EFFECT OF AFFINITY BETWEEN THE STAMP AND INK MOLECULES ON MICRO CONTACT PRINTING

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ABSTRACT

In this paper, we experimentally highlight the affinity of the stamp and ink molecules, or self-assembled monolayer (SAM) in micro contact printing. We found that in a short contacting time, the ink molecules were not fully transferred from the stamp to the substrate. This is considered to be affected by the affinity of the molecules with the stamp. In order to investigate this phenomenon, we prepared several types of SAM, and stamps made of PDMS and PDMS covered with parylene. We used the diffusion coefficient to characterize the increase in the patterning area and experiments showed the coefficient differed with both ink molecules and stamps. This knowledge will be of great help for accurate micro contact printing.

KEYWORDS: Micro contact printing, self-assembled monolayer, affinity, diffusion

INTRODUCTION

The manufacturing technology of nano/micro structures to provide surfaces various functions is currently extensively studied with applications to micro total analysis systems in mind. Reliable and low-cost technologies include micro contact printing (μCP) that is simple, reproducible, and cost-effective, requires simple equipment and processes, and was first introduced by G. Withesides et al. in 1994 [1]. It achieves high quality and definition of patterns of molecules on the surface at nano and micro scale. The molecules, or the ink in the printing, that can be transferred to the surface from the stamp cover peptides, proteins, DNA, and, in particular, self-assembled monolayer (SAM) [2]. SAM forms a monolayer of molecules after being transferred to the surface. It consists of a functional group, alkane chain, and binding group. The binding group determines the surface material on which the SAM can be formed. The functional group modify the chemical properties of the surface, which include the surface energy, chemical reactiveness, bio affinity, etc.

The accuracy or transfer rate, i.e., how well the stamp pattern is transferred onto the substrate, is one of the critical criteria in μCP. We experimentally found that not sufficient contact time between the stamp and the substrate resulted in poor accuracy and this trend depended on species of SAMs and the stamp surface. We considered the affinity of the ink SAM and the stamp was most dominant and evaluated the affinity by the diffusion coefficient of the SAM molecule with respect to the SAMs and the stamp surfaces (with or without parylene coating).

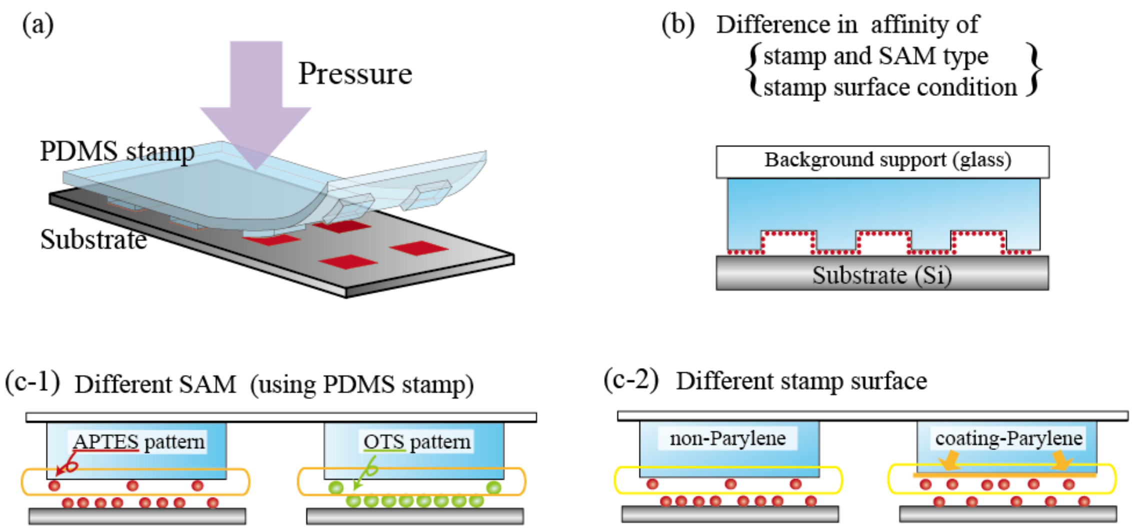


Figure 1. Schematic images of this study. (a)-(b) Schematic image of micro contact printing (μCP). (a) Concept image of micro contact printing.(b) Concept of this study. Patterning accurate is defined by affinity of stamp and SAM type, or stamp surface condition. (c-1) Schematic images of difference in affinity of stamp and SAM-ink types. (c-2) Schematic image of difference in stamp surface condition, Parylene coating or not.

FABRICATION AND PRINTING

The µCP processes can be divided in three steps that are; stamp fabrication (Figure 2 (a)), inking, and contacting process as shown in Figure 2 (b). First we fabricated PDMS stamps by curing SILPOT 184 W/C on SU-8 (SU-8 10, Microchem) mold. It had square patterns of 20 µm × 20 µm, and a height of 5 µm. For a stamp with parylene, we deposited parylene C using Lab Coater.

Next we dipped PDMS stamp in SAM solution for 30s and dried [3]. We used 3% aminopropyltriethoxysilane (APTES), octadecyltrichlorosilane (OTS) and 3% glycidoxypropyltrimethoxysilane (GPTMS) as SAM (Table 1). SAMs of silane compound can organize self-assembled on Si substrate, so they can be applied to the fabrication of several micro/nano electronic devices. Then the stamp was brought into contact with a silicon substrate using custom-made micro contact printing machine (PA400km, Nanometric Tech. Inc.) as shown in Figure 3 that allows the stamp to be pressed uniformly and at constant pressure. The pressure was set to be 1 kPa in our experiments. After the contact for designated periods, SAM was heat treated for 60 s at 100 C.

Then we observed and measured printed pattern each contact time by laser microscope. Figure 4 shows the laser-microscopic images of the patterned SAMs by using PDMS stamp.

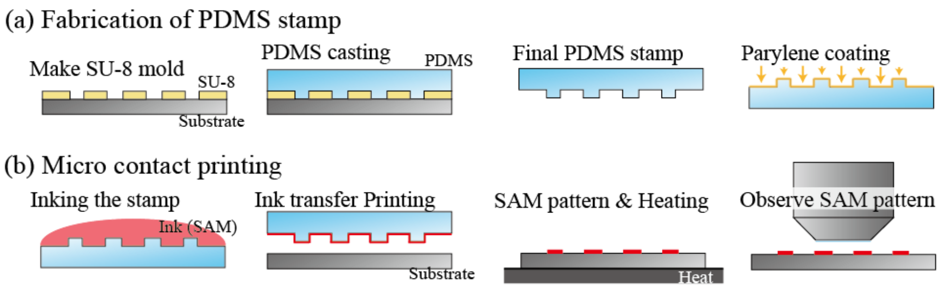


Figure 2. Images of micro contact printing process. (a) Fabrication process of PDMS stamp. We made SU-8 pattern as the mold, and we poured PDMS on the mold and cured it. Then we deposited Parylene coating on stamp surface. (b) Inking and micro contact printing process.

Table.1 Structural formula and molecule weight of using SAMs

	APTES (3-aminoprophyltrieethoxysilane)	OTS (octadecyltrichlorosilane)	GPTMS (3-glycidoxypropyltrimethoxysilane)
Structural fomula	OCH_2CH_3 $NH_2\text{-}(CH_2)_3\text{-}Si\text{-}OCH_2CH_3$ OCH_2CH_3	Cl $CH_3\text{-}(CH_2)_{17}\text{-}Si\text{-}Cl$ Cl	CH_2 OCH_3 $>CH\text{-}CH_2O\text{-}(CH_2)_3\text{-}Si\text{-}OCH_3$ O OCH_3
Molecule weight	221.37	387.93	236.34

Figure 3. Image of custum-made micro contact printing machine. It allows the stamp to be pressed uniformly and at constant pressure.

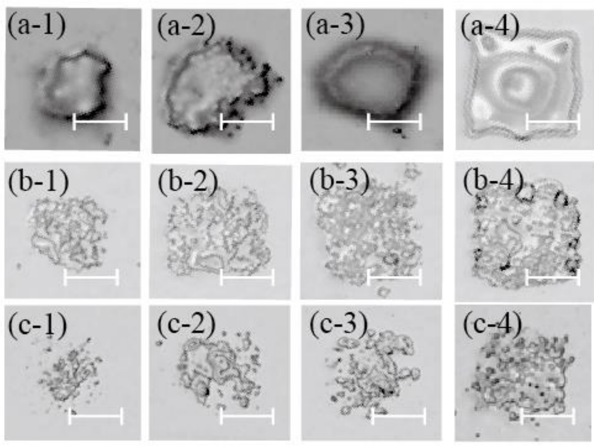


Figure 4. Diffusion effect of SAM on a silicon substrate for different contact time by laser microscope. (a-) APTES patterning. (b-) OTS patterning (c-) GPTMS patterning. (-1) Contact time is 5s. (-2) Contact time is 10s. (-3) Contact time is 30s. (-4) Contact time is 50s.

RESULT AND DISCUSSION

Figure 3 (a) shows the relationship between the contact time and patterning area with respect to the ink molecules (APTES, OTS, GPTMS) when PDMS stamps were used. It took 100 s for the patterned SAMs to have a same pattern with the stamp for all the SAMs but the rate was different. We thought this difference of patterning rate of SAMs comes from the difference of affinity between ink molecules and PDMS stamp, so next we changed the surface condition of PDMS stamp by coating parylene C and contact-printed in the same way. As shown in Figure 3 (b) and (c), the patterning rate were also different between them for both APTES and OTS. SAM of GPTMS couldn't pattern by using parylene coated PDMS stamp.

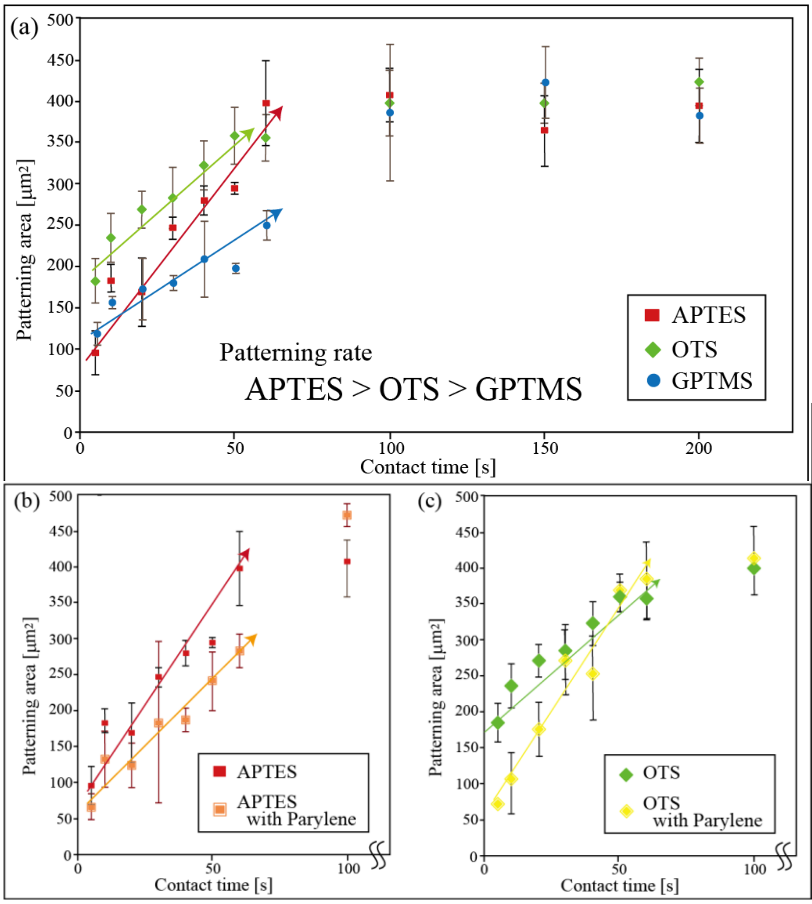
Then we evaluated the results with respect to the diffusion using the diffusion coefficients given by diffusion equation (1). The results are summarized in Figure 5.

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right) \tag{1}$$

By comparing the diffusion coefficients (D), I found that there are some differences depending on SAM types or stamp surface, and this coefficient is a guide to evaluate the affinity between the SAM ink and stamp.

CONCLUSION

In this study, we evaluated the affinity of stamp and SAMs in contact printing. The data base of the diffusion coefficients for various SAMs and stamps will be of great help to design micro fabrication processes using µCP technology.



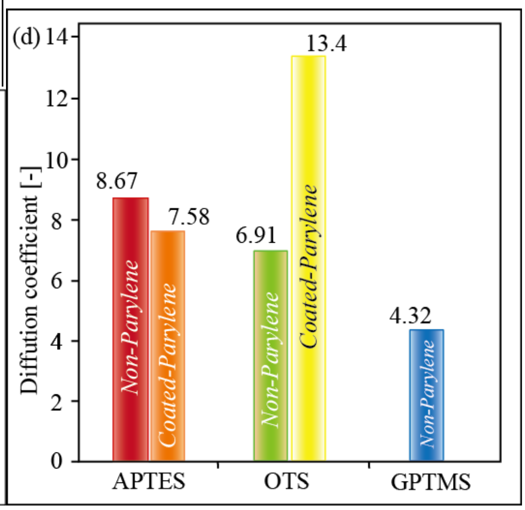


Figure 5. (a) Result of the difference in diffusion time of APTES, OTS and GPTMS pattening. (b) Result of the difference in surface condition, coating Parylene or not on APTES. (c) Result of the difference in surface condition, coating Parylene or not on GPTMS. (d) Diffusion coefficient of this study. It shows that the diffusion coeffient and patterning speed is different depending on SAM type and stamp surface condition.

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