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WeA5 — Diamond II
Nanofluidics I (Oral Session)
Chair: Arai, Fumihito — Nagoya Univ.
Co-Chair: Lam, Raymond H. W. — City Univ. of Hong Kong

13:00-13:15 — WeA5.1
--Enter the Title of the Paper--A COPLANAR MICROFLUIDIC CHANNELS APPLIED FOR SURFACE MODIFICATION OF OXIDIZED GALINSTAN, pp. 410-413.
Li, Guangyong — MEMS and Nanotechnology Lab. School of Mechanical Systems
Parmar, Mitesh — MEMS and Nanotechnology Lab. School of Mechanical Systems
Lee, Dong-weon — Chonnam National Univ.

13:15-13:30 — WeA5.2
Patterned Ultrathin Metal Membranes with Hexagonally Packed Sub-50nm Nanopore Arrays Based on Hydrophilicity-Templated Self-Assembly Monolayer, pp. 414-417.
Yang, Zengfei — Peking Univ. Shenzhen Graduate School
Qian, Chuang — Inst. of Microelectronics, Peking Univ.
Wu, Wengang — Peking Univ.

13:30-13:45 — WeA5.3
A Microfluidic Long-Term Bacteria Culture Device with Controllable Humidity and Dissolved Oxygen, pp. 418-421.
Cui, Xin — City Univ. of Hong Kong
Lam, Raymond H. W. — City Univ. of Hong Kong

13:45-14:00 — WeA5.4
An Improved Method for Measuring Boundary Slip on Hydrophobic Surface with Atomic Force Microscope, pp. 422-425.
Pan, Yunlu — Harbin Inst. of Tech.
Zhao, Xuezeng — Harbin Inst. of Tech.
Li, Dayong — Harbin Inst. of Tech. Univ. of Scienc

14:00-14:15 — WeA5.5
Influence of Polystyrene (PS) Solution Concentration on the Formation of Nanobubbles, pp. 426-429.
Li, Dayong — Harbin Inst. of Tech. Univ. of Scienc
Pan, Yunlu — Harbin Inst. of Tech.
Zhao, Xuezeng — Harbin Inst. of Tech.

14:15-14:30 — WeA5.6
Design of a Combined DEP-Raman System for Cell Stretching Manipulation, pp. 430-433.
Zhang, Xiaofei — North Univ. of China
Zhang, Yang — North Univ. of China
Bai, Guohua — North Univ. of China
Tan, Qiulin — North Univ. of China
Xiong, Jijun — North Univ. of China
Sun, Dong — City Univ. of Hong Kong

WeA6 — Diamond III
Simulation and Modeling of Nanostructures and Nanodevices (Oral Session)
Chair: Wang, Albert — Univ. of California
Co-Chair: Li, Yiming — National Chiao Tung Univ.

13:00-13:15 — WeA6.1
Molecular Dynamics Simulation of the Thermal-Caused Material Removal Process by the SPM-Based Electric Nanofabrication, pp. 434-437.
Yang, Ye — Shanghai Jiao Tong Univ.
Zhao, Wansheng — Shanghai Jiao Tong Univ.

13:15-13:30 — WeA6.2
Simulation of the Nucleation of the Precipitate Al₃Sc in an Aluminum Scandium Alloy Using the Kinetic Monte Carlo Method, pp. 438-441.
Esteves, António — Univ. of Minho
Moura, Alfredo Manuel da Silva Gonçalves — Inst. of Pol. and Composites (IPC), Univ. of Minho,

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A Coplanar Microfluidic channel applied for Surface Modification of oxidized Galinstan

Guangyong Li, Mitesh Parmar and Dong-weon Lee*, *Member, IEEE*

***Abstract*—In this paper, a gas permeable PDMS (polydimethlysiloxane) based microfluidic device has been reported for surface modification of oxidized Galinstan. A microchannel with Galinstan droplets was surrounded by another coplanar channel filled with HCl solution. Due to the excellent permeability of PDMS, the HCl vapor easily passed through a thin PDMS wall between two channels (interchannel wall) to achieve continuous chemical reaction with oxidized Galinstan. The PDMS wall thickness was optimized after studying the recovery of non-wetting characteristics of HCl treated Galinstan droplet and HCl permeability through different thickness of PDMS films. The novel microfuidic device was fabricated using conventional micro-molding technology. The Lab VIEW controlled syringe pump system was used for characterizing behavior of HCl vapor treated Galinstan in the microchannel. The experimental results demonstrated that the method easily removes the oxide layer of oxidized Galinstan and can effectively move HCl-treated Galinstan droplets in microchannel.**

I. Introduction

Galinstan is a liquid metal eutectic GaInSn alloy (68.5%, 21.5 and 10% by weight, respectively). Due to outstanding properties such as low melting point (-19 °C), low electrical resistivity (0.435 μΩ·m), higher boiling point (1300 °C), higher thermal conductivity (16.5 W/m·K) and ultralow vapor pressure ($<10^{-6}$ Pa at 500 °C), the low toxicity of Galinstan can be ignored compared to highly toxic mercury. As a special liquid metal alloy, it has been investigated for various applications including RF micro switch [1], pump [2], microvalve [3], resonators [4], antennas [5], energy harvesting [6] and tunable frequency selective surface (FSS) [7]. FSS is the planar filter surface designed for microwaves. The working mechanism of tunable FSS device can be represented with equivalent circuit based on variation in capacitance and/or inductance. The variation in capacitance depends largely on the movement of Galinstan. Hence, the easy movement of Galinstan is of utmost importance.

On the other hand, the surface of Galinstan is instantly oxidized in ambient conditions and it behaves more like gel rather than true liquid; adhering to almost any solid surface. This oxide layer is solid and remains elastic unless it experiences a yield stress. The viscous nature is largely originated from gallium oxide (Ga_2O_3 and Ga_2O) and it has a significant sticky problem for easy movement of liquid metal. This instantaneous oxidation is a challenge to overcome. In recent years, some methods have been developed to overcome this issue. According to Liu *et al.*, Galinstan behaves like true liquid metal in sub-ppm oxygen environment [8]. However, this requires a vacuum sealed hermetic packaging which can be extremely costly. Hence, efforts were made to use either oxidized Galinstan or to remove the complete oxide layer. Kim *et al.* reported a micro pillar array based super-lyophobic polydimethlysiloxane (PDMS) micro-tunnel for oxidized Galinstan [9]. However, this has a limitation in applying to 3-dimensional structures. Chen *et al.* presented a Teflon coated channel to overcome this sticking of oxidized Galinstan since it is surrounded by Teflon solution [10]. Nevertheless, this Teflon solution interferes in accurate movement of the oxidized Galinstan. Zrnic *et al.* found that the oxide layer can be removed by the treating the surface with diluted hydrochloric acid (HCl) [11]. Unfortunately, the surface of HCl-treated Galinstan is easily oxidized again in the air.

In this paper, a novel device having a gas permeable PDMS microchannel for surface modification of oxidized Galinstan is presented. Galinstan droplets in the microchannel can be constantly maintained in a true liquid phase at room temperature when Galinstan oxide is treated continuously by HCl filled coplanar surrounding channel. In addition, the recovery of Galinstan droplet non-wetting characteristics is discussed before and after treating the oxidized Galinstan with HCl solution.

II. Experimental

A. Contact angle

The contact angle is an experimentally observable quantity that describes the wetting property of a liquid in contact with a solid surface and surrounded by another immiscible fluid (most commonly a gas). Classical Young's equation (Eq. 1) is widely used to describe the contact angle of a liquid droplet on flat solid surface [12]:

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

where θ is contact angle; γ_{SG}, γ_{SL}, and γ_{LG} are surface tension of solid-gas, solid-liquid and liquid-gas interfaces, respectively.

In order to optimize the thickness of microchannel walls, the HCl permeability studies along with the recovery of non-wetting characteristics of Galinstan droplet were conducted. For this, the contact angle changes of ~8 μl oxidized Galinstan droplet were measured on PDMS films (with varying thicknesses 200, 300, 400, 550 and 850 μm)

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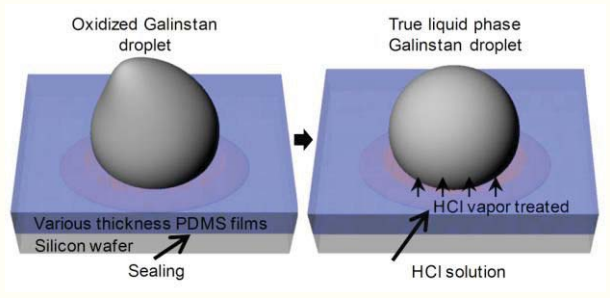

Figure 1. Schematic of oxidized Galinstan droplet into true liquid phase Galinstan droplet.

covered on top of HCl solution (200 µl) in an air environment as shown in Fig. 1. Here, the wettability study was performed by measuring the droplet contact angles using CCD camera (15 *frames / second*) along with in-house developed image processing MATLAB program.

B. *Behavior of Galinstan in microchannel*

To demonstrate the behavior of HCl vapor treated Galinstan in microchannel, a coplanar microchannel based PDMS device was designed. Here, the Galinstan channel was surrounded by a coplanar channel filled with HCl solution. As mentioned before, the thickness of interchannel PDMS wall can be a deciding factor in oxide removal of oxidized Galinstan. After the careful study of HCl permeability through PDMS films of different thickness, the interchannel wall for 37% HCl concentration was optimized at 200 µm.

Based on above analysis, the coplanar microchannel device was fabricated using conventional micro-molding technology outlined in Fig.2. The coplanar microchannel mold was made from SU-8 2050 photoresist (PR) on the silicon wafer. PDMS solution, using standard rapid prototyping method, was coated on the microchannel mold. After curing, the top PDMS based coplanar microchannel layer was gently peeled off from the mold. The top PDMS layer (thickness: 3 mm) comprises of

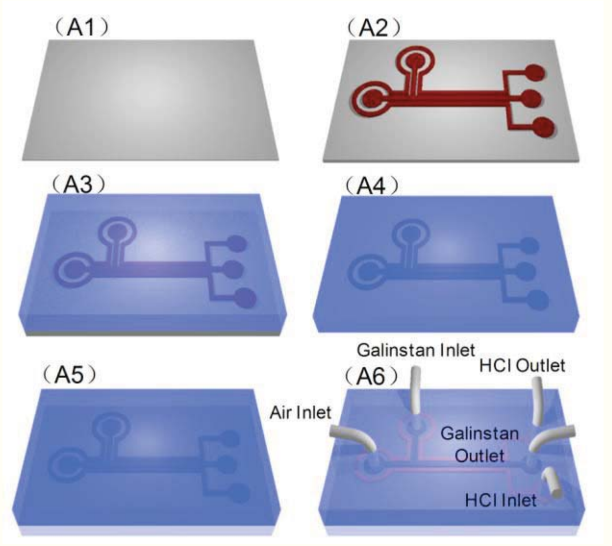

Figure 2. Fabrication sequence of PDMS channel: (A1-A6) SU-8 PR mold, PDMS coating, peeled off from the mold, PDMS-Glass bonding, Channel injected Galinstan surrounded by another coplanar channel filled with HCl.

two coplanar channels (cross-sectional area: 600 µm width*100 µm height) and 5 ports (diameter: 2.4mm) to inject Galinstan and to apply air pressure. Finally, the top PDMS channel layer and the glass slide (as foundation base) were bonded together after a brief activation in oxygen plasma.

After fabrication, the experimental setup comprising of Lab VIEW controlled syringe pump and the CCD camera were used to characterize the behavior of HCl vapor treated (HCl-treated) Galinstan in microchannel, as can be seen in Fig. 3. The movement of HCl-treated Galinstan behavior depends on air pressure. For this characterization and enhancing the feasibility of Galinstan applied to electronic device, we need to consider the conditions under which Galinstan will be filled and separated in microchannel.

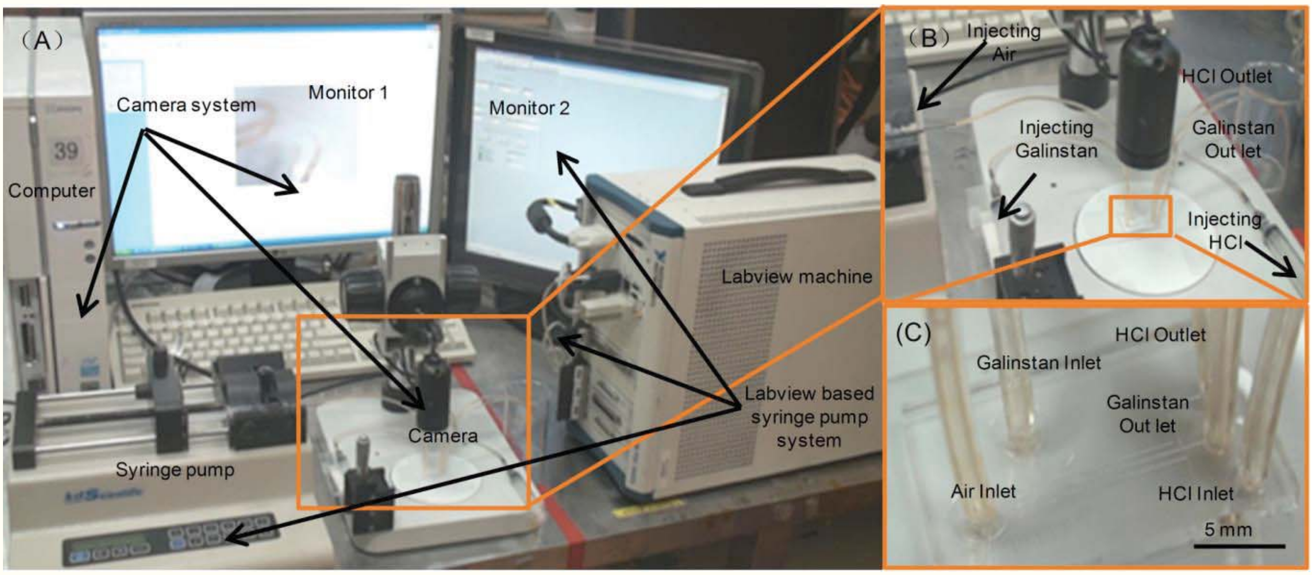

Figure 3. (A) Experimental set up; (B) Camera system; (C) Coplanar microchannel device.

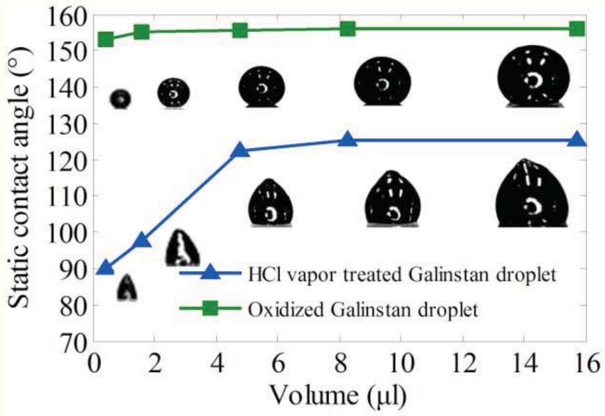

Figure 4. Contact angles of HCl treated Galinstan droplet and oxidized one for various Volume.

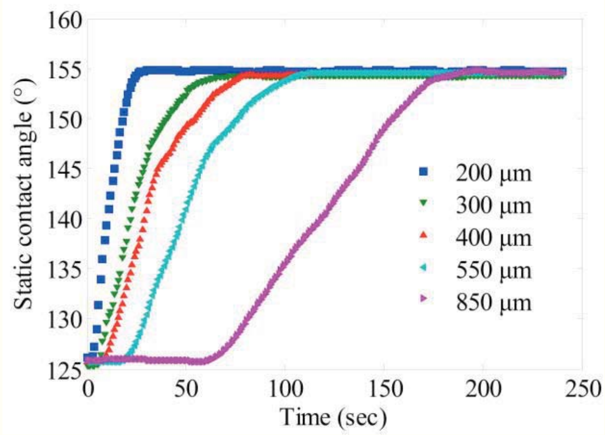

Figure 5. ~8 μl Galinstan droplet contact angles as a function of diffusion time of 37wt% HCl for various thickness PDMS

The time of HCl vapor passing through PDMS channel wall was determined by observing the change in the shape of Galinstan before and after 37 wt% concentration of HCl solution treated in microchannel. Although Galinstan pouring readily out of a bottle, the ability to inject Galinstan into a microchannel would depend on certain pressure applied to Galinstan in the channel. According to ideal gas equation, this pressure was calculated by recording the compressed air volume. In order to analysis the feasibility of Galinstan applied to electronic device, injecting and separating of 37 wt% HCl treated Galinstan in microchannel were considered.

III. RESULT AND DISCUSSION

A. *Static contact angle*

Comparison of contact angles between oxidized Galinstan droplets and 37 wt% HCl-treated Galinstan (reduced Galinstan oxide) droplets with various volumes are shown in Fig. 4. There is a noticeable change of contact angle indicating the change in wetting characteristics of the droplet. The change of contact angles depending on PDMS thickness is observed as a function of time, as shown in Fig. 5. It shows ~8 μl reduced Galinstan oxide droplet contact angle change (from ~125°for oxidized Galinstan to ~155° in case of reduced Galinstan oxide) with time for different thickness PDMS films.

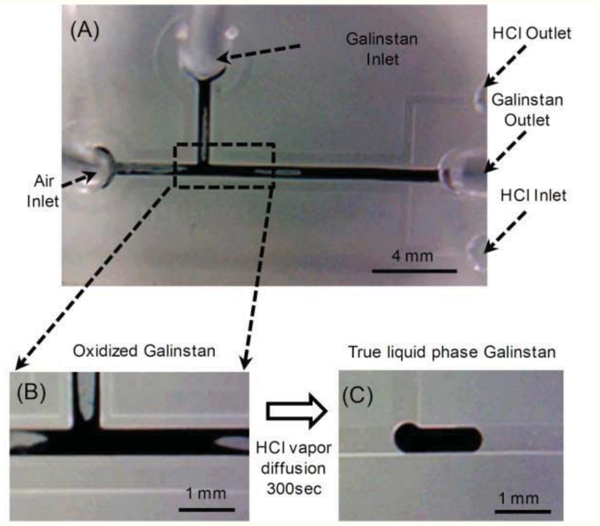

Figure 6. (A) Top view of the coplanar microfluidic channel, (B) naturally oxidized Galinstan in the channel, and (C) true liquid phase Galinstan after HCl vapor diffusion.

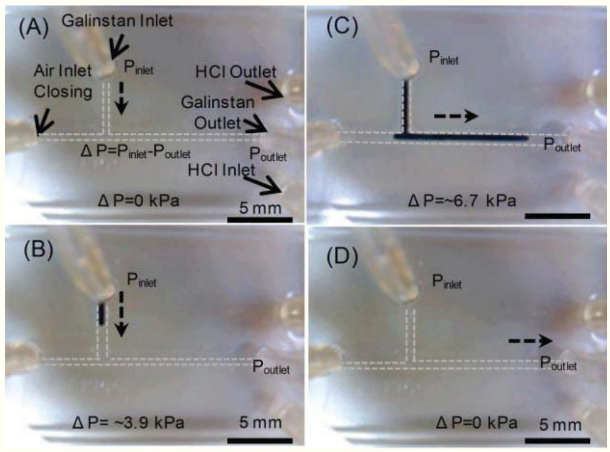

Figure 7. Injecting Galinstan into microchannel and its dependence on applied air pressure

As expected, HCl vapor quickly passes through 200μm PDMS film compared to higher thickness PDMS films.

B. *Behavior of Galinstan in micro-channels*

Fig. 6 shows the time of HCl vapor passing through PDMS channel wall and the shape changing of Galinstan oxide before and after 37 wt% HCl solution treatment in microchannel. As expected, the solid-like oxidized Galinstan become true liquid phase after HCl vapor diffusion for 300 sec.

We have also analysed the ability to inject Galinstan into microchannel and its dependence on pressure under the condition. During the analyses, 37 wt% HCl is present in the coplanar channel and it was assumed that the Galinstan is continuously treated with the HCl solution. Fig 7 shows the injection of Galinstan into microchannel and its dependence on the applied air pressure. Initially only a part of ~ 1 μl Galinstan droplet was filled in the narrow channel until the difference of pressure reached to ~ 3.9 kPa (Fig.7 (A-B)).

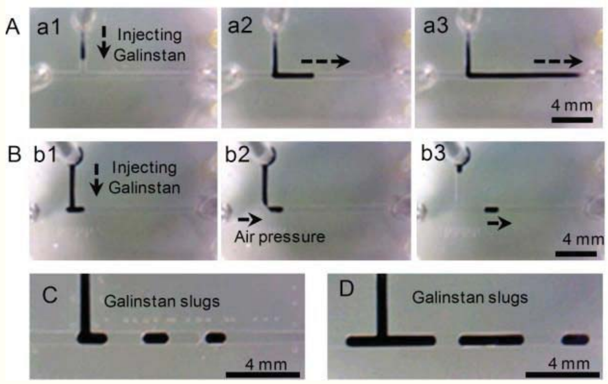

Figure 8. Injecting(A) and separating(B) of HCl treated Galinstan in microfluidic channel; (C) Same volume Galinstan droplet; (D) different volume Galinstan droplet.

Because Galinstan need to overcome a load resistance when it was filled from a wide channel into a narrow channel. Galinstan could be filled in the channel slowly before the difference of pressure increases to ~6.7 kPa (Fig. 7(C)) However, when the pressure exceeding to 6.7 kPa, Galinstan passed through the channel rapidly (<1 sec.) as can be observed in Fig.7(D). On the contrary, Galinstan will meet no difficulty when it flows from a narrow channel to a wide channel. After that, the behavior of injecting and separating HCl treated Galinstan in microchannel was observed as shown in Fig. 8. The experiment results demonstrated that 37 wt% HCl easily removes the oxide layer of oxidized Galinstan and make HCl-treated reduced Galinstan oxide a non-wetting, Newtonian liquid metal alloy.

IV. CONCLUSION

In this study, coplanar microchannel using gas permeable PDMS is applied for the surface modification of oxidized Galinstan. The microchannel with Galinstan droplets was surrounded by another HCl-filled coplanar channel. The interchannel PDMS wall thickness was optimized after the HCl (37 wt%) permeability study through different thickness of PDMS films. The optimized thickness of PDMS is found to be about 200μm. Due to the good permeability of PDMS, the HCl vapour effectively passed through the interchannel PDMS wall to achieve continuous chemical reaction with oxidized Galinstan. Based on basic experiments, a simple microfluidic device was fabricated using the conventional micro-molding technology. A Lab VIEW-controlled syringe pump system was used for the movement of HCl vapor treated Galinstan in the microfluidic channel. Finally, separation and size control of Galinstan droplets in the microfluidic devices was successfully demonstrated using the syringe pump system. The experiment results demonstrated that this novel microfluidic platform can easily remove the oxide layer of oxidized Galinstan and make HCl-treated Galinstan a non-wetting, Newtonian liquid metal.

V. REFERENCES

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