAc. Therefore, zPVA is naturally compatible with the carrier film and forms a robust bond. Second, during transfer, PVA becomes soft and can readily conform to the host surface upon contact. This feature is useful when transferring the circuit because it allows electrical connections with surface-mounted components to remain intact even as the substrate stretches and folds. When applied over the benchmark circuit of Figure 4A, the zPVA film could conduct over the z axis of all lines, starting from the 300 μm wide line without causing a short circuit with adjacent lines.

To demonstrate its application in robotics and HMIs, we incorporate the printed E-skin into the 3D printed shell of a prosthetic hand that includes LEDs and capacitive tactile inputs used for easy human−machine interaction for control of the closing and opening functions. We also use the circuit as an "electronic tattoo" that self-adheres to a human forearm and is capable of acquiring EMG signals. Such demonstrations also represent improvements over previous efforts to incorporate skin-like structures with gas sensors,[32] temperature sensors,[33] proximity, and pressure sensing.[34−36] With the presented method, E-skins with distributed sensing elements might be rapidly printed and transferred over 3D surfaces.

In the case of biomonitoring tattoos, we observe that the functionality of the circuit is limited to a few hours, depending on the skin condition (e.g. sweating), the part of the body over which the tattoo is applied, and amount of physical activity. When the TTP is applied to the body, the skin is in direct contact with the 5 μm plastic layer. However, the skin forms a stronger bond with the PVA adhesive, which is typically coated on the surface of the TTP film (by manual transfer using a separate sheet of PVA-coated paper) prior to application over the skin. However, for biomonitoring tattoos, the adhesive layer cannot be applied because it is electrically insulating and interferes with detecting bioelectric signals.

CONCLUSIONS

Epidermal electronics and E-skins represent promising technologies for more ubiquitous physical human−machine interaction. We present a rapid, low cost, and highly customizable approach to create ultrathin E-skins that can be transferred to natural human skin or the surface of rigid 3D objects. To demonstrate its potential role in robotics, we presented several applications involving skin-mounted bio-potentials acquisition and control of a robotic hand prosthesis. Because the circuits are thin and stretchable, they can be transferred to nondevelopable features like the surface protrusions shown in Figure 5. This transfer is accomplished with hydrographic printing, which has been popular for visual design and decorative arts in industries like automotive. Although promising, the extension of hydrographic transfer to printed electronics is still in its nascent stages and requires further study on factors like wear resistance and long-term durability. Moreover, the zPVA interface requires further characterization of its mechanical properties and electrical compatibility with a wider range of materials.

MATERIALS AND METHODS

Printing the Circuits. In order to produce a stretchable thin-film circuit, a circuit template is first printed on a TTP substrate (Silhouette) using a desktop LaserJet printer (MFC-L2700DW; Brother) and toner (TN2320; Brother). Next, silver epoxy (Atom Adhesive-DUCT AD1) is deposited over the substrate (Figure 2A). With a hot air blower, silver epoxy is dried for ∼10 s, and the excess is removed with a lint-free cloth. Alternatively, circuits can be left at room temperature for 24 h, or cured at oven at 40° for 2 h. Silver epoxy bonds over the previously laser printed circuit and is easily removed from the rest. This selective adhesion eliminates the need for a stencil or screen printing. Although our previous method with AgNP inks allow for direct inkjet printing of silver traces, the inks are significantly more expensive than Ag pastes and epoxies and do not adhere as well to the substrate. Atom Adhesive-DUCT AD1 was selected mainly because of the good adhesion properties (adhesion tensile strength: 1000 N/cm^2) and rapid curing time.

After fabrication of the Ag circuit, EGaIn is deposited over the substrate. The EGaIn is a eutectic alloy of 76 wt % gallium and 24 wt % indium. The LM alloy selectively wets to Ag traces when exposed to a weak (2 wt %) acetic acid solution or hydrochloric acid vapor (Figure 2A, and Movie S1).

Interfacing with *z*PVA. Interfacing includes methods for either integration of surface mount components directly over the circuit prior to transfer, or interfacing the lead wires with a flex circuit or a traditional PCB. Interfacing can be achieved using silver epoxy or zPVA.

Silver Epoxy. We used silver epoxy (Atom Adhesive-DUCT-AD1), which is the same material used in the laser printing method. Deposition can be done using a prefabricated stencil or material deposition in the desired locations. The components are then placed over silver epoxy to make a connection with the conductive circuit using tweezers. Silver epoxy can be cured at room temperature in 10−60 min (depending on the curing temperature). Also, using a hot air gun, it can be dried in 2 min.

zPVA. zPVA is a thin-film anisotropic conductive glue introduced for the first time in this article that conducts only through z axis. To prepare zPVA, 15 μm diameter silver-coated nickel microspheres (Potters) (27 wt %), are mixed with EGaIn (10 wt %) and added to the PVA gel (63 wt %). EGaIn is first mixed with the silver-coated nickel particles in a planetary centrifugal mixer (Thinky) for 2 min at 2000 rpm. The PVA gel is prepared by mixing 10 wt % PVA powder with 90 wt % water using a hotplate and a magnetic stirrer for 90° and 100 rpm for ∼20 min, until after evaporation of water, a PVA gel is obtained (approximately 15 wt % PVA solution). The particles are then mixed with this gel using the centrifugal mixer for 2 min and 2000 rpm with the percentage already explained above. To make zPVA conductive on the z axis, a bipolar magnetic field is placed under the surface where zPVA is deposited. This allows the material to form conductive columns. Unlike solder pastes and conductive pastes, which require heating over 100 °C to fuse components to the circuit, zPVA cures at room temperature in approximately 10 min. Thus, it is compatible with a wide range of substrates and plastics. Because of its excellent adhering proprieties, zPVA provides a robust connection between the components and the substrate over which the circuit is printed.

LM Alloying. Prior to bonding microelectronics to the circuit, a drop of LM can be alloyed over the component or flex circuit pads. To do so, the component or flex circuit is placed in a water-diluted NaOH bath (10 wt %) to remove the oxide. A drop of LM is then added to the bath and rubbed over the pads similar to what was already described in ref 37.

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ACS Appl. Mater. Interfaces 2018, 10, 38760−38768

Transferring or Hydroprinting. To transfer the circuits, both hydrographic paper or TTP can be used. The former one is suitable mostly for transfer over surfaces in a water tank, while the latter can be used both for transfer over the skin and objects. Here we used TTP (Silhouette). After creation of "Ag−In−Ga" circuit with the aforementioned methods, and populating the circuit with the necessary microelectronics or flex circuit islands, the whole circuit is floated over the water tank. Depending on the host surface, selective cuts over the paper may be applied prior to transfer, which allows spreading the circuit on more complex surfaces.

FPCB Fabrication. Flexible circuits were fabricated by the chemical development process, using a standard copper-coated polyamide film (C.I.F AN210). The photoresist (Positiv20) is then spray-coated over copper. The resulting circuit is dried in the oven for 15 min at 70 °C. The desired circuit pattern is then printed over the copper sheet, using a Xerox standard wax printer (ColorQube 8570). Afterward, the circuit is exposed to the UV light for 20 min, and it is submerged in a 10 wt % NaOH solution, until the photoresist is cleaned. Finally, it is submerged in an iron(III) chloride solution (Edison Delta) until excess copper is dissolved. Finally, the wax is removed with industrial acetone. Measurements of the sheet resistance of the *z*PVA film were performed using a Hewlett Packard E3631A and a four-point measurement scheme.

Protective Coating. Depending on the application, circuits can be coated with a protective layer to increase its resistance to wear. In the case of biopotential measurements, the circuit cannot be coated, but in case of the transfer over plastic pieces (Movies S1 and S3), where direct touch with the conductive electrode is not necessary (capacitive measurement), the circuit is coated by a plastic spray (Plastik 70 KONTAKT CHEMIE).

EGaIn LM. In order to produce eutectic gallium indium (EGaIn), gallium and indium were purchased from (Rotometals). EGaIn was obtained by stir mixing 76 wt % gallium and 24 wt % indium at 190 °C on a hotplate for 12 h.

Electromechanical Testing. Lines of 80 mm by 1 mm were printed over the TTP with the method referred in this article. This is then transferred over a 500 μm thick cured PDMS by application of water on the backing paper and removing the paper. Finally, a second layer of 500 μm thick PDMS is applied by a thin-film applicator. We then let the sample to cure for 4 h at 50 °C. The process for preparation of the sample with the *z*PVA interface includes spray coating of 40 mm by 1 mm line of LM on a 500 μm thick PDMS. Separately, a 200 μm film of *z*PVA was applied over the contact pads of an "Ag−In−Ga" trace (80 mm by 1 mm). Afterward, we placed the TTP over PDMS and aligned the square contact pads of the LM trace and "Ag−In−Ga" trace, and placed a flat magnet below PDMS. The backing paper is then removed by applying water. A second 500 μm thick PDMS layer is then applied over the sample with a thin-film applicator, which is cured for 4 h at 50 °C. Schematics of both types of samples is shown in Figure 3.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b13257.

SEM images of the cross section of the TTP, schematics of interfacing *z*PVA, flex-PCB and rigid PCB, functional thin-film circuits with LEDs floating over water, schematics of the setup used for *z*PVA film *z*-axis resistance measurement, schematics of steps for transferring the circuits over an object (PDF)

Fabrication and hydroprinting of Ag−In−Ga ultrathin circuits (AVI)

Application of hydroprinted electronics for the EMG tattoo over the body and control of prosthetic hand (AVI)

Application of the hydroprinted circuit over a 3D printed piece with nondevelopable surfaces (AVI)

Ag−In−Ga circuits water resistance (AVI)

Transfer of a circuit populated with SMD chips (AVI)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

EGaIn, eutectic gallium−indium
EMG, electromyography
FPCBs, flexible printed circuit boards
HMIs, human−machine interfaces
IoT, internet of the things
LED, light-emitting diode
LM, liquid metal
PEDOT:PSS, poly(3,4-ethylenedioxythiophene)/poly-(styrene sulfonate)
PVA, polyvinyl alcohol
RFID, radio frequency identification
AgNP, silver nanoparticle
TTP, transfer tattoo paper

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