A SUPER-LYOPHOBIC PDMS MICRO-TUNNEL AS A NOVEL MICROFLUIDIC PLATFORM FOR OXIDIZED GALINSTAN®

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ABSTRACT

We report a micro pillar array-based super-lyophobic poly(dimethyl siloxane) (PDMS) micro-tunnel as a novel microfluidic platform for oxidized Galinstan®. Liquid-metal alloy, Galinstan® was expected to be widely utilized in many MEMS applications due to its favorable properties. However, the fact that Galinstan® gets easily oxidized and wets on almost nearly any surface is the difficult challenge for utilization of Galinstan®. We studied various pitch distance micro pillar arrays and evaluated lyophobicity of Galinstan® using static contact angle and sliding angle. A unique approach to fabricate 3-dimensional (3-D) lyophobic micro-tunnel structure was designed using flexible PDMS, which can overcome the limitation of current lithography techniques. It was demonstrated the movement of oxidized Galinstan® without wetting.

INTRODUCTION

Galinstan®, a non-toxic metal eutectic alloy, is in liquid phase at room temperature and has been investigated for various applications including biology [1], RF switch [2], magnetohydrodynamic (MHD) pump [3], and tunable frequency selective surface (FSS) [4]. Although it has great potential for a variety of applications, surface of Galinstan® is easily oxidized in air and it behaves more like gel rather than true liquid. This super-fast oxidation is a challenging problem to overcome and device development using Galinstan® has slowed down significantly. It was reported that Galinstan® behaves like true liquid in the below 1 ppm of oxygen environment [5]. This requires a good hermetic packaging for microfluidic platform for Galinstan®. Viscous oxide surface skin of Galinstan® is known to adhere to almost any surface [3]. Microfluidic channels filled with diluted hydrochloric acid (HCl) showed removal of oxide skin in eutectic GaIn alloy [6], but such HCl filled microfluidic channel may not be applicable for most applications. Oxide-free Galinstan® is crucial for certain applications like micro switches. However, in other applications such as micro-cooling and FSS, maintaining true liquid phase of Galinstan® is not necessary. Unfortunately, up to this point, there was simply no known on-demand control method of movement of oxidized Galinstan® in microfluidic platform.

Although there have been countless literatures on super-hydrophobic surfaces [7, 8], to the best of our knowledge, there was no published report on super-lyophobic surface for Galinstan®.

In this paper, we investigated PDMS-based super-lyophobic surfaces using contact and sliding angle based on Wenzel and Cassie's models, and proposed a novel 3-D micro pillar array-based super-lyophobic PDMS micro-tunnel for oxidized Galinstan®.

THEORY

Classical Young's equation (Eq. 1) is widely used to describe the contact angle of a liquid droplet on flat solid surface [9].

$$\cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \quad (1)$$

where θ is contact angle and γ_{SG} , γ_{SL} , and γ_{LG} are surface tension of solid-gas, solid-liquid and liquid-gas interfaces, respectively. Since the Young's equation only works with the flat homogeneous surface, other expanded approach is needed to describe contact angle of a droplet on rough surfaces.

When a liquid can fully wet the surface texture, the equilibrium contact angle of a liquid droplet is described by the Wenzel model (Eq. 2) [9].

$$\cos\theta_W = r\cos\theta \quad (2)$$

where r is a roughness factor, which is defined as the ratio of actual area of a rough surface to the flat, projected area. Droplets in this fully-wetted Wenzel state typically display very high hysteresis because the contact line of the droplets becomes severely pinned on surface asperities.

When a liquid cannot penetrate into the surface texture, on the other hand, the droplet forms a highly non-wetting regime known as a Cassie state. The droplet in the Cassie state displays a very high contact angle as well as low hysteresis, because the surface texture entraps numerous pockets of air underneath the droplet leading to a composite solid-liquid-air interface. If f_S is the fraction of the solid in contact with the liquid, the Cassie equation can be represented as eq. (3) [9].

$$\cos\theta_C = f_S(1+\cos\theta) - 1 \quad (3)$$

Therefore, to achieve super-lyophobic surface that allows easy movement of Galinstan® droplets, liquid droplet on the roughened structures should be in the Cassie state.

DESIGN

Galinstan® property

Galinstan® is a registered trademark of the Geratherm Medical AG. Galinstan® is eutectic alloy of gallium, indium and tin and it is liquid at room temperature [5]. The composition rate of Galinstan® used in this work is 68.5% of gallium, 21.5% of indium and 10% of tin. Based on its favorable properties such as non-toxicity, higher boiling point (1,300 °C) and thermal conductivity (16.5 W/m · K), lower electrical resistivity (0.435 μΩ · m) [10] compared to mercury, it was expected to be utilized in many MEMS applications as an alternative of toxic mercury. Although these properties are attractive, a major problem in the

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development of practical applications is an undesirable affinity for oxidation. It oxidizes upon contact with air and forms a viscous oxide layer that adheres to almost any surface. The oxide layer thickness can be varied from 1.9 to 2.5 nm in low and high humidity environment and the viscous effect is largely originated from gallium oxide (Ga_2O_3) [11]. This viscous oxide renders significant problem for actuation and movement of liquid metal in the channel.

3-D PDMS micro-tunnel structure

Due to significant wetting characteristic of oxidized Galinstan®, it is essential to achieve low contact area super-lyophobic surface for oxidized Galinstan® operation in a microfluidic platform. Instead of using a flat super-lyophobic surface, it is highly desirable to have super-lyophobic sidewall and super-lyophobic top surface. Since current lithographic techniques are incapable of creating such structures, we propose a simple method to generate 3-D PDMS lyophobic micro-tunnel microfluidic platform for the manipulation of oxidized Galinstan®.

FABRICATION

Micro pillar array

AZP4620 photoresist (PR) was triple spin coated on a thermally grown oxidized Si wafer to get approximately 100 µm thick PR. The PR was significantly under-baked in a convection oven at 90 ºC (typical soft-bake temperature is 110°C on a hot plate). Then, the PR was severely under-exposed with the exposure dose of 800 mJ/cm^2 (typical exposure dose is > 3,000 mJ/cm^2 for > 100 µm thick PR). The PDMS was casted over the PR mold and it was cured at room temperature for one day. The replicated PDMS showed irregular surface micro pillar array (Fig. 1c). Fluorocarbon (FC) polymer (C_xF_y) was deposited on top of the PDMS micro pillar array to enhance lyophobicity.

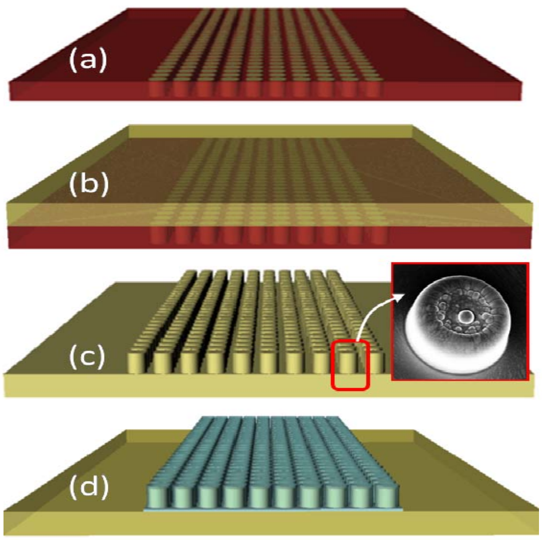

Figure 1: Fabrication sequence of the super-lyophobic PDMS pillar array: (a) under-baked under-exposed PR mold, (b) PDMS coating, (c) replicated PDMS, (d) FC polymer deposition on the replicated PDMS pillar array.

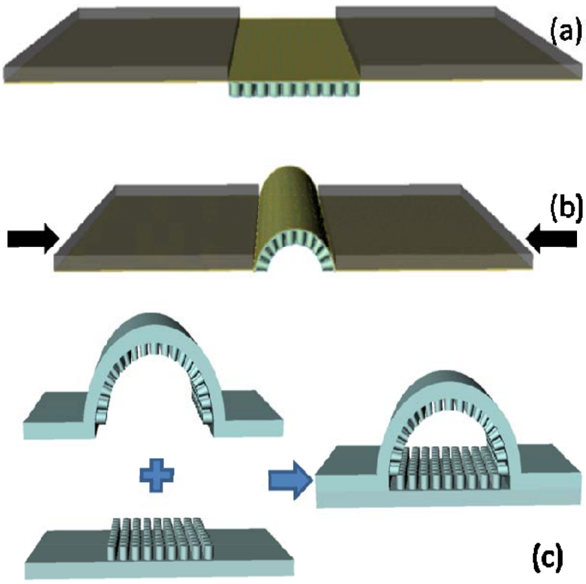

Figure 2: Fabrication sequence of the super-lyophobic micro-tunnel: (a) glass slides attached on either side of the PDMS, (b) PDMS bent, (c) PDMS-PDMS bonding to create the micro-tunnel platform.

3-D lyophobic tunnel structure

For the fabrication of micro pillar surrounded 3-D lyophobic tunnel, top and bottom layer were separately fabricated and bonded together (PDMS-PDMS bonding). Glass slides were aligned to the outlines of patterned top micro pillar array and bonded on either side (Fig. 2a). Then, glass slides were pushed inward to bend the PDMS micro pillar array and it was attached to bottom PDMS micro pillar array to form the micro-tunnel (Fig. 2c). Immediately after bonding, it was placed in a 110°C convection oven to increase adhesion. The micro-tunnel is 2.2 mm wide and 3.2 mm high.

Fig. 3a shows an optical image for one end of the PDMS pillar array micro-tunnel. Fig. 3b shows Galinstan® droplet placed inside the micro-tunnel using a pipette. It is clearly evident that oxidized Galinstan® droplet does not wet on the inner surface of the micro pillar surrounded micro-tunnel.

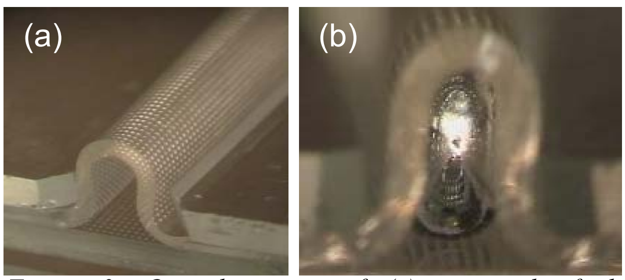

Figure 3: Optical images of (a) one end of the super-lyophobic PDMS micro-tunnel and (b) Galinstan® droplet placed in the micro-tunnel

EXPERIMENT

In order to study lyophobicity of various pitch distance in the range of 50 ~ 525 µm micro pillar array, the contact and sliding angle was measured for 7.8 µL oxidized Galinstan® droplet.

The contact angles of each sample surface were measured using a goniometer (ramé-hart 200-F1 model). Fig. 4 shows contact angle images of the liquid metal on different pitch distance pillar arrays.

The diameter of each micro pillar was 75 µm except for 50 µm pitch distance pillar array whose diameter was 25 µm. We quantified the lyophobicity of various PDMS micro-pillar surfaces by studying contact and sliding angles, and then down-selected the best candidate for the PDMS micro-tunnel structure. The movement of oxidized liquid metal by applying N_2 gas pressure in the micro-tunnel was recorded from the bottom of tunnel structure using a microscopy connected camera.

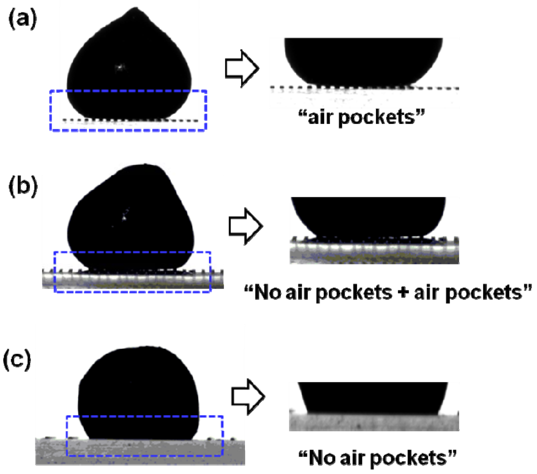

Figure 4: 7.8 µL oxidized Galinstan® droplet on (a) 175 µm pitch pillar array, forming a non-wetting Cassie state (air pockets), (b) 275 µm pitch pillar array, on which the droplet partially fill in surface texture (air pockets and no air pockets area), and (c) 525 µm pitch pillar array (no air pockets), where the droplet fully wets the surface texture.

RESULTS AND DISCUSSION

Fig. 4 shows the contact images of Galinstan® on micro pillar arrays with various pitch distances. Galinstan® droplet is not a spherical shape due to oxidized surface. The droplet on a 175 µm pitch distance micro pillar array clearly formed a Cassie state, confirmed by the presence of air pockets underneath the droplet (Fig. 4a). We believe the droplets on pillar arrays with pitch distances smaller than 175 µm formed a Cassie state, as it becomes more difficult for a liquid to penetrate between micro pillars when the pitch becomes smaller. On the other hand, the image of Galinstan® droplet on a micro pillar array with 525 µm pitch distance showed that the droplet penetrated between pillars, forming a fully wetted Wenzel state (Fig. 4c). We also observed an intermediate state between Cassie and Wenzel states on 275 µm pitch distance micro pillar array (Fig. 4b). There were no air pockets on the left-side and air pockets were observed on the right-side underneath the Galinstan® droplet.

Fig. 5 shows contact and sliding angle as a function of pitch distance. The contact angle of liquid metal on the flat FC polymer deposited surface was 125.4°. The lowest (132°) and highest (163 °) contact angle were measured on 525 µm and 175 µm pitch distance micro pillar array, respectively. Fully wetted Wenzel and air suspended Cassie states were confirmed in sliding angle study. While the oxidized Galinstan® droplet did not move at all on pillar arrays with pitch distances larger than 275 µm, the droplets easily rolled of the pillar arrays with smaller pitch distances. The drastic difference in the sliding angles on these two-types of surfaces confirms that the Galinstan® droplets indeed formed Cassie regimes on micro pillar arrays with pitch distances < 275 µm. The lowest sliding angle (17.4°) was obtained on the 175 µm pitch distance pillar arrays. Based on contact images and sliding angle of liquid metal droplet, three different regimes can be distinguished.

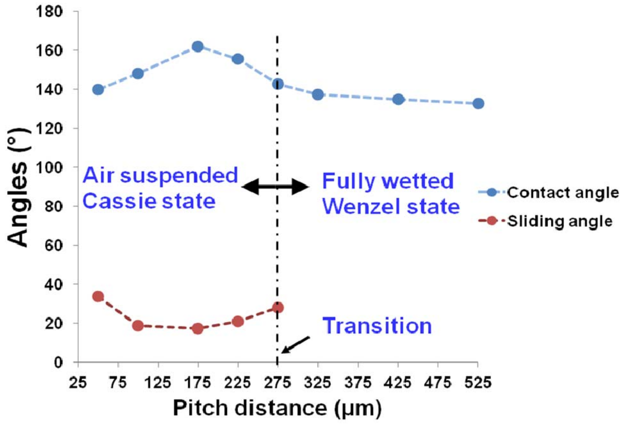

Figure 5: Contact and sliding angle as a function of pitch distance for 7.8 µL oxidized Galinstan® droplet.

Fig. 6 shows comparison of experimental data and theoretical Wenzel and Cassie plots. Red and blue colored graphs indicate contact angle as a function of roughness and fraction calculated from the geometry of micro pillars, respectively. Circle shape dots represent measured data points and cross shape lines indicate calculated data from Wenzel and Cassie models. The numbers in the graph indicate pith distance in micrometer. The contact angles of droplets showed a drastic difference between the Cassie and Wenzel states. We also observed a qualitative agreement between the measured contact angles and predicted trends from Eqs. 2 – 3: For the droplets in a Wenzel state (range of pitch distance from 525 to 325 µm), contact angles increased from 132° to 137° as the surface roughness increased from 1.08 to 1.22. For the droplets forming a Cassie state (range of pitch distance from 225 to 50 µm), contact angles increased to an extremely high value of 163° as the fraction of the solid-liquid interface decreased. Several uncertainties such as the vibrational perturbation during the deposition step as well as highly hysteretic behavior of oxidized Galinstan® can be attributed to some deviations between measured contact angles and predicted values. The observed super-liquid repellency is the cause of the low sliding angle discussed above.

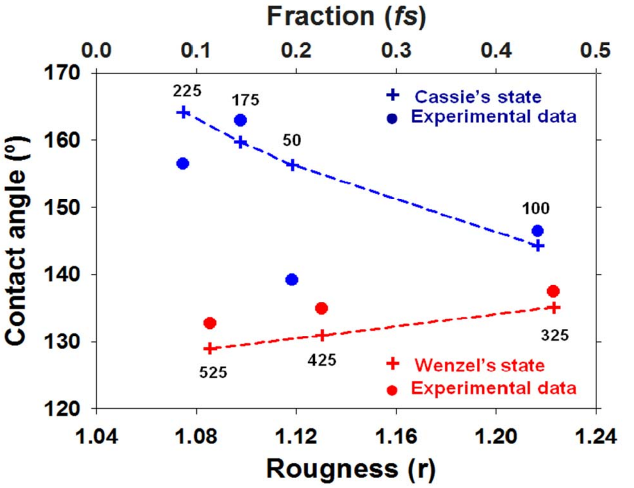

Figure 6: Comparison of Wenzel and Cassie states to experimental data for contact angles (numbers in the graph indicates pitch distance in μm).

Based on study of lyophobicity of various pitch distance micro pillar arrays, 3-D lyophobic micro tunnel with an array of micro pillars (175 μm pitch distance) was fabricated and tested. Fig. 7 shows a series of still images from a video of the moving Galinstan® droplet with applied N_2 pressure. Note that there is no trace of oxidized Galinstan® on the micro-tunnel. The speed of the Galinstan® droplet was measured to be 3.78 mm/sec.

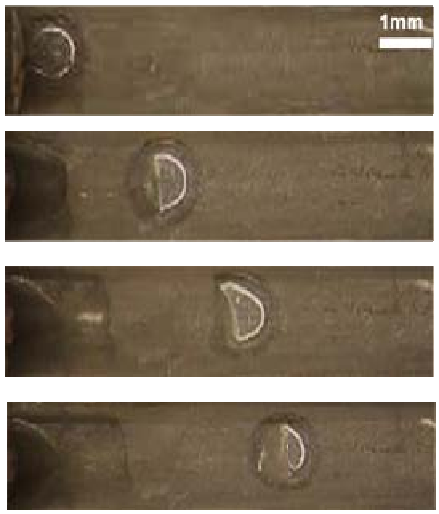

Figure 7: A series of still images taken from a video of moving Galinstan® droplet in the super-lyophobic PDMS micro-tunnel.

CONCLUSION

In this paper, a super-lyophobic PDMS micro-tunnel structure textured with micro pillars was proposed as a novel microfluidic platform for the manipulation of oxidized Galinstan® droplets. Contact and sliding angle were studied to explore super-lyophobic surface for various pitch distance pillar arrays. 3-D lyophobic tunnel structure was designed to have low contact area and fabricated by applying a new approach. The movement of oxidized Galinstan® was demonstrated without any wetting residue in the 3-D lyophobic tunnel structure. This work has a great potential to solve one of the most challenging problems in the liquid metal based microfluidics.

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