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Hot-embossing performance of silicon micromold coated with self-assembled n-octadecyltrichlorosilane

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ABSTRACT

Self-assembled monolayer (SAM) coatings of *n*-octadecyltrichlorosilane [OTS, $CH_3(CH_2)_{17}SiCl_3$] were deposited on Si micromolds for micro hot-embossing by dipping the Si molds into an anhydrous toluene solvent containing OTS. The coated samples were designated as OTS20, OTS40, OTS60 and OTS80 with respect to deposition time of 20, 40, 60 and 80 min to study the effect of deposition time on the coating quality. The composition, surface roughness, friction coefficient, thermal stability and surface energy were measured using X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), nanotribological test and contact angle test, respectively. The thermal stability of the OTS coatings was determined by measuring water contact angle after heating at various temperatures. The XPS and AFM results showed that a prolonged deposition induced a denser and thicker coating structure and more aggregation of OTS, which also increased the surface roughness. A comparative study of the uncoated and OTS60 coated Si micromolds depicted that the OTS coatings had a good potential to improve the surface quality and efficiency of the molds. The OTS60 coating was evaluated after heat treatment at embossing temperature of 130 °C for a better understanding of the failure mechanism of the micromolds, which showed that the surface properties of the molds remained unchanged at the embossing temperature. Further characterization of the damaged Si micromolds showed that the peel-off of the coatings after a number of replications was the main reason for the failure of the molds. It was found that periodic re-cleaning of the micromolds and re-deposition of the OTS coatings on the coated Si micromolds could extend the lifetime of the molds up to about 112 embossing operations per mold.

1. Introduction

Surface phenomena become more significant for a micromold as its dimensions scale down and surface-to-volume ratio becomes large. In this case forces associated with the mold surface, such as adhesive and friction forces, become dominant for the performance of the micromold [1,2]. The problems with low yield, poor reproducibility, premature failure and limited lifetime of a mold are induced by high friction and surface adhesion generated during demolding [3–5]. Si micromolds are common for fabrication of polymer-based microfluidic devices by either hot-embossing or injection molding because of the well established fabrication methods for Si, e.g. deep reactive ion etching (DRIE), for favorable surface finish and accuracy [6,7]. However, a typical Si mold has a short lifetime because of its high brittleness and poor tribological performance. The above problem has been attempted by means of solid lubricating coatings, which was limited by the line-of-sight issue [8]. In this respect self-assembled monolayers (SAMs) are a preferred kind of solid lubricant, because a sub-nanometer uniform coating can form spontaneously on the surfaces of Si micromolds by simply immersing them into a solution comprising an organic solvent and an active surfactant. A Si mold coated with an SAM can have very low friction coefficient and surface energy, good thermal stability and high rupture strength due to a strong chemical bonding between the layer and the Si substrate [9–12]. SAM coatings have recently attracted great attention as molecular lubricants in MEMS, nanoimprint lithography (NIL) and bio-technology to deal with friction and adhesion related problems [9,13–15]. Many researchers have studied various SAM coatings among which OTS is a well established solid lubricant in MEMS applications [9,16,17]. Because of that, OTS was chosen for this study.

A typical hot-embossing process applies a temperature above the glass transition temperature (T_g) of a workpiece and a high pressure to form microfeatures into the workpiece, where both

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workpiece and micromold are subjected to heating before embossing, followed by a cooling process before demolding [18]. Some research works on the thermal stability of OTS coatings by measuring their wettability after heating at various temperatures have been reported [19,20], but the understanding of the surface tribological and anti-rupture properties as well as variation in composition of these coatings after heat treatment at embossing temperature is required for improvement of the fabrication efficiency.

This work optimized the deposition time of OTS coatings based on the performance of the coatings. To further improve the replication performance and better understand the failure mechanism of the SAM coated micromolds, this paper also proposed a simple process of periodic re-deposition of the OTS SAMs on the molds.

2. Experimental details

2.1. Sample preparation

Si micromolds, prepared by DRIE as described elsewhere [2], were first cleaned thoroughly in deionized (DI) water followed by cleaning in a piranha solution, a mixture formed with a 98% H_2SO_4 solution and a 30% H_2O_2 solution in a volume ratio of 7:3, at room temperature (22–24 °C) for 45 min. After that the Si micromolds were rinsed in DI water again followed by rinsing in an anhydrous toluene solvent. The cleaned molds were then immediately dipped into a solution comprising an anhydrous toluene solvent (Sigma–Aldrich) and 0.1 mM OTS (Meryer Chemical), and a self-assembled monolayer (SAM) was formed on the mold surfaces. The SAM coated molds were sequentially rinsed in the anhydrous toluene followed by DI water. The immersion durations of the Si molds in the OTS solution during the dip coating process were 20, 40, 60 and 80 min and the OTS SAM coatings prepared were designated as OTS20, OTS40, OTS60 and OTS80, respectively.

The OTS coated micromolds were periodically re-cleaned ultrasonically in the anhydrous toluene solvent for 15 min and then re-coated in the 0.1 mM OTS solution for 1 h after every 20 embossing operations.

2.2. Characterization

The OTS coated Si substrates were thermally treated at various temperatures from 90 to 270 °C with a step increment of 30 °C in ambient atmosphere to evaluate the thermal stability of the coatings. Before the thermal anneal was started, the OTS coated Si substrates were placed on the top of the hot-plate of the hot-embossing machine that was open to the ambient environment. Thereafter, the samples were heated to each desire temperature and maintained at that temperature for 60 min. At the end of thermal anneal, the OTS coated Si substrates were cooled down to room temperature (~22 °C), which took about 30–60 min depending on the heating temperature.

X-ray photoelectron spectroscopy (XPS) (Kartos Axis Ultra) was used to study the chemical states of the OTS coated samples using a monochromatic Al Kα excitation of 1486.71 eV at 90° detection angle with pass energies of 160 and 40 eV for wide and detail scans, respectively. The atomic percentages of the elements in the OTS coated samples were calculated from the integrated areas of the respected XPS bands.

The surface topography and roughness of the OTS coated Si micromolds were measured by atomic force microscopy (AFM) (Digital Instruments, S3000) using a Si_3N_4 cantilever with force constant and resonance frequency of 40 N/m and 300 kHz, respectively. The AFM images were acquired in tapping mode with a scan rate of 0.7 Hz and a scan area of 1 μm × 1 μm inside a closed chamber at ambient atmosphere condition. Thicknesses of OTS coatings were measured by AFM at randomly selected areas and average height difference was taken to measure the thickness.

Table 1
Atomic percentages of O, C and Si and atomic ratios of C/Si, C/O and Si/O of bare Si and OTS coated Si micromolds.

Sample	O (at.%)	C (at.%)	Si (at.%)	C/Si	C/O	Si/O
Bare Si	28.44	10.47	61.09	0.17	0.37	2.15
OTS20	23	22.64	54.36	0.42	0.98	2.36
OTS40	14.29	50.36	35.35	1.42	3.52	2.47
OTS60	13.1	58.66	28.23	2.08	4.48	2.15
OTS80	12.71	64.54	22.75	2.84	5.08	1.79
Heat treated OTS60	13.46	58.39	28.15	2.07	4.34	2.09
Damaged OTS60	26.8	15	58.2	0.26	0.56	2.17

The friction and adhesion of the OTS coated samples were measured with a nanotribometer (CSM) using a polymethyl methacrylate (PMMA) ball of 2 mm in diameter. During a friction test the PMMA ball was slid on the sample surface along a circular track of 0.5 mm in radius at a sliding speed of 2 cm s^{-1} under a normal load of 25 mN for 500 laps. During an adhesion test, the PMMA ball was brought in contact with and then separated from the sample surface and, at the same time, the deflection of the cantilever beam caused by the adhesion was recorded. The recorded cantilever deflection was then converted to an interaction force in terms of the spring constant of the cantilever used. The adhesive interaction behavior between the surfaces of the PMMA ball and sample in contact was determined from the force–cantilever displacement curve.

The tribological behavior of the OTS60 coated sample heated at 130 °C (hot-embossing temperature) was also evaluated by nanotribometer (CSM).

Static contact angles of DI water and ethylene glycol drops on the OTS coated sample surfaces were measured at five different locations randomly selected for each sample, from which the surface energies of the samples were determined. The dispersive (γ_{lv}^{d}) and polar (γ_{lv}^{p}) surface tension components of DI water and ethylene glycol (Merck) were 21.8, 51 and 29.3 and 19 dyne/cm, respectively.

3. Results and discussion

The atomic percentages of all the elements in the OTS coated samples determined from the XPS measurements are summarized in Table 1. Significant amounts of oxygen are observed from all the samples, which are expected to be from the native oxide layers of the exposed Si substrates. The Si concentrations measured

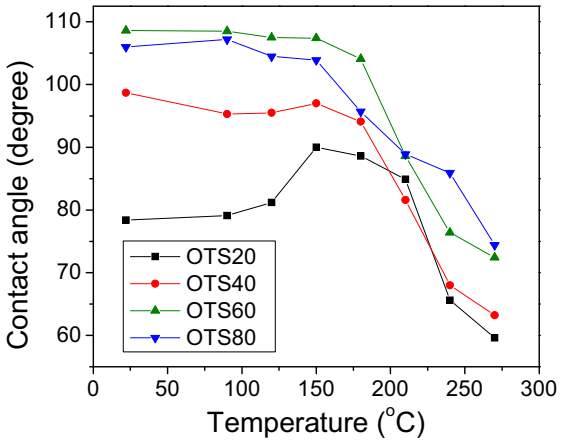

Fig. 1. Temperature-dependent water contact angles of various OTS coated Si micromolds.