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Submicron-scale Polymeric Patterns for Tribological Application in MEMS/NEMS

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Abstract: Submicron-scale patterns made of polymethyl methacrylate (PMMA) were fabricated on silicon-wafer using a capillarity-directed soft lithographic technique. Polyurethane acrylate (PUA) stamps (Master molds) were used to fabricate the patterns. Patterns with three different aspect ratios were fabricated by varying the holding time. The patterns fabricated were the negative replica of the master mold. The patterns so obtained were investigated for their adhesion and friction properties at nano-scale using AFM. Friction tests were conducted in the range of 0-80 nN. Glass (Borosilicate) balls of diameter 1.25 mm mounted on cantilever (Contact Mode type NPS) were used as tips. Further, micro-friction tests were performed using a ball-on-flat type micro-tribo tester, under reciprocating motion, using a soda lime ball (1 mm diameter) under a normal load of 3,000 mN. All experiments were conducted at ambient temperature (24 ± 1°C) and relative humidity (45 ± 5%). Results showed that the patterned samples exhibited superior tribological properties when compared to the silicon wafer and non-patterned sample (PMMA thin film) both at the nano and micro-scales, owing to their increased hydrophobicity and reduced real area of contact. In the case of patterns it was observed that their morphology (shape factor and size factor) was decisive in defining the real area of contact.

Keywords: Nano, micro, adhesion, friction, soft lithography, tribology

Introduction

Nano- and micro-scale tribology plays an important role in many emerging fields, such as micro/nano-electromechanical systems (MEMS/NEMS) [1-2]. These systems are comprised of elements that are small in size and operate at micro/nano-scale. At these scales of size, the ratio of surface area to volume is high and the surface forces such as adhesion and friction strongly influence the tribological behaviour of the components. These forces are critical in such applications, as they decrease the performance and consequently reduce the durability of MEMS/NEMS devices [1-3].

In the past, many researchers have proposed different approaches towards reducing the surface forces at micro/nano-scale by undertaking topographical and chemical modifications of surfaces. Examples of topographical modification include laser texturing [1], micro-dimple formation [4] and ion-beam roughening of surfaces [5]. Chemical modification includes use of molecular coatings (Langmuir or self-assembled monolayers (SAMs)) as lubricants [3,6].

The topographical modification of surfaces is largely concerned with modifying the local geometry of surfaces in order to imitate the surface topography of 'lotus leaf' that has an unique ability to avoid getting wet by the surrounding water (Fig. 1) [7]. Inspired by the lotus surface, topographical modification of polymeric surfaces has been effective in improving their tribological behaviour [5]. To generate a topographical change of surfaces, various methods based on lithography technique are available such as photolithography, electron beam lithography, nanoimprint lithography and block copolymer lithography [8-10]. Here, we report on the investigation of the tribological characteristics of nano-patterned poly(methyl methacrylate) (PMMA) polymeric surfaces fabricated using a simple capillarity-directed soft lithographic technique, in the context of their possible application for micro/nano-scale devices.

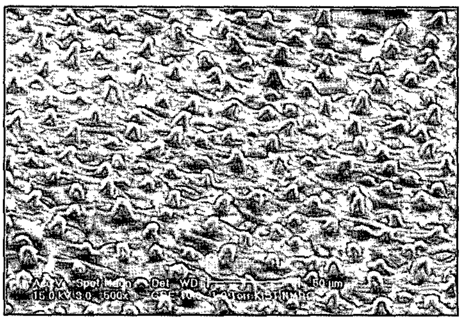

Fig. 1. Protuberances on the lotus leaf that generate a 'water-repellent' surface.

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Experimental

Test specimens

Sub-micron sized patterns of poly(methyl meth-acrylate) (PMMA) with three different aspect ratios on silicon wafer were fabricated using a simple capillarity-directed soft lithographic technique called capillary force lithography [11-12]. Polyurethane acrylate (PUA) stamps were used to fabricate these patterns. The details regarding the fabrication of

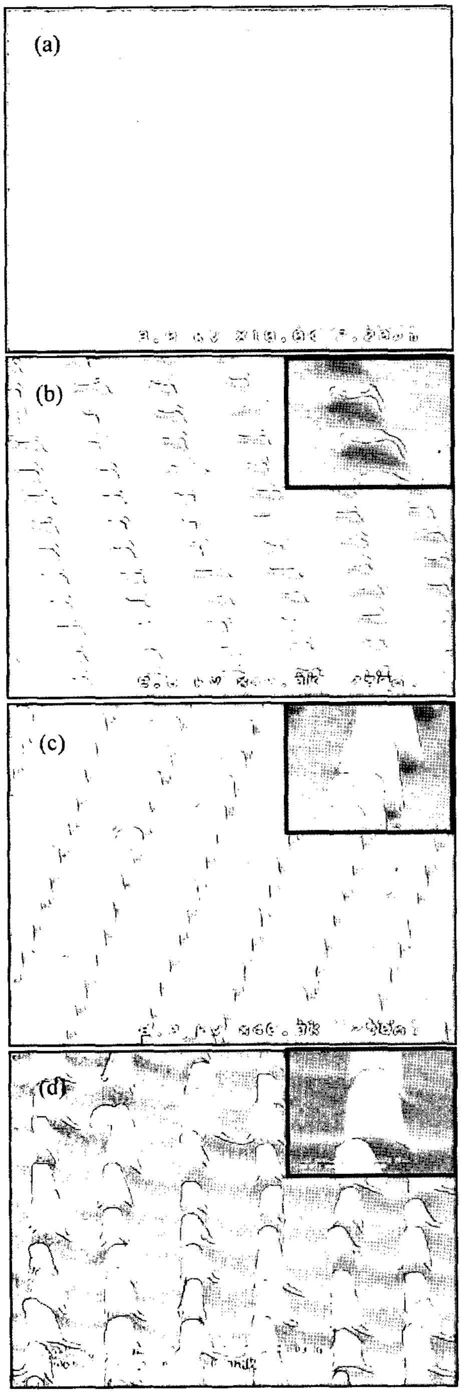

Fig. 2. (a) PMMA thin film. (b-d) show the morphology of patterns fabricated at holding times of 15, 30 and 60 minutes respectively.

Table 1. Water contact angles of silicon wafer, PMMA thin film and of the patterns fabricated at holding times of 15, 30 and 60 minutes

Material	Water contact angle (Deg)
Si wafer	22
PMMA Thin film	68
15 minutes	91
30 minutes	94
60 minutes	99

the stamp (mold) are given in ref. [13]. The processing sequence of pattern formation is briefly described here. The fabrication process involved spin coating of silicon substrates (size~5×5 cm^2) with a 10% poly(methyl methacrylate) (PMMA) solution in toluene. A UV cured mold was then placed on the coated samples under a slight pressure (~10 g/cm^2) to make conformal contact. The mold had cone-shaped nanopillar features with a lateral dimension of ~150 nm at base end and ~50 nm at top and with a height of ~500 nm. Keeping the temperature above T_g of PMMA, typically at 120°C, the samples were left undisturbed for various holding times. The samples fabricated were examined using scanning electron microscopy. Figure 2 (a-d) shows the surface of a PMMA thin film spin-coated on silicon wafer and the morphology of patterns obtained for holding times of 15, 30 and 60 minutes respectively. The insets in the micrographs show the respective patterns at higher magnification. It could be seen from this figure that the aspect ratio of the patterns increases with the holding time. Table 1 shows the static water contact angle of the silicon wafer, PMMA thin film and patterned samples measured using the sessile-drop method. The measurements were repeated for 5 times and the average values are shown.

Test apparatus and methods

Silicon wafer, PMMA thin film and the patterned samples were tested for their adhesion and friction properties (load 0-80 nN, speed 2 μm/sec, scan size 5 μm×5 μm), at nano-scale using atomic force microscopy (AFM). Borosilicate ball (diameter 1.25 μm) mounted on cantilever (Contact Mode type NPS) was used as tip. At micro-scale, friction was measured using a soda lime ball (radius 0.5 mm) under reciprocating motion (load 3,000 μN, speed 1 mm/sec) using a micro-tribotester. All experiments were conducted at controlled temperature of 24 ± 1°C and relative humidity 45 ± 5%.

Results and Discussion

Figure 3 shows the adhesion force at nano-scale of the silicon wafer, PMMA thin film and patterns of three different aspect ratios. It could be observed that the patterns exhibit adhesion force, which is significantly lower than that of the thin film and silicon wafer. Under tribological contact, adhesion force is caused due to various forces such as capillary, electro-static and van der Waals forces [3]. Amongst these forces, the capillary force, which occurs as a result of water condensation from the environment that leads to the formation of meniscus

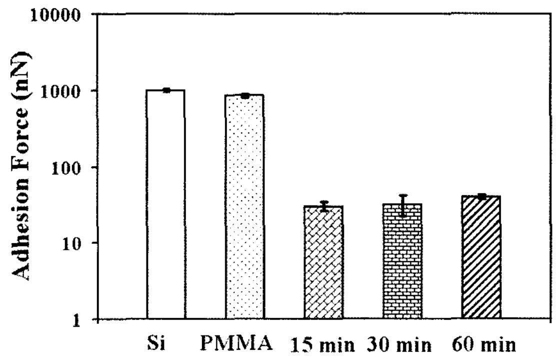

Fig. 3. Adhesion force of the test materials at nano-scale.

bridge, is the strongest [3]. In the present case, the patterned samples exhibit lower values of adhesion owing to their hydrophobic nature (Table1). This suppresses the capillary force to a large extent. Under such circumstances, where the capillary force is unlikely to dominate the adhesion force, the van der Waals forces would play a major role [14]. From Table 1 it could also be seen that silicon wafer is the most hydrophilic material followed by the PMMA thin film, due to which their adhesion property is more dominated by capillary force [3]. This makes them exhibit higher values of adhesion when compared to the patterned surfaces.

Figure 4 shows the nano-scale friction force of the test materials as a function of applied normal load. It could be observed from this figure that values of friction force exist even at zero applied normal load for all the test materials. This is mainly attributed to the influence of the intrinsic adhesive force on the friction force [15]. The inherent adhesion in the case of patterns is comparatively less than the other two materials owing to their hydrophobic nature (Table 1).

From Fig. 4 it could be seen that the patterned samples exhibit values of friction that are lower by an order of magnitude than those of the silicon wafer and PMMA thin film. According to the fundamental law of friction given by Bowden and Tabor [16], for a single asperity contact, the friction force is directly dependent on the real area of contact. Equation 1 gives the expression for the friction force.

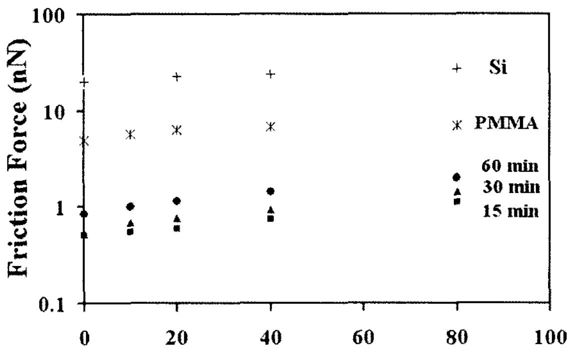

Fig. 4. Friction force of the test materials as a function of applied normal load at nano-scale.

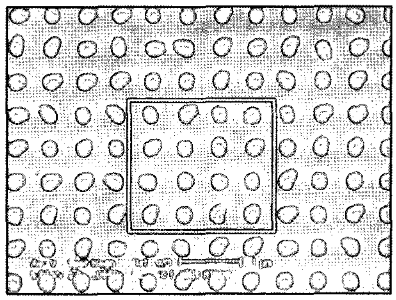

Fig. 5. Top view of the pattern fabricated at holding time of 15 minutes.

$$F_f = \tau A_r \quad (1)$$

where, τ is the shear strength, an interfacial property and A_r the real area of contact.

Thus, in the present case the main reason for the patterns to exhibit lower values of friction than silicon wafer and PMMA thin film is due to their reduced contact area. Figure 5 shows the top view of the patterns taken using a scanning electron microscope. Considering a typical area (area within the box) and assuming that the patterns are circular in shape (radius ~100 nm), the area projected by the patterns within the selected area (box) reduces by almost seven times compared to the nominal area of the sample. This large reduction in the contact area results in lower values of friction in the patterned samples. Further, in addition to their hydrophobic nature (Table 1), the reduction in the contact area plays an important role in reducing the adhesion of the patterned samples when compared to the other two materials (Fig. 3).

Amongst the patterns, the friction force increases with the aspect ratio (holding time) at any given load (Fig. 4). This could be attributed to the increase in the contact area with increase in the aspect ratio. Further, the contact area of the patterned samples is determined both by their size and shape. Considering the size factor, during sliding, patterns with higher aspect ratio (partially-grown (Fig. 2(c)) and fully-grown (Fig. 2(d)) would undergo elastic deformation, thereby causing increased contact area and hence increased friction (Fig. 4).

The insets in Fig. 2 (b-d) show high magnification scanning electron micrographs of the patterns. It could be seen from these figures that the morphology of the patterns has dimples (depressions) on their surface. Further, the size of the dimples decreases with the increase in the holding time (aspect ratio). Considering this shape factor, the presence of dimples in the low aspect ratio pattern (Fig. 2 (b)) and the partially-grown pattern (Fig. 2 (c)) results in lower contact area in that order, when compared to the fully-grown pattern (Fig. 2 (d)). This renders the fully-grown patterns to exhibit higher friction force than the other two samples (Fig. 4). Thus, both the size and shape factors are decisive in determining the contact area of the patterns. The increase in the contact area with the aspect ratio also explains for the increase in the adhesion force with the aspect ratio (holding time) (Fig. 3). The increase in the friction force with the applied normal load in the patterned samples as seen in Fig. 4 is probably due to the increased

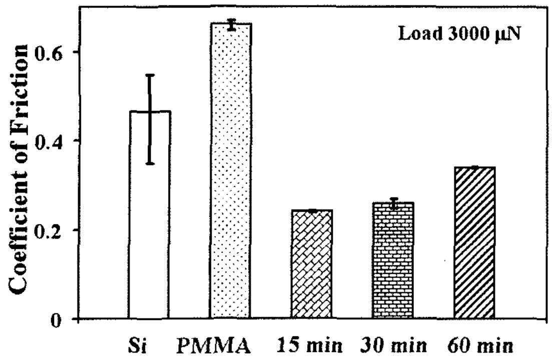

Fig. 6. Coefficient of friction of patterns at micro-scale.

elastic deformation of the patterns that would eventually increase the contact area.

Figure 6 shows the coefficient of friction of the test materials at the micro-scale, estimated as the ratio of friction force to the applied normal load. It could be seen that the coefficient of friction of the patterns shows significant reduction when compared to that of the silicon wafer and PMMA thin film, even at this scale. This is due to the reduced contact area in the case of the patterns. Amongst the patterns, the coefficient of friction increases with the holding time (aspect ratio), which is due to the increase in friction force through the contact area. Unlike in the case of the patterned surfaces, it was observed that both silicon wafer and PMMA thin film exhibited wear, which influenced their friction severely. Figure 7 (a) and (b) shows the worn surfaces of silicon wafer and PMMA thin film.

Thus, topographical modification of surfaces by shape-engineering proves very effective in enhancing the tribological performance both at nano and micro-scales through increased hydrophobicity and reduced real area of contact.

As mentioned earlier, MEMS/NEMS are micro/nano-scale devices that are comprised of elements, which are small in size and operate at micro/nano-scale. During the operation of these devices, most of their components undergo impacting or rubbing motion against each other [17-18]. In most of these devices, silicon is a material of choice because it is compatible with integrated-circuit technology [1,3]. However, silicon oxidizes readily to form a hydrophilic surface, making it susceptible to adhesion [1,3,6]. In making micro/nano-components from silicon such as gears, linear racks and rotating platforms [19], wear and friction become important in addition to adhesion, owing to its poor tribological properties [1,3,6]. Thus, protective coatings are required to enhance its tribological behaviour. Several kinds of coatings have been tested and used to protect silicon under tribological contact in micro/nano-scale devices [3,6]. Amongst these, self-assembled monolayers (SAMs) have proved effective [3,6]. However, the mechanical stability of these monolayer coatings under shear stress is only modest [20] and that their surfaces exhibit significant wear under extended sliding contact [21-22]. Hence, there is always a need for development of new robust materials for tribological applications in micro/nano-scale devices. Considering the enhanced tribological properties of the patterned surfaces investigated in this work, we believe that in the future, these nano-engineered surfaces would be potentially useful for various micro/nano-scale tribological applications. Regarding their nature of application, they maybe used on components that have relatively a large surface area at these scales and which undergo tribological contact. For example, application of patterned surfaces in confined areas i.e. on inaccessible surfaces such as that at the micro-engine drive gear (Fig. 8) [23] may not be possible. Figure 9 shows a MEMS device, a few components of whose have a relatively large surface area, where the nano-patterns could be used.

Figure 9 (a) shows two pixels of a digital micromirror device (DMMD) [24]. The electrostatically activated pixels are operated in a bistable mode, where the equilibrium positions occur when the yoke is rotated ±10° into contact with the electrodes [24].

Such an operation causes the tip of the yoke to scrub back and forth on the electrode surface resulting in the wear of electrode surface (Fig. 9(b)) [24]. At present, perfluoro-decanoic acid (PFDA) is used as the lubricant in this application [24]. However, this molecular coating is vulnerable to ionic or

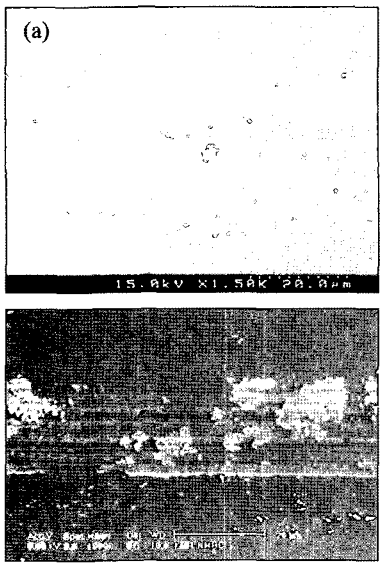

Fig. 7. (a) shows the worn surface of silicon wafer and (b) shows the worn surface of PMMA thin film.

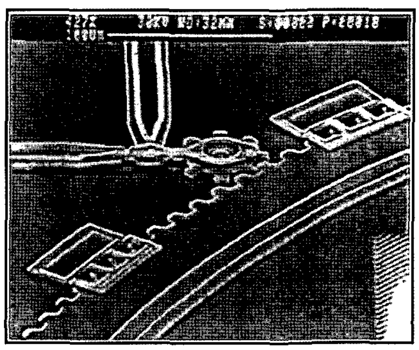

Fig. 8. Micro-engine drive gear [23].

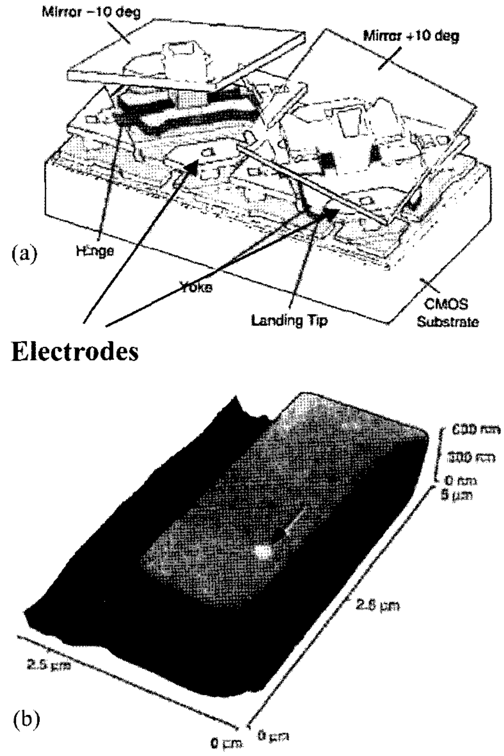

Fig. 9. (a) Digital micromirror device and (b) AFM image of electrode. The arrow indicates wear scar [24].

solvent chemical attacks [24]. Moisture can break the bond to the surface and solvate the coating material, thus removing it from the surface [24]. Hence, to ensure reliable application of PFDA in DMMD, a hermetic chip package is used [24]. Exposed to open environment (moisture) PFDA exhibits severe friction and wear [25-26]. Given this situation and application, the nano-engineered patterns maybe a promising substitute, as (1) they are hydrophobic in nature and are not affected by moisture and (2) the surface of the electrodes (Fig. 9(b)) is sufficiently large enough for their application.

Conclusions

Tribological properties of PMMA thin film and nano-patterns with three different aspect ratios were evaluated at nano and micro-scale using AFM and micro-tribotester, respectively. The test results are summarized as follows:

1. The superior adhesion and friction behaviour exhibited by the patterned samples at nano-scale, over that of the silicon wafer and non-patterned thin film, is due to their hydrophobic nature and reduced real contact area.
2. The size and shape factors of patterns were decisive in determining their contact area. The contact area increased with the aspect ratio (holding time) of the patterns.
3. The nano-scale adhesion and friction of the patterned samples increased with the aspect ratio due to the increase in the contact area.
4. At micro-scale, the patterns, due to their reduced contact area exhibited improved friction property over the silicon wafer and non-patterned thin film, a feature similar to that observed at nano-scale.
5. The micro-scale coefficient of friction of the patterns increased with the aspect ratio through the contact area.

Acknowledgments

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