PLASMA-TREATED PDMS AS INTRINSICALLY NON-WETTING SURFACE FOR GALLIUM-ALLOY LIQUID METAL MICROFLUIDICS

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ABSTRACT

We repolt the *CFJ02* plasma t1·eatment of polydimethylsiloxane (PMDS) smface as a new method to create an intrinsically non-wetting surface for gallium-based liquid metal microfluidics. It was found that *CFJ0 2* pla sma on PDMS for > 120s creates nanoscale roughness which exhibits a non-wetting prope1ty against liquid metals. Static contact angles and contact angle hysteresis (CAH) of the plasma-treated PDMS surfaces using gallium-based liquid metal droplets were found to be > 144° and < 16.8°, respectively. Rolling test with 15° inclined surfaces were used to confinn non-wetting prope1ty of the surface.

KEYWORDS

Liquid metal, Galinstan, PDMS, Microfluidics, Plasma.

INTRODUCTION

Gallium-based liquid metals have been the focus of intense research in recent years due to its nature as an excellent electrically and thermally conductive fluid and its nontoxicity when compared with other liquid metals, such as mercmy. However, gallium-based liquid metals naturally oxidize in ambient air [I], fomiing a few nanometers thin oxide shell consisting Ga2O and Ga2O3 [2]. Thi s oxide shell has the prope1ty of being strongly adhesive to a variety of materials [3] and are a hindrance in areas such as liqliid metal microfluidics, which requires the liquid metal to freely move in a microfluidic channel. Liquid metal microfluidics show great promise for creating flexible, stretchable, and reconfigurable electronics [4,5], thus it is critical to find an easy solution to move liquid metal cleanly and precisely.

There have been attempts to counter the wettability of the oxide layer of the liquid metals using caustic agents, such as HCl [6,7], introducing foreign thin fihns such as Neve1wet® [8] or Ga nanopa1ticle [9], or multistep fabrication of hierarchical micro/nanoscale structures [IO]. However, these methods may not be readily compatible with other methods and reqliirements of the device. For example, while Ga nanopa1ticle coating is an attractive method, the Ga coating is conductive and not applicable to many electronics and radio frequency (RF) applications.

This work shows that a single *CFJOi* plasma treatment conve1ts any PDMS smface into an intrinsically non-wetting surface against oxidized gallium-based liquid metals.

FABRICATIO N

PDMS pre-polymerand polymerizingagent from the SYLGARD™ 184 Silicone Elastomer Kit were mixed, using the standard I0:I ratio by weight of pre-polymer to polymerizingagent, then degassed in a vacuum chamber for I hour. The mixture was gently poured into a 105 mm x I05 mm x 2 mm square polypropylenemold, set on a flat smface to slowly cure for 24 hours at 25°C to enhance elasticity, then baked at 65°C for 30 minutes in a convection oven. After allowing the mold to cool to room temperature, the I05 mm x I05 mm x 2 1mn PDMS slab was peeled from the mold and cut into three I05 mm long, 35 mm wide, and 2 mm thick PDMS strips. Six similar strips were fab1icated from two PDMS slabs. One strip was cut into five equally sized smaller pieces. PDMS strips and smaller pieces were subsequently treated to a 3:1 ratio *CFJ0 2* plasma (at 250 W, 100 mT01T, 3 seem 0 2, 9 see m CF 4). Groups of PDMS samples were plasma treated with durations of0 s, 60 s, 120 s, 900 s, and 3,600 seconds.

Initially all PDMS strips exhibited non-wettability immediately after plasma treatment. However, over a period of days, some of the strips with less exposure time lost their non-wettability property. Due to this transient property, the samples were characte1ized after 7 days by which time the prope1ty is stabilized. Dming that week, the samples were kept in a polypropylene case, in ambient air, at room temperature (- 25°C). SEM micrographs and contact angle measurements were can ied out for all samples. Rolling test was also canied out for all samples to double confum their smface nonwetting prope1ty.

MICRO/NANOSCALE STRUCTUREOF PLASMA-TREATED PDMS SURFACE

Figme I shows SEM micrographs of PDMS surfaces that have been exposed to the *CFJ0 2* plasma. The PDMS exposed to the 60 s plasma treatment (Figure Ia) has fairly uniform nanoscale pillar stmctm·e with typical structm·al height of - 212 nm and a width of about - 75mn. While this surface was initially non-wetting, over the period of a week, tliis prope1ty was lost, and any pmtion of the smface that was tested a week later wetted liquid metal instantly.

Lopes et. al have repo1ted simulations indicating that the Cassie-Baxter state (non-wetting state) cannot be sustained for pillar heights and spacings below a cli tical fraction of the droplet radius [11]. By applying these criteria to plasma treated PDMS, if the plasma treatment time is not long enough to create surface roughness of a certain height and spacing, the surface will not meet the criteria for the Cassie-Baxter state non-wettability. However, note that this does not explain the initial transient non-wettability.

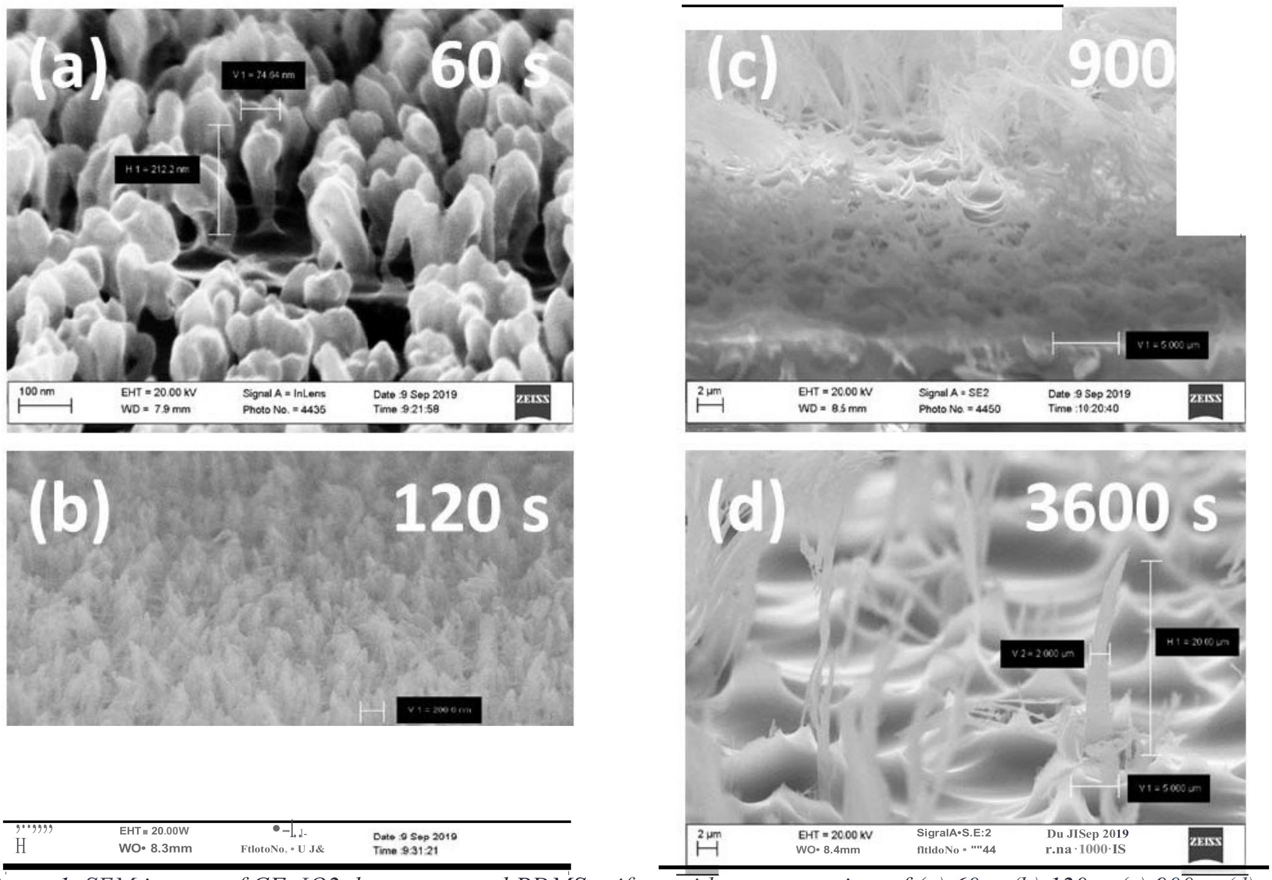

Figure 1. SEM images of CF,,IO2plasma -treated PDMS suiface with treatment time of (a) 60 s, (b) 120 s, (c) 900 s, (d) 3,600 s.

The PDMS exposed to the 120 s plasma treatment (Figure l b) show nanower and sharper surface-etched sub-micronscale PDMS filaments. Such densely-packed, sh01i, spiked structures appear to have length on the order of a micron or less making it velylikely for it to sustain a Cassie-Baxter state for liquid metal over the entire surface.

The PDMS pieces exposed for 900 s (Figure le) and 3,600 s (Figure l d) show an extremely "hai1y" surface that has a dense collection of heavily etched PDMS li bbons roughly 5-10 µm and >20 µm long, respectively. These interconnected networks of flat-edged filaments likely create a roughened surface meeting Cassie-Baxter cliterion, allowing for the nonwetting of liquid metal.

Thus, the non-wettingproperty of the PDMS samples is due to the smface roughness created by the CF*J02* plasma, and requires an exposure time long enough to create a swface roughness that meets the Cassie-Baxter state criteria.

STATIC AND DYNAMIC CONTACT ANGLE MEASUREMENTS

All contact angles were measured using theKRUSS Drop Shape Analysis System DSA30B (Hamburg, Gemiany) using their DSA4 image analysis software. A SY3601 syringe (4.706 mm diameter, 1.0 rnL, Henke Sass WolfGmbH) was loaded with Gallirun-based liquid metal alloy (Ga 66.5%, In 20.5%, Sn 13%; Smaii-Elements GmbH). The needle used for the measurements was the KRUSS NE47 needle with polypropylene inner tubing with a stainless-steel metal jacket (0.7 mm outer diameter).

Wettability/non-wettability regimes of each plasma-treated PDMS strips were chai·acterized by dropping ~8 µL liquid metal droplets, naturally oxidized in ambient air, on to the PDMS strip's smface, which lay on the horizontally-leveled stage of the DSA30B system. To test stretched PDMS snips, the ends of a snip were clamped, across the entire width of the sn·ip, to opposingends of a vise, which had an initial separation of 20 mm. The vise screw was gently twned to separate the vise ends until they were about 25 mm apait, giving about 25% sn·ainto the PDMS snip (Figm·e 2). The vise was then placed on the leveled stage of the DSA30B system for contact angle measurements.

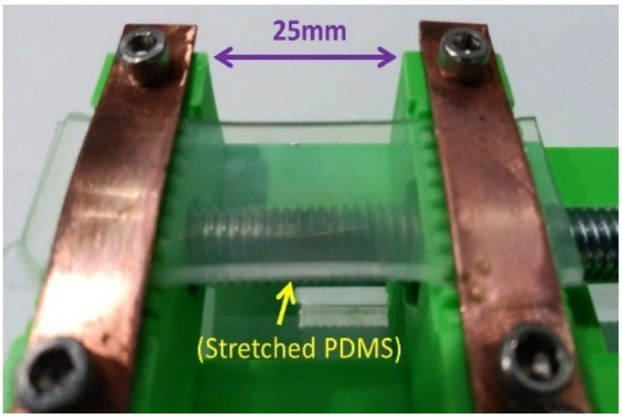

Figure 2. Vise with clamped PDMS strip stretched 25mm.

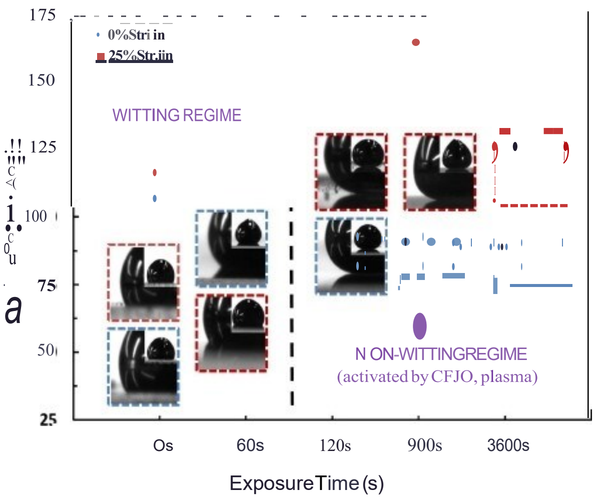

Figure 3. Static contact angle of ~8 µL surface oxidized liquid metal droplets on various plasma-treated PDMS suifaces.

The static contact angle for each strip, in resting and stretched state, was estimated by averaging the measured left and right contact angles of a liquid metal droplet. The static contact angles were found to be greater than 144° for the PDMS samples with 120 s or longer plasma treatment (non-wetting regime), while the angles were

135.8° or lower for the samples with 60 s less plasma treatment (wetting regime)(Figure3).

Dynamic contact angle was measured by initially placing the needle tip about 1 mm from the PDMS snip surface, forming a sessile drop by first depositing ~8 µL on to the smface, depositing ~5 µL more dming the advancing contact angle measurement phase, then retrieving ~13 µL during the receding contact angle measurement phase. Figure 4 shows dynamic contact angle measurements for each PDMS strip, in stretched and resting state. Contact angle hysteresis (CAH) were less than 16.8° for the samples with 120 s or longer treatment (non-wetting regime). However, CAH for the PDMS samples with 60 s or less plasma n·eatment showed large CAH of 95.8° or higher, typical for a wetting surface.

These contact angle measurements allow us to define an activation exposure time of about 120 s of *CFJ02* plasma treatment. This is the minimum time needed to convert a PDMS surface from the wetting regime to the non-wetting regime. Fmthermore, it is clear that the wetting/non-wetting propelties of plasma n·eated PDMS surfaces does not seem to be affectedmuch by strains at 25%.

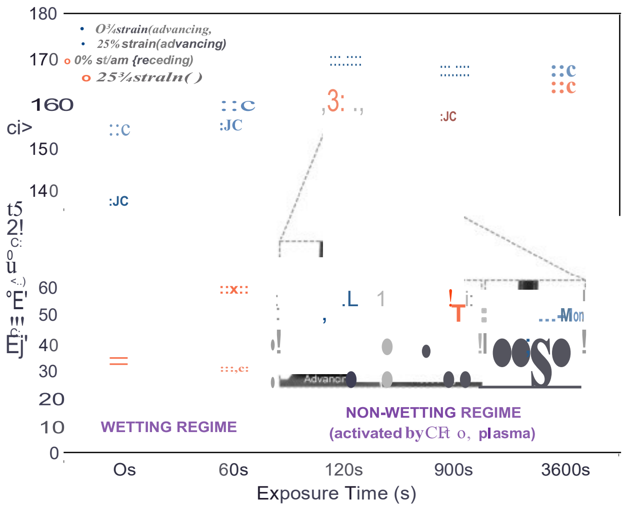

Figure 4. Dynamic contact angle of suiface oxidized liquid metal droplets on various plasma-treated PDMS suifaces.

ROLLING TEST

To confum non-wettability of a PDMS snip, rolling tests were performed by dropping ~8 uL of liquid metal droplets using a syringe on to each plasma treated PDMS sn·ip, in the unstrained state, and under a 15° incline (Figure 5). Samples with 60 s or less plasma n·eatment had the liquid metal droplet instantly stick to its smfa ce, exhibiting a clear wetting prope1ty (Figure 5a). Samples with 120 s or longer plasma n·eatment had liquid metal droplets readily roll off on the inclined surface without

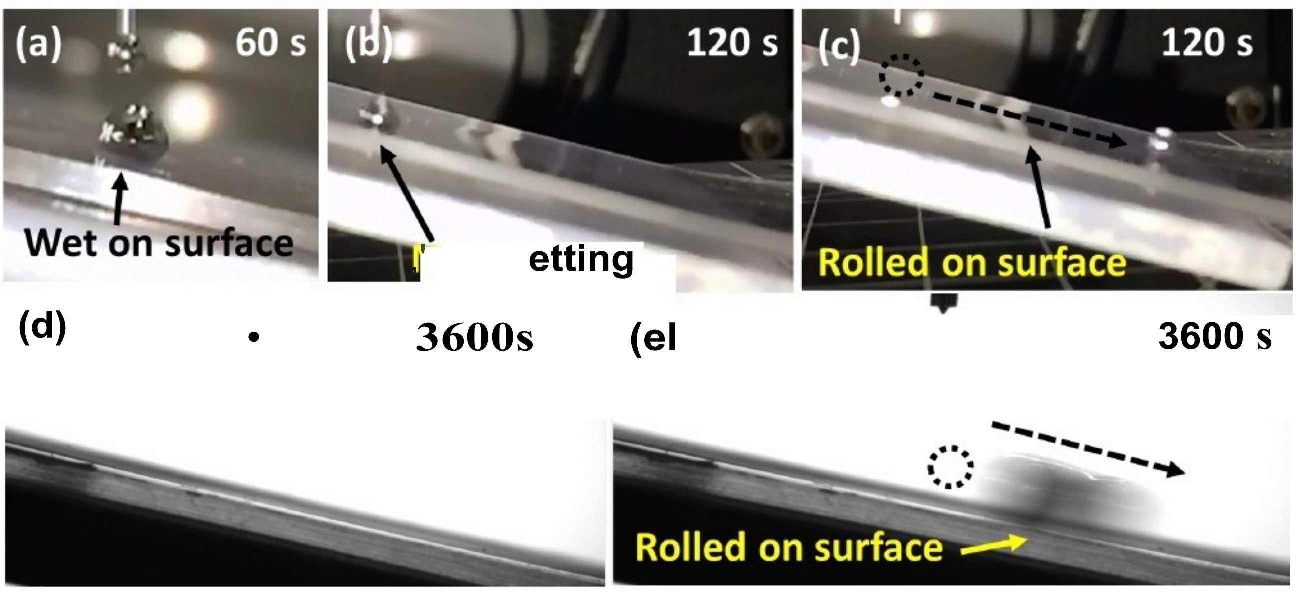

*Figure **5**. Optical images of the rolling test of the liquid metal droplet on (a) 60 sand (b, c) 120 s (d, e) 3,600 s plasma-*

treated suifaces tilted at the angle of 15°. Liquidmetal droplet stuck on 60 s suiface (a) while rolled on 120 s surface (b, c)and 3,600 s suiface (d, e).

leaving any apparent residue on the PDMS, exhibiting a clear non-wetting property (Figure 5b-e). This result clearly demonstrates that the plasma-treatment indeed creates the non-wetting property, and that the duration of exposure plays a critical role in maintaining that property.

CONCLUSION

In thi s w ork , CF J0 2 plasma-treated PDMS surfaces were demonstrated to have long-tenn non-wetting prope1ies against oxidized gallium-based liquid metal droplets. The treated PDMS smfaces were shown to have wettability/non-wettability regimes that were quantitatively characterized by static and dynamic contact angle measurements, and shown to have a regime transition based on the duration of plasma exposure. It was fuiher shown that the wetting/non-wetting prope1iy does not change much under an applied strain. SEM micrographs of the plasma treated surfaces show that the plasma etches the PDMS smface to create nanoscale to microscale filaments and that these filaments collectively work together to create a non-wetting rough surface against liquid metal. This nonwetting property can be readily created on any PDMS surfaces regardless if the surface is flat or with topology. This simple method promises to be a valuable tool in liquid metal microfluidic applications.

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