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ARTICLE TYPE

Rapidly Patterning Conductive Components on Skin Substrates as Physiological Testing Devices via Liquid Metal Spraying and Pre-designed Mask

Cangran Guo, Yang Yu and Jing Liu*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX, Department of Biomedical Engineering, School of Medicine, Tsinghua University, Beijing 100084, China
****E-mail: jliubme@tsinghua.edu.cn. Tel.: +86-010-62794896, Fax: +86-010-82543767***

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The newly emerging skin-electronic devices with flexible features are usually fabricated on a very thin substrate, which however do not directly contact with the skin. This may generate large coupling impedance with the skin and high signal noise for a sensitive enough detection of weak physiological signals. Here from an alternative way, we proposed a method to directly pattern liquid metal conductive components as sensors on skin through spray-printing strategy. This quick forward way of making flexible electronics on skin is enabled via stainless mask which is pre-designed via chemical etching with line width resolution of 100μm and can be used to deposit desired electrical components. Several most typical geometric metal graphics spanning from simple to complex structure which serve to compose complex electrical circuits or devices, are fabricated in a moment. Particularly, GaIn24.5-based liquid metal wires deposited on the pig skin under different situations were quantified, and the mechanisms for the spray-printing of bioelectronics were interpreted. Further, stretching experiments were performed which shows that the resistance of the printed film would take a square growth with the tensile length of the pig skin in a specific range. Lastly, an inter-digital array (IDA) electrode sensor, with distance between two fingers of the inter-digital fingers as 0.5mm and length of the finger as 11mm, was fabricated and applied to measure impedance spectroscopy of the pig skin. This study demonstrates the unique value of the present Lab on Skin for physiological measurement. It illuminates a promising route of directly printing electronics pattern on skin that will be very useful in a wide variety of practical situations like skin sensors, actuators, skin electrical circuits and so on.

1 Introduction

Conventional biomedical conductive components generally own advantages of high conductivity and definition process ability. However, they also imply shortcomings requiring complex fabrication conditions. In particular, the classical microelectronics manufacture technologies such as lithography, evaporation, etching, screen printing, micromachining or electroplating etc. heavily rely on special equipments and clean room infrastructure. And most of the existing electrophysiological measurement devices are rigid sensors or circuits, which may sometimes encounter troubles such as coupling performance, contact comfortableness, manufacturing complexity and cost etc. Such electrodes may cause discomfort and even hurt to human body due to their mechanically rigid fixing. Recently, the flexible electronics is increasingly investigated and gradually applied to bio-electronic measurement.[1-5] The flexible transistors can be made as electronic skin to mimic the sensitivity of real human skin. Generally, the electronic epidermal devices are integrated with a collection of multifunctional sensors, which can be used to detect the temperature or pressure,[6] record heartbeats, brain activity and more electrophysiological signals or made as actuators in an array such as micro-heaters.[7-10] It is well known that skin has the largest flexible and robust surface areas, which covers and protects the biological body from external potential injury, and also serves as an important physiological sensor. So far, most of the skin-electronic devices ever reported are based on solid metals or inorganic semi-conductors. The stretchable skin electronics are usually fabricated on a very thin and flexible substrate, which have intelligent processing capabilities such as sensing and acting. For such an application modality, the electronic devices are isolated from the skin by the substrates. In certain situations, the skin may not be able to directly measure the signal from outside the body. Actually, most of the electrophysiological signals are detected with the electrodes contacting the skin. If the patterned conductive components could be directly printed on the target skin, the interface impedance of the skin and electronic components will be very low. The signal from the human body could thus be well transmitted to the outside for better analysis.

In this paper, a pervasive method for printing electronics directly on skin to make conductive patterns via atomized spraying is proposed. This technology allows manufacturing various more complex components quickly on skin as shown in Fig. 1. Considering the requirement at room temperature, most of the existing electronics fabrication methods such as evaporation and sputtering would not work well. In addition, the previously researched functional inks are mainly based on organic substances,[11] polymers,[12] nano-particles[13] and so on. These electrical inks can be prepared by loading nanoparticles into the base fluids such as silver ink or organic electronic conductive materials such as: poly (3, 4- ethylenedioxythiophene): poly (4-styrenesulfonate) (PEDOT: PSS). However, a big issue exists in such composite inks or organic conductive lines as well as other patterns, because they rely heavily on the high temperature annealing or other more complex process such as evaporation. Besides, these electronic inks' conductive performance is still not good enough. Overall, until now there is no an ideal way of using these materials to fabricate electronics directly on skin. As an alternative, the liquid metal is easy to compose electronics directly on flexible substrates even skin with special convenience at room temperature.[14-19] Such conductive ink owns many unique merits like good electrical conductivity, mechanical flexibility, biocompatibility, low cost and so on, which overcomes in a large extent the shortages facing the conventional materials.[14,15] This kind of flexible electronics has wide application in making RF electronics,[16, 17] injected electrical wire for flexible packaging of solid-state integrated circuit chips [18] and bio-electrodes. [19] The liquid metal ink is increasingly applied to fabricate flexible electronics with the methods to realize direct writing by brush, desktop printing, ball writing,[20] injection[18, 21, 22] and stamp.[23] And most of the present printing methods could not fabricate the electrical components on skin, whose geometry is rather irregular and not easy to deposit a circuit. The spray-printing method has been proven to be a very good way to fabricate flexible electronics. It is feasible in fabricating printed circuit board.[24] PEDOT: PSS transparent electrodes are used for solar cells based on the method of spray-printing.[25] The method is also very useful in other situations: ink of copper indium diselenide nanocrystals as the light-absorbing layer for manufacturing photovoltaic devices, [26] the printing ink to form metallic silver films,[27] the liquid metal to print electronics directly on several desired substrate. [28] This paper takes the lead in using the atomized spraying technology to directly print the room temperature liquid metal to fabricate electronics on skin in room temperature without requesting a thermal annealing process. The fabricated electronics can be used as testing "Lab on Skin" to form bio-electrodes, sensors, skin circuits and so on. It is expected that such ubiquitous technology will stimulate a series of unconventional application in future bioelectronics.

2 Materials and methods

2.1 Materials

The currently chosen printable ink is made of gallium-indium alloy. Liquid metal has a high degree of electric conductivity far superior to other flexible conductive materials. For the fabrication, gallium and indium metals with purity of 99.99 percent were taken as raw materials with a relative weight ratio of 75.5:24.5 in line with the chemical compositions. The detailed procedures were outlined as follows. All beakers were prepared clean with the deionized water. Then the gallium and indium metals were mixed together in the prepared beaker and heated at 100°C until they were fused completely. The melting point of GaIn24.5 is measured around 15.5°C (See Table 1), which keeps in liquid state at room temperature. When the liquid metal are exposed to the air, GaIn24.5 will quickly form a thin layer of oxide skin, which can help liquid metal maintain the formed shape in a large extent. About 8 ml 30% NaOH solution was added to the metals in order to prevent the configured GaIn24.5 ink from naturally being oxidized. With such low melting point behaviour, all the spraying experiments can be carried out in liquid state at room temperature. Pig skin is chosen here as the electronic substrate in the experiments, which is used as the substitute materials for studying human skin due to its similarity in material response to human skin. Fresh pig skin was purchased from a local supermarket. The skin was preserved in 0.9% normal saline solution with a temperature of 4°C. The lumbar area of the pig skin was cut to make specimens. All of the fat layer, and hairs were removed carefully from the specimens using a surgical scalpel.

Table 1 Physical properties for GaIn24.5

Material	Melting point (°C)	Density (kg/m3）	Surface tension （N/m）	Dynamic viscosity （Pa·s）
GaIn24.5	15.5	6280	0.624	1.6956×10−3

2.2 The process of fabricating liquid metal film

The basic process for spray-printing liquid metal conductive layer on biological skin is depicted in Fig. 1. The liquid metal was atomized with the equipment of airbrush (from MEIJI PIECE GUN Company, Japan) and the air pump which were purchased from Shenzhen, China. A stream of liquid metal was disrupted by high-energy gas jets into fine micro-droplets and fell onto the pig skin surface as expected. After atomization, the liquid alloy was broken into micro-droplets, and deposited on the substrate, which finally formed into conductive layer.

2.3 Mask fabrication and replica molding of liquid metal pattern on skin

Metal chemical etching is used to fabricate the stainless steel mask, which allows any picture, photo, or pattern to be copied onto target substrate. The metal mask is fabricated with a 200μm thick steel sheet, which is pre-treated to remove the oil on the surface. The metal sheet is washed by de-ionized water. Dry photo-resist membrane layer is heated and attached on metal sheet surface with stress from the hot press roll. The designed picture (See Fig. 1 (a)) from the film is transferred to the metal sheet with dry photo-resist membrane layer by exposure and development (Fig. 1(b)). After the dry photo-resist membrane was removed, the next step is chemical etching by following the equations such as:

$$2FeCl_3+Fe=3FeCl_2$$

$$2FeCl_3+Cu=2FeCl_2+CuCl_2$$

Here, ferric chloride ($FeCl_3$ solution) has served as the mordant. The mask is fabricated with desired picture designed in advance. Usually the bottom geometries are slightly larger in width than the top geometries so as to compensate for the mask alignment errors. The liquid metal spraying experiments are carried out in a fume hood. The metal mask and the pig skin substrate are cleaned with de-ionized water and dried with N_2. The pig skin substrate is covered by the prepared mask.

The mask must be tightly positioned closely to the substrates to guarantee printed electronics with clear boundaries. Then the electronic components are prepared by the so-called spray-printing method (Fig. 1 (c)) until finally deposited on skin surface (Fig. 1 (d)).

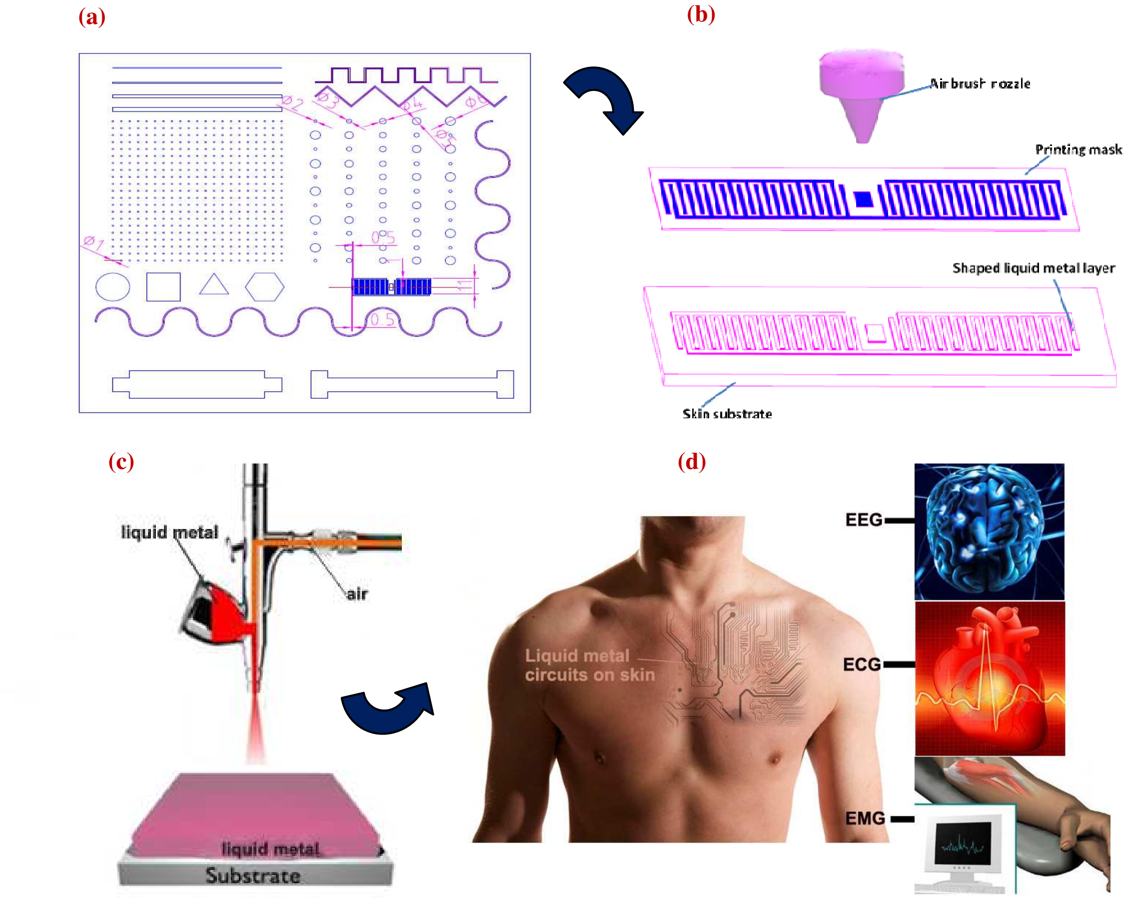

Fig.1 (a) The designed mask for spray-printing. (b) Technical principle of fabricating interdigital electrode on substrate via a mask. (c) The mechanical principle of atomization of liquid metal to form conductive layer by an airbrush and an air pump. (d) The schematic conception of fabricating liquid metal circuits on human skin.

3 Results and discussion

To demonstrate the diverse capability of the liquid metal spraying printer in manufacturing circuit components on skin, here we choose to print several most typical metal geometric graphics which can be used to compose complex electrical circuits or devices. In skin electronics, a sensor or antenna is generally composed of various basic electrical elements such as straight line, circle or complex curve. With a pre-designed stainless mask, the corresponding electronic wires or signs (Fig. 2a) can be quickly printed out on skin via spray-printing. Traditional inter-digital array (IDA) biosensor is often manufactured with very complex process and equipment. Here, an IDA electrode was fabricated to measure impedance spectroscopy of the pig skin (See Fig. 2b). Such biosensor could generate sensitive enough electrochemical signals due to its low ohmic drop, rapid reaction kinetics, and a high signal-to-noise ratio.[29, 30] The quick and straight-forward fabrication of interdigital array microelectrodes (IDAM) is demonstrated. The distance between the two fingers of the IDAM is 0.5mm and the length of the finger is 11mm. As shown in Fig. 3a-d, the diameter of the micro-droplet which impacted the skin surface was in micro-meter level.

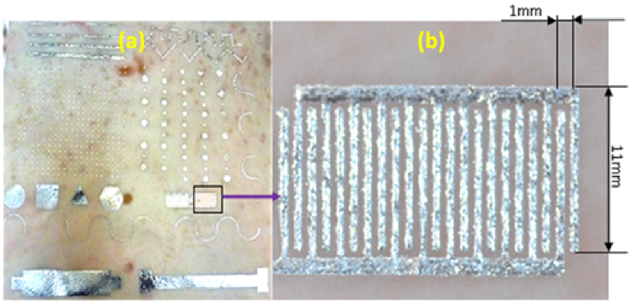

Fig.2 Geometric graphics for liquid metal components on skin using spraying methods. (a) Picture of typical geometric metal graphics of liquid metal on pig skin surface. (b) Inter-digital array microelectrodes (IDAM) of liquid metal on pig skin surface.

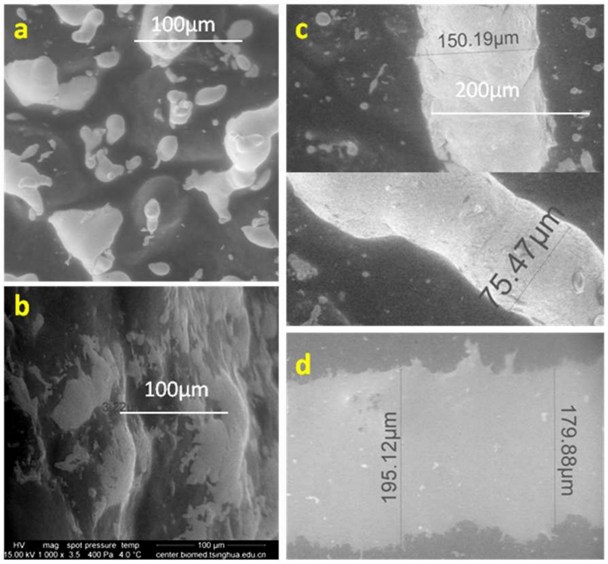

Fig.3 Basic microscopic SEM features of liquid metal spray-printing (LMSP). (a) SEM of spraying printed liquid metal micro-drops on pig skin under 100µm scale; (b) vertical direction SEM of spraying printed liquid metal film on pig skin under 100µm scale to measure the film thickness; (c) SEM image of using LMSP straight line on pig skin; (d) SEM image of using liquid spraying printed straight line on paper.

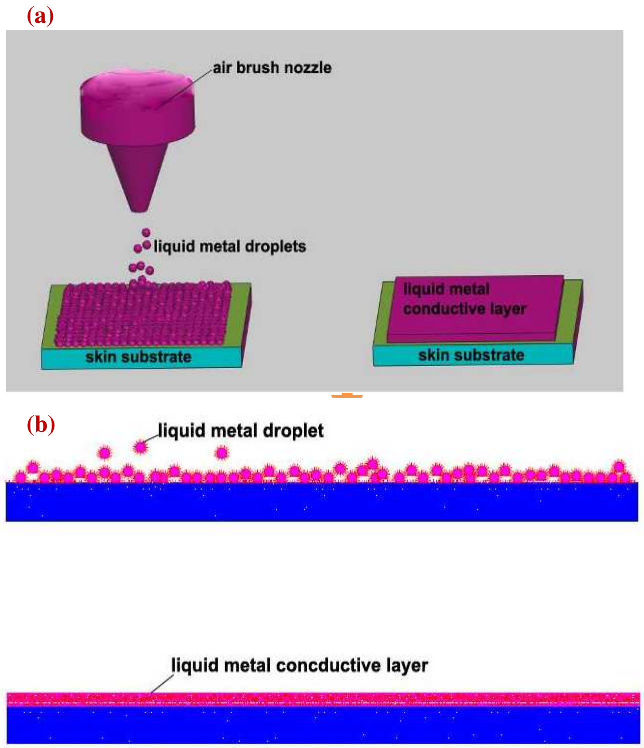

Fig.4 Fundamental process for spraying liquid metal film on substrate. (a) Process of spraying to form liquid metal film. (b) Principle of liquid metal micro-droplets adhered to the substrate and merged film.

The thickness of the thin film is 2µm, which is obtained from the SEM image of the thin film's cross section as shown in Fig.3 b. The width of the straight line of liquid metal is around 100µm. Overall, the fabrication accuracy with spray-printing is expected to be around 10µm. As the SEM figure indicates (Fig. 3c & Fig. 3d), the surface tension of the liquid metal micro-droplet is much larger when it is spray-printed on the skin than that on a paper. Therefore, the straight line of liquid metal on the skin is much smoother than on paper. As shown in Fig. 4 (a), the liquid alloy is disrupted into micro-droplet by air-brush with its surface oxidized rapidly in the air. The oxidized liquid metal micro-droplets have polar atoms on the surface, which are somewhat chemically reactive. In addition, the skin surface may also contain certain polar molecules (see Fig. 4 (b)). As the micro-droplets of liquid metal impact the skin surface, the atoms or molecules can be firmly adsorbed on the skin surface under the Van der Waals force. After that, the adsorption film of liquid metal conductive layer is formed. For the small size of liquid micro-droplet, its surface is more active than when it is in normal big size, and the oxidation process as mentioned above become more quick. So it is easier to adhere to the substrates. But the surface oxide would guarantee the purity inside. The liquid metal flow is influenced by the gas flow through the nozzle, so the size of micro-droplet is related to the design of atomization nozzle. Generally the cohesive strength of the liquid metal and skin surface is described by the work of adhesion, [31] *i.e.*

$$W_d = \gamma_L + \gamma_S - \gamma_{SL} \tag{1}$$

where, γ_S , γ_L are the surface tension of the solid and the surface tension of the liquid metal, γ_{SL} the solid-liquid interfacial tension, and the work of adhesion of a liquid metal micro-droplet to a solid surface could be given by Young-Dupre equation as

$$W_d = \gamma_L (1 + \cos\theta) \tag{2}$$

where, γ_L is the surface tension of the liquid and θ the contact angle, W_d is the work of adhesion.

Then the adhesion force is:

$$F_a = \frac{dW_d}{dx} \qquad (3)$$

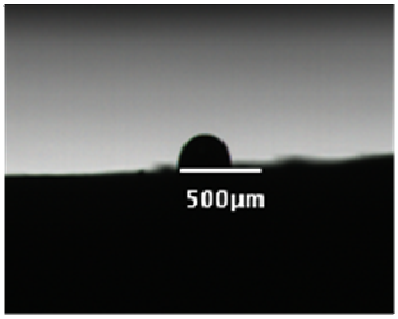

Fig.5 Liquid metal droplet sitting on pig skin surface, 100.5°

The contact angle between a liquid metal drop and the skin surface is a measure of the angle to characterize the adhesion strength. In most cases, a larger contact angle means the weaker attraction between the liquid metal and the skin surface. Conversely, a lower contact angle means a stronger attraction. As shown in Fig. 5, the static contact angle between a liquid metal drop and the skin surface is measured as 100.5° by a contact angle meter (JC2000D3, POWEREACH). This is because the micro-droplets are oxidized rapidly in the air with polar atoms on the surface. When the liquid metal drop is placed on skin surface, an attraction develops between the polar molecules in the droplet and the surface. The adhesion strength may be larger than the value which is obtained by only calculating with the static contact angle. The attraction and force of gravity will make the drops to form a thin film. As shown in Fig. 6, the experimental results further explain the adhesion principle of spray-printed liquid metal on skin as compared with different methods through depositing GaIn24.5 to the pig skin. Our previous work confirmed that GaIn24.5-based liquid metal prepared with oxidation reaction could be directly and easily written on a flexible substrate. It also can be deposited on skin but still difficult to fabricate more complex patterns. (See Fig. 3 (c)) The surface tension of the skin is much bigger than other substrates such as paper, cloth, polymeric materials and so on. As an alternative, it is easy to quickly make very complex patterns with the methods of spray-printing method. In this way, people can print out various shapes and patterns conveniently on the skin according to demands of the target electrical devices. The energy conservation equation before and after liquid micro-droplet impacts the skin surface can be written as:

$$E_k^i + E_p^i + E_s^i = E_k^f + E_p^f + E_s^f + W_d \qquad (4)$$

where, E_k^i, E_p^i, E_s^i are the kinetic, potential, surface energies of liquid metal micro-droplet impacting to the skin surface before and E_k^f, E_p^f, E_s^f are the afterwards.[32]

The mass of the micro-droplet is not changed after it impacts the skin, for the case, one has:

$$W_d \approx E_k^i + E_p^i + E_s^i \qquad (5)$$

The kinetic and surface energy before impact can be described as:

$$E_k^i = \frac{1}{2}\rho_L \mathrm{U}_0^{\,2}\left(\frac{\pi}{6}d_0^3\right) \qquad (6)$$

$$E_s^i = \pi d_0^2 \gamma_L \qquad (7)$$

where, ρ_L, γ_L, d_0 are the liquid metal density, surface tension and diameter of the impacting liquid metal micro-droplet, respectively. U_0 is the velocity of micro-droplet impacting the skin surface. Here, as the liquid metal micro-droplet impacts the solid surface, one has

$$E_p^i \approx 0, E_p^f \approx 0 \qquad (8)$$

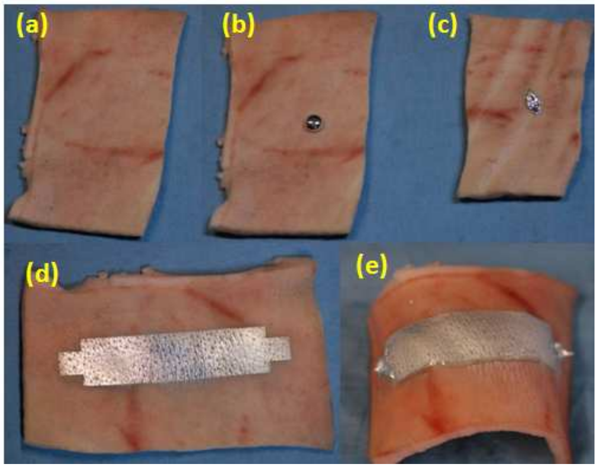

Fig.6 Optical images of comparing GaIn24.5-based liquid metal ink deposited on pig skin under different situations. (a) Optical images of naked pig skin without any GaIn24.5. (b) Optical images of non-oxidized GaIn24.5 injected on pig skin. (c) Optical images of oxidized GaIn24.5 written on pig skin. (d) Optical images of GaIn24.5 spray-printed on pig skin. (e) Optical images of GaIn24.5 spray-printed pig skin in bent states.

Then we can get:

$$\gamma_L(1+\cos\theta)=\frac{1}{2}\rho_L \mathrm{U}_0{}^2\left(\frac{\pi}{6}d_0^3\right)+\pi d_0^2\gamma_L \qquad (9)$$

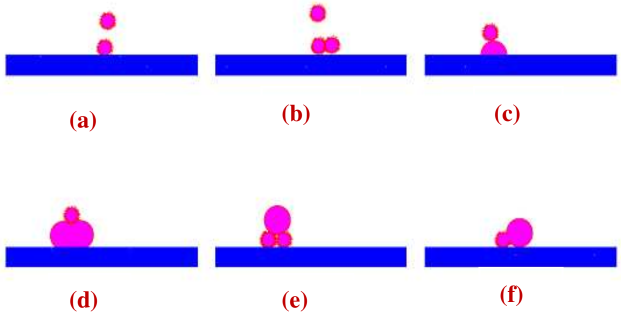

Fig.7 Mechanism of liquid metal micro-droplets impacting the skin substrate. (a) The first micro-droplet impacts the skin surface. (b) The second micro-droplet impacts the skin surface as well as the first micro-droplet. (c) The micro-droplets impact two merged liquid metal. (d) The micro-droplets impact several merged liquid metal micro-droplets. (e) A large micro-droplet impact two small ones which are not merged yet. (f) A large micro-droplet impacts a small one and then merged subsequently.

As discussed above, the size of micro-droplets is determined by the physical properties of the main gas-liquid two-phase such as density, viscosity, surface tension, and the velocity of gas flow around the droplet state decisions. The liquid metal micro-droplets in the gas stream are mainly atomized by the influencing factors such as the pressure of the gas, the liquid surface tension and viscous forces.

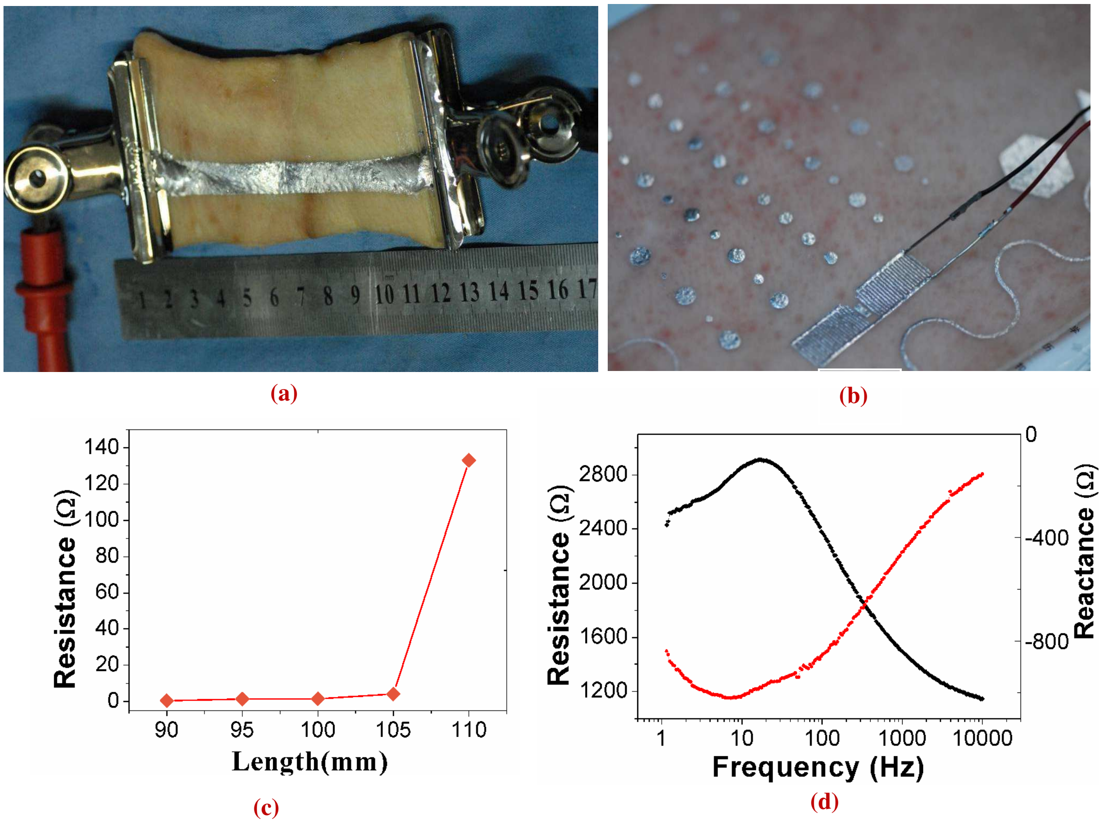

Fig.8. (a) Schematic stretching experiments apparatus of liquid metal on pig skin. (b) Schematic for measurement of impedance spectroscopy of pig skin using IDA. (c) Curve of resistance of the liquid metal line with the length of pig skin. (d) Representative electrical impedance spectroscopy of the IDA electrode. The black line represents resistance of pig skin detected and the red line the reactance.

As the liquid metal micro-droplets impact the surface, a liquid film spreads outwards (See Fig.7 (a)). When the second liquid metal micro-droplet impacts the first micro-droplet, the two liquid micro-droplets will merge (See Fig.7 (b)), and the film will then spread and become thicken (See Fig.7 (c) and Fig.7 (d)). When the second liquid metal micro-droplet impacts the substrate, which is far from the first one, another larger micro-droplet may impact the two micro-droplets which affected the former substrate, and they merged to a film. If the second liquid metal micro-droplet is a larger one it may merge with the first to form a film. In summary, according to the SEM measurement on the liquid metal as spray-printed on pig skin, there usually occur six situations of liquid metal micro-droplets impacting on the pig skin substrate (See Fig.7 (a)-Fig.7 (f)). To characterize the electrical properties of the printed electronics on skin, additional experiments were performed as set up in Fig.8 (a) and (b). Fig.8

(c) shows the resistance results of liquid metal on pig skin according to the measurements. It can be evidently observed that resistances increase with the skin stretched in length. The resistance will increase squarely within the range from 0.4Ω to 4.1Ω with the tensile length of the pig skin in a narrow range from 90mm to 105mm.

Theoretically, the definition of resistance can be described by the following formula:

$$R = \frac{\kappa L}{S} \tag{9}$$

Here, R is the resistance. L is the length of liquid metal conductor. S is the cross sectional area of the liquid metal conductor. κ is the resistivity. The length, width and height changes of liquid metal conductor are in accordance with variation of the elastic skin body. When the tensile force increases, the elastic skin body will adapt to the liquid metal conductor.

The volume and length relation reads as:

$$S = \frac{V}{L} \tag{10}$$

Here, the volume of the liquid metal conductor is invariant. And the resistivity is constant. Then one has

$$\frac{R}{R_0} = \frac{\frac{\kappa L}{S}}{\frac{\kappa_0 L_0}{S_0}} = \frac{\kappa V_0}{\kappa_0 V}(\frac{L}{L_0})^2 \tag{11}$$

Clearly, the resistance varies squarely with tensile length of the pig skin, which coincides with the measured data. So this stretchable liquid metal pattern has good prospects used as pressure sensor of skin. For impedance measurement, we adopted the SRS Model SR780 2-Channel Network Signal Analyzer to get the data. [33] The impedance spectroscopy of pig skin can be detected with the IDA (see Fig.8d). The impedance of skin reflects the electrical properties of skin, which could be used to evaluate the pathological changes of tissues. The results show that the peak resistance of pig skin is 2900Ω at the frequency of 20Hz and the peak reactance of pig skin is 1000Ω for the frequency of 10Hz, which provide a very convenient way to measure the physiological parameters of the skin.

4 Conclusions

In summary, the present study has established a quick forward method to fabricate directly conductive components on skin with spray-printing via pre-designed stainless mask and liquid metal ink. The mask was fabricated using chemical etching method with an accuracy of 100μm, which serves well to deposit specific conductive patterns. And the liquid metal ink was verified as a perfect material in quite a few emerging skin biomedical practices. We also interpreted the related spraying printing mechanisms and the behaviors of the printed conductive components. According to the SEM images of the liquid metal spray-printing, it was disclosed that the accuracy of the manufactured liquid metal electrical components had reached micro-meter level. Further, it was found that the resistance of the printed film ranging from 0.4Ω to 4.1Ω would increase squarely with the tensile length of the pig skin from 90mm to 105mm. An IDAM was fabricated to measure impedance spectroscopy of the pig skin with the distance between the two interdigital fingers as 0.5mm and the length of the finger as 11mm, respectively. The impedance spectroscopy of pig skin was detected with the IDAM, which demonstrated its suitability for the on skin physiological measurement. These results promise an important route of quickly and directly making bioelectronics devices as “Lab on Skin” in a variety of practical applications like skin sensors, actuators, and even more complex skin electrical devices in the coming time.

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