VISUAL OBSERVATION OF PDMS TIP IN LIQUID MICROCONTACT PRINTING

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ABSTRACT

Microcontact printing has been shown to be a viable lithographic technique for the fabrication of microstructures, through the deposition of molecules by conformal contact between a surface and an elastomeric stamp. However, the diffusion of the molecules on the substrate and the deformation of the stamp during the contact are severe drawbacks when considering the resolution of the technique. In this paper, we show the effect of the diffusion of the molecules on the size of gold patterns on silicon and we observe *in-situ* the deformation of the PDMS stamp in liquid and air environment using an interferential microscopy technique.

1. INTRODUCTION

Microcontact printing [1] is a versatile technology used to create molecular micropatterns through the conformal contact of a microstructured elastomeric stamp with a wide range of substrates [2]. Low-cost and straightforward, this technique is used in several engineering domains, from chips microfabrication [3] to biophysical studies [2].

An elastomeric material, commonly PDMS, is molded in a hard microfabricated template in order to create a to a high precision soft replica of the master. After detaching the stamp from the mold, it can be *inked* with the chemical material that is to be printed. The stamp is then pushed toward the substrate with a controlled pressure and time in order to transfer the *ink* molecules to the substrate and then removed. The molecules are located where the conformal contact between the stamp and the surface takes place with a submicrometer resolution.

Although the PDMS stamp can be fabricated with high precision [4], the limitation of the resolution of the microcontact printing technique is a consequence of two phenomena occurring during the stamping [2] : the deformation of the stamp under pressure and the diffusion of the *ink* molecules on the substrate during the contact [5,6]. The effect of the diffusion can be avoided with a decrease of the contact time, a decrease of the *ink* concentration or a different solvent [7]. On the other hand, if it is easy to avoid large scale deformation by modifying the design of the stamp [8], it is difficult to quantify in real time the deformations of the surface of the stamp during the contact.

In this article, we apply Reflection Interference Contrast Microscopy (RICM) to visualize *in-situ* the deformation of a PDMS stamp during the inking process on a glass surface. RICM, developed in 1964 by Curtis *et al.* [9] to study the adhesion patterns of biological cells, allows imaging the Newton rings created by an object in close vicinity of a transparent surface and then reconstructing its three-dimensional profile [10]. RICM was recently used to study the adhesion [11] and detachment [12] of elastomeric colloidal particles on glass substrates.

In this article, we introduce the RICM and we apply it to the study of the deformation of the tips with the applied pressure and we show we can reconstruct the tip profile from the analysis of the interference patterns. Then, we compare these results with the ones obtained by performing a microcontact printing experiment on a gold surface and we conclude on the role of the deformation on the pattern area in air and water environment.

2. PDMS STAMP FABRICATION

In this study, we use a millimetric PDMS stamp having microscopic pyramidal features, in order to make easier the study of the deformation during the stamping process (fig. 1). We fabricate the silicon master with pyramidal grooves by photolithography and anisotropic KOH etching. A fine control of the etching time allows controlling the final surface of the pyramidal tip, which is set to 3.5x3.5 μm^2 in our experiments. Then we pour a PDMS/Curing agent (9:1wt/wt, Dow Corning Sylgard 184) mixture onto the master and we cure it at 180°C for three hours. Finally, we detach the stamp from the master and we attach it on a glass slide for easy handling. Each single PDMS tip molded from the master has a pyramidal structure with 3.5 x 3.5 μm^2 square surface on the top. The stamp itself has a square shape and a total surface of 3x3 mm^2.

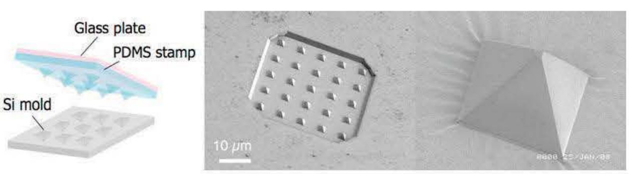

Figure 1: Schematic view of the molding process of a PDMS stamp and SEM image of the stamp itself. On the center image, we see clearly the supporting area around the tips. The tips have a pyramidal shape ending up with a flat surface of 3.5x3.5 μm^2.

3. RICM IMAGING OF CONTACT AREAS

Reflection Interference Contrast Microscopy

The principle of Reflection Interference Contrast Microscopy (RICM) is depicted on fig. 2. An object, in this study a PDMS stamp, in contact with a glass substrate is observed by reflection microscopy with epi-illumination with monochromatic light. The incident beam is partly reflected at the glass interface, the object reflects the transmitted part and interference fringes, also called Newton rings, are created on the glass surface. The RICM allows

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imaging patterns smaller than the micron and allows reconstructing the vertical profile of the object over several microns far from the glass substrate.

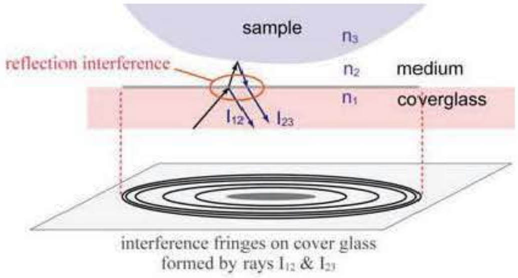

Figure 2: Schematic representation of an RICM experiment. The proximity between the stamp and the glass surface creates interference patterns under monochromatic illumination. The interference fringes inter-distance depends on the vertical profile of the stamp.

Optical Setup

We observe the RICM interference patterns on an inverted light microscope Olympus IX 51. We create a monochromatic illumination with an epifluorescence mercury lamp and a set of filters allowing only a single wavelength (λ=570 nm) going through the optical setup. We perform the image acquisition with a QImaging Retiga EXi 12 bit-camera and the image analysis with the NIH ImageJ software.

Glass substrates

The RICM study of the stamp deformation is done on commercial glass coverslips used for microscopy. Prior to the experiment the coverslips are rinsed with ethanol and deionized water. The experiments in liquid are done in cell culture chamber having a coverslips at the bottom.

***In-situ* Observation of the Stamping Process**

We press a PDMS stamp without ink molecules on a glass slide with a stamping force ranging from 1 to 20 mN and controlled by calibrated weights. By RICM, we take a picture of each tip and we measure numerically the contact area in air (a) and (b) and we report the results on the figure 3.

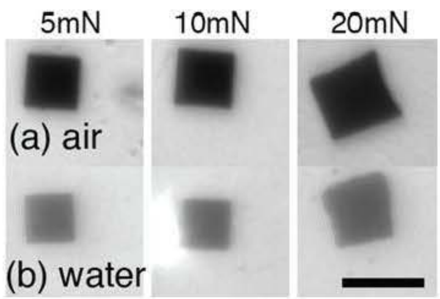

Figure 3: RICM images of the PDMS tip in contact with the glass slide for different stamping pressures in air and water. The difference of contrast is due to the different refractive index of air and water. (Scalebar: 5 µm)

The difference of contrast between the pictures in air (a) and in water (b) relies in the difference of refractive index between air and water.

We see that the contact area increases with the applied force. Moreover, as the increase of the area is more important in air condition, the shape of the stamp is modified for an applied force of 20 mN as the structure collapses.

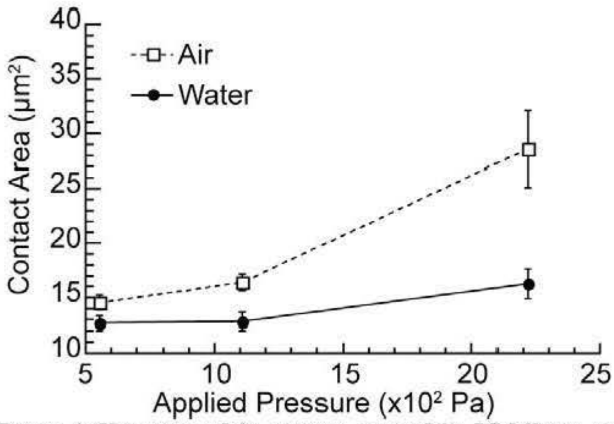

Figure 4: Variation of the contact area of the PDMS tips as a function of the stamping pressure.

On figure 4, we report the evolution of contact area of the tip as a function of the experimental environment and the applied pressure. Neglecting the buoyancy force, the applied pressure is expressed as the applied weight divided by the total area of the stamp. In air, the deformation of the stamp leads to an important increase of the stamping area with the applied pressure. In water, this deformation doesn't occur since liquid is entrapped within the stamp thanks to the PDMS support.

Reconstruction of the stamp profile

The RICM technique allows bringing more quantitative information than the contact area solely. Indeed, we can also observe on a tip image the interference fringes and analyze their spacing since it depends on the vertical profile of the tip itself, as shown on figure 5(inset).

On figure 5(top) we plot the intensity profile of the interference pattern along one direction of the tip image starting from the center of the contact area, for an experiment in water with an applied force of 20 mN.

The figure 5(bottom) shows the numerical reconstruction of the profile of the stamp over several hundred of nanometers far from the glass substrate based on the image analysis of the interference fringes inter-distance shown on figure 5(top): each local minimum of the graph corresponds to a height difference on the profile equal to half of the illumination wavelength [10].

As inferred from the asymmetric RICM image, the profile of the stamp itself is not symmetric, and hence the applied force is not uniform on the stamp.

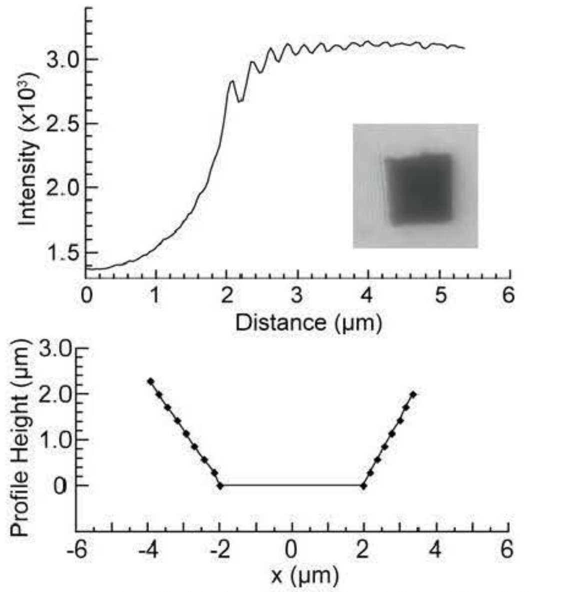

Figure 5: (Top) Intensity profile of the interference fringes along one direction of the stamp RICM image for a stamping in water with a force of 20 mN. (Inset) RICM image of the tip in contact with the glass slide: the center part corresponds to the contact area with the glass. (Bottom) Stamp profile reconstructed from the interference pattern analysis.

4. GOLD PATTERNS ON SILICON

Silicon substrates

In order to study the effect of the pressure and stamping time on the shape of gold patterns by microcontact printing, we thermally evaporate a 50 nm thick gold layer with a 10 nm thick chrome adhesion layer (Nilaco, Japan) on silicon wafers cleaned by a Piranha mixture (H_2SO_4/H_2O_2 1:1 vol.).

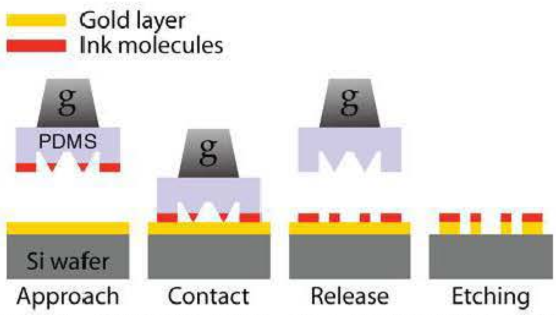

Figure 6: Schematic view of a microcontact printing experiment: (a) approach, (b) contact and transfer, (c) release and (d) etching of the gold layer. The pressure on the stamp is controlled by calibration weights. Gold is solely etched where no molecules are bound to it.

Microcontact Printing Experiment

We cover the PDMS stamp with a SAM molecule, hexadecanethiol (HDT, 100 mM in ethanol), which has the ability to self-assemble on the gold surface [1]. Then we apply the stamp on the gold surface with a controlled pressure and time in air or deionized water environment (Figure 6). We detach the stamp from the sample and finally we immerse the sample into a gold etching solution (KOH 1M, $Na_2S_2O_3$ 1M, $K_3Fe(CN)_6$ 0.01M, $K_4Fe(CN)_6$ 0.001M) for 150 seconds until complete etching of the gold layer where no SAM molecules are adsorbed.

Gold patterns on silicon

On Figure 7, we show the gold patterns obtained with an applied force ranging between 5 and 20 mN during 5 seconds in air (a) and water (b) and observed with a JEOL JSM 740 field-effect scanning electron microscope. The patterns are larger in air than in water environment and the molecular diffusion of the molecules tends to round the patterns.

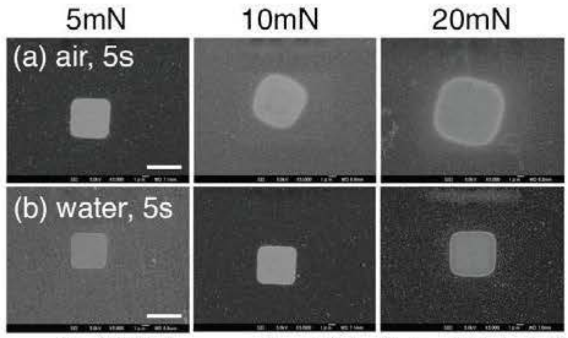

Figure 7: SEM images of gold patterns fabricated by microcontact printing of SAM molecules in air and liquid environment. The contact time, the applied pressure and the environment have an influence on the pattern size and its shape. (scalebar : 5 µm)

On figure 8, we report the evolution of the gold pattern area as a function of the experimental environment, the stamping time and the applied pressure. In air, the pattern area increases by a factor 2 over the applied pressure range and we can see a strong influence of the molecular diffusion since the area increases with the stamping time. When the stamping process is performed in water, nor the applied pressure, neither the molecular diffusion has a strong influence on the pattern area.

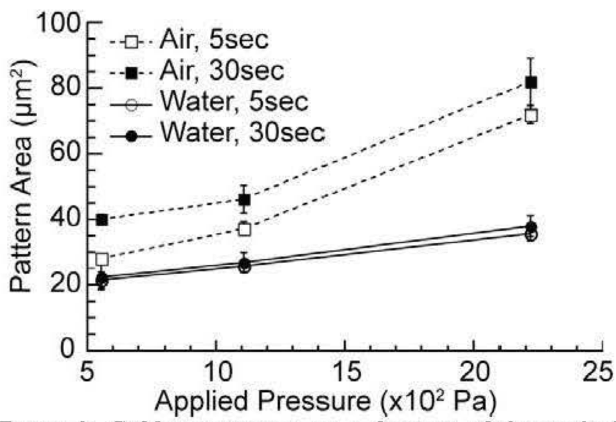

Figure 8: Gold pattern area as a function of the applied pressure. The data are averaged over the 25 tips and the error bar represents the standard deviation of the area.

5. DISCUSSION

Performed in air or in water, the contact area of the stamp and the gold pattern area have the same trend toward the applied pressure. In our experimental configuration, the PDMS tips collapse in air environment, leading to a change of the shape of the tip and a broadening of the contact area. However, in water, since the liquid is trapped between the stamp and the substrate, the shape of the tip is less deformed and doesn't collapse. Compared to the experiment on gold surface, the diffusion accounts for less than the stamp deformation itself on the final surface area of the patterns, especially in air.

6. CONCLUSION

In this article, we have shown that the RICM technique can be used to analyze the tip deformation of a stamp in microcontact printing experiments. The analysis of the contact area showed that depending on the experimental conditions, the pressure can deform and make collapse the tip, with dramatic effect on the patterns surface area. We confirmed this with the analysis of the surface area of gold patterns in the same conditions.

RICM is a powerful technique allowing the reconstruction of the tridimensional profile of the stamp in the close vicinity of the substrate. Used as a monitoring instrument, and not as an analysis technique, it can be really helpful during microcontact printing experiments in order to control the stamping conditions *in-situ*.

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