Feature development on prepatterned elastomer surfaces upon ion implantation

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1. Introduction

Polydimethylsiloxane (PDMS) is a silicone elastomer with many attractive properties such as machinability, low cost, resistance to corrosion, making it suitable for various industrial and biomedical applications [1–6]. In some situations, it is necessary to modify the surface properties such as wettability, chemical compositions, and surface energy of the PDMS samples [7]. A possible way to alter the surface physicochemical properties is by plasma implantation [8], but the technique can induce significant changes to the surface morphology of the samples [9]. In fact, many studies concerning the effects of plasma treatment on the surface pattern growth have been made, as surface texturing can be applied to affect the roughness, biocompatibility, and optical properties of materials [10,11]. Plasma ion implantation on PDMS can induce periodic structures [12], the periodicity of which can be adjusted by process parameters such as bias voltage or implantation duration, but the resultant patterns are generally disordered. Bowden et al. [13] used PDMS samples patterned in bas-relief structure which were exposed to oxygen plasma to generate oriented ripple patterns, but the process was somehow complicated.

The aim of the present work is to suppress the development of such induced wavy structures during plasma ion implantation through a simple surface prepatterning step. Besides, the prepatterning step could be employed for controlling the development of ripple growth during the plasma ion implantation process, which may be used as stamps for biopatterning of surfaces [14] to transfer patterns of protein solutions. The spontaneous formation of compound and ordered structures was characterized by atomic force microscopy (AFM). The correlations between spontaneous pattern formation with oxygen plasma treatment parameters, such as bias voltage and processing time, were studied on prepatterned PDMS samples.

2. Experiments

2.1. Materials

Fig. 1(a) illustrates the process flow of pattern generation on PDMS samples. Elastomeric PDMS (Sylgard 184, Dow Corning) were prepared by mixing siloxane base and curing agent in the weight ratio of 10:1. The mixture was casted onto master molds with gratings of periods (heights) 1.5 \( \mu \)m and 0.75 \( \mu \)m (140 nm and 105 nm), respectively. In this work we discuss mainly the results concerned with samples prepatterned with 1.5 \( \mu \)m gratings. Control samples with flat surfaces were made by preparing PDMS on cleaned glass slides. Subsequently the samples were cured at 75 °C for 1 h.

2.2. Plasma implantation treatment

Fig. 1(b) depicts the oxygen plasma ion implantation setup. In the ion implantation system, the control and prepatterned samples were laid side-by-side on the sample stage. A negative voltage was applied to the stage which attracted positive plasma ions into the samples. The PDMS surfaces were subjected to oxygen plasma treatment with different bias voltages (0–10 kV) and processing durations (15 or 30 min). The base pressure in theimplantation chamber was 2.4 \( \times \) 10\(^{-3}\) Pa. The oxygen pressure was maintained at 0.1 Pa during implantation with a flow rate of 10 sccm. In this...
work, we adopted a pulsed, high frequency quasi-direct-current oxygen plasma ion implantation procedure. The sample voltage pulse width was 50 \mu s and the frequency was 100 Hz. This technique prevents the accumulation of charges on the sample surfaces and minimizes the sample overheating [15].

3. Result and discussion

The nanoimprinting process has been employed in our previous works [16,17], with the successful transfer of patterns to receiving substrates. A similar technique was used to prepare PDMS samples in this work, which were subsequently subjected to ion implantation treatment. Fig. 2 illustrates the AFM micrographs of the control (unpatterned) PDMS samples after subjected to oxygen plasma treatment at different bias voltages and processing durations. Spontaneous formation of ripple patterns can be observed. Both the periodicities and depths of the ripple patterns on the surface increased with rising bias voltage or implantation time, but the features showed ordering only in localized regions. Besides, many cracks were generated on the sample, which significantly increased the surface roughness. It has been reported [12] that oxygen plasma treatment of PDMS samples leads to the formation of a brittle, oxidized, silica-like surface layer (Fig. 1(b)). The compressive stress in the surface layer develops into a wavy behavior, which could be explained by the thermal expansion coefficient mismatch between the oxidized, incompressible implanted layer and the unoxidized, bulk PDMS when the samples are cooled down. Upon cooling, the PDMS contracts more than the brittle surface layer since the thermal expansion coefficient of unoxidized PDMS layer is greater than that of silica [11], leading to a large compressive stress in the top surface layer. A spontaneous surface buckling instability [18] is induced for releasing the stress.

Fig. 3 presents AFM images of samples with initial surface prepatterns (gratings of period 1.5 \mu m and depth 140 nm), after exposure to oxygen plasma with different bias voltages and durations. No ripple pattern was induced by the oxygen plasma treatment when the prepatterned sample was implanted at a bias voltage of 5 kV, up to 30 min of implantation time (Fig. 3(a) and (b)). This is in stark contrast with the control sample, which showed induced ripples even when it was exposed to the plasma without any applied bias voltage (Fig. 2(b)).

On the other hand, ordered compound structures were formed when the sample was exposed to a plasma of bias voltage 10 kV for 15 min, and the pattern showed high uniformity essentially across the whole sample surface (about 1 cm²) (Fig. 3(c)). This is in contrast with the unpatterned control sample (Fig. 2), which showed irregular ripple patterns. An ordered hierarchical pattern was observed in prepatterned samples, which was caused by the confinement provided by the surface features. The orientation of the tracks induced by plasma treatment was perpendicular to the prepatterned features, therefore the orientation of spontaneously pattern growth can be controlled.

The height variation (peak-to-trough distance) of the track patterns on the PDMS surfaces upon ion bombardment is shown in Fig. 4. Generally the track heights decreased with rising bias voltage and implantation time, except for the 1.5 \mu m PDMS features implanted at 5 kV which showed an increased height variation, repeatable in several samples fabricated under identical conditions. This peculiar behavior coincided with the absence of spontaneous ripple formation in the sample, which could be due to the increasing compressive stress in the PDMS during the implantation process before it is released through ripple formation.

An explanation on why this phenomenon has occurred would require more in-depth analysis on the onset of ripple feature formations in prepatterned surfaces, which is under progress.

Fig. 5 shows the AFM micrographs of three samples with different initial surface morphologies but which samples have undergone
identical oxygen plasma treatment processes (10 kV bias for 15 min). Parameters of the induced winkle features are shown in Table 1. The periodicity of ordered spontaneous ripple patterns was larger on the prepatterning surface when compared with the control sample; the peak-to-trough amplitude of the ripples on prepatterned samples, on the other hand, was dramatically suppressed from around 700 nm to less than 200 nm. This result revealed that the presence of initial surface morphologies has inhibited the depth development of wrinkled structures pattern.

The capability of surface prepatterning in suppressing the development of high-roughness and disordered ripple patterns is of importance in many studies. Very often elastomer surface have to be plasma-treated before they are used [7]. Unfortunately this would induce damaging and irreversible changes to the sample morphologies, which often complicates the interpretation of experimental results. With the presence of mild surface modulations it is possible to suppress the occurrence of very severe surface roughness, which would be otherwise induced even in the absence of bias voltage during implantation (Fig. 2). When wrinkling occurs on prepatterned samples at very high bias voltages the surface modulations formed were much reduced compared with the control samples (without prepatterning) (Table 1). We therefore conclude that the surface prepatterning can provide a simple route for suppressing the development of implantation-induced ripple patterns.

4. Conclusions

In summary, the ripple patterns on plasma implanted PDMS surfaces can be suppressed through a simple surface prepatterning step. Ripple pattern was not induced on the prepatterned samples even when it was plasma implanted under a bias voltage of 5 kV.
for 30 min. As when wrinkled patterns were induced in the prepatterned surfaces by exposing to the oxygen plasma under a bias voltage of 10 kV, the induced ripples were oriented perpendicular to the prepatterns. As compared with the control flat PDMS sample plasma implanted under the identical biasing conditions of 10 kV for 15 min, the height of ordered waves developed on the prepatterned samples was reduced by more than 3 times. Such a prepattern/plasma implantation process is attractive for potential applications in the field of micro/nano fabrication, by offering a new way to produce ordered hierarchical structure without any conventional lithographic methods. The technique should also prove useful where ion implantation is necessary but mild surface modulations are not of significant importance, such as the culturing of cells [19].

Acknowledgements

Financial supports from The Hong Kong Polytechnic University (J-BB9P, A-PM21) and HKRGC GRF (PolyU 5232/09E) are acknowledged.

References